Quantum Mechanics

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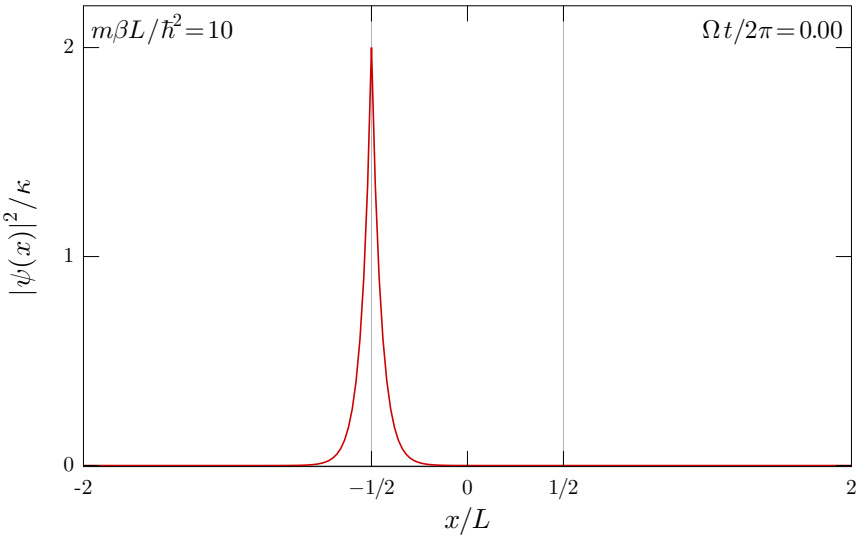
Using This Book

Embedded Multimedia

Video examples are useful in visualizing the results of calculations. Throughout this book, you will see movie references like the one below (there are 6 movies in this book). As an example, the movie clip below is a simple animated plot.



What you see here is two graphical objects. On the left is the better option, *in principle*, the embedded video clip. Unfortunately, it may also be the *complicated* option. You can try clicking on it now to see if it will work. If it does, you're golden, and you can skip to the next section. If not, keep reading.

On the right, you see a complicated-looking square. This provides *two* ways to access the sound clip, both via the web.

- First, this acts as a **clickable URL** from within the pdf document. Click on it, and your pdf reader should automatically switch to a web browser, which will load an online copy of the movie clip in mp4 format.
- Second, this is a **QR code**, which you can scan with a smart phone or tablet. This will get you the same URL as the click. This option is handy if you've printed out the book, because you can use your mobile device to read the URL off the paper and play the sound sample. You can also scan the code off your computer screen, if it's zoomed in enough, and if for some reason this is easier than just clicking on the code. Note that the QR codes are fairly small (printed at 7 mm on paper) so they aren't too obtrusive in the document. This means, however, that not all devices and reader apps will be happy with these codes—a high-resolution camera and decent app are necessary. The **i-nigma** app seems to work well (in iOS and Android).

Now back to the embedded movie on the left.

Why is the state of embedded multimedia in PDF documents so terrible? In part, it is Adobe's habit of releasing software that leaves a *lot* to be desired, in terms of both security and aesthetics. But also, few developers of alternative PDF viewers have provided better options. It is as if PDF multimedia is stuck in 1990's limbo—PDF multimedia hasn't improved much since then (even *regressing* somewhat), but it *has* gotten more complicated.

This document is generated using LaTeX; I include some details of this process in the description below in case it is useful to counter any problems that may crop up. The more popular methods of embedding multimedia in pdf, particularly via LaTeX, involved Flash, which finally met its demise at the end of 2020. The embedding method is a relatively austere method given by Alex Grahn in a discussion on Stack Exchange[1] The main option for viewing these files with embedded sound clips functioning is Adobe Acrobat (or the free Acrobat Reader[2]), but sadly, this software is bloated, slow, and renders text poorly. So we will review some of the options for viewing these files:

- Adobe Acrobat DC (recent versions, on macOS/Windows, commercial/expensive) works reasonably well in playing back the clips. Playback controls are not available.
- Adobe Acrobat Reader (recent versions, on macOS/Windows, free) should reproduce the functionality of Adobe Acrobat DC, but in practice may be considerably buggier.
- On iOS devices and in macOS, PDF Expert[3] handles multimedia well and renders text nicely. Highly recommended. The iOS version is free, a subscription is not needed for multimedia. The macOS version is currently not free, but may move to the same subscription model (subscription should not be necessary).
- In Windows, PDF-XChange Editor[4] handles multimedia fine (the free version works, upsell version not necessary).
- Things that seem like they should work, but don't: Preview.app on OS X, ezPDF in iOS; Foxit Reader on MacOS and Windows.
- In Linux, success has been reported in installing recent Windows versions of Acrobat under Wine[5,6]

  If you have success (or not) in other readers or operating systems, please let me know.

3D Diagrams

Some of the three-dimensional diagrams have two slightly different copies side by side (examples are figures on p. 272, reproduced below, and p. 406). The idea is to relax or cross your eyes and try to overlap the two images to get a 3D stereo view.[7] This first pair is rendered in the way that the other 3D figures are rendered throughout the book; this pair is intended to be viewed ''wall-eyed,'' or with your eyes wider than they would be when focusing on the screen. To fuse the images you can try to relax your eyes and try to ''look beyond the screen'' until they cross, assuming you're viewing this on a laptop or tablet.

[1] https://tex.stackexchange.com/questions/516029/media9-is-becoming-obsolete-dec-2020-any-alternatives-for-embedding-video-audio

[2] http://get.adobe.com/reader/

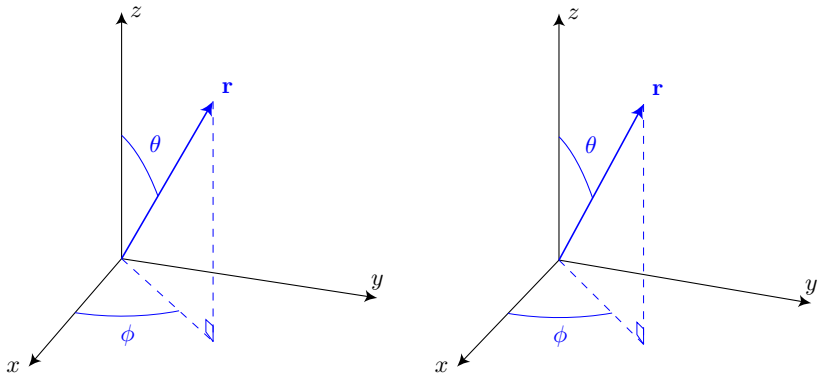
[3] http://pdfexpert.com

[4] https://www.tracker-software.com/product/pdf-xchange-editor

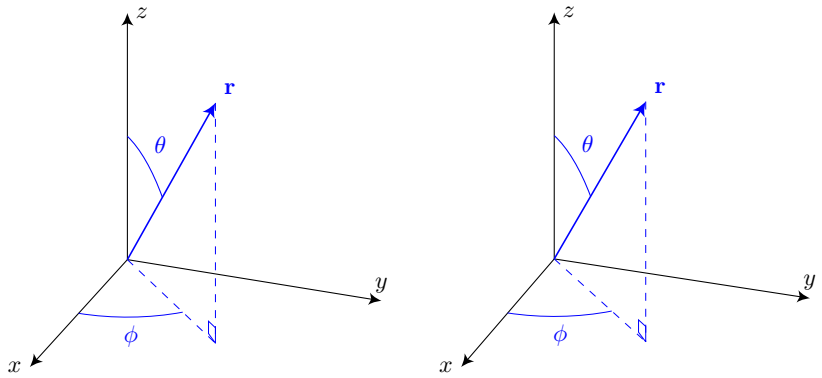
[5] https://www.winehq.org

[6] https://tex.stackexchange.com/questions/442851/is-there-a-way-to-display-both-videos-and-javascript-animations-on-a-beamer-gene/446179#446179

[7] For a bit more information on rendering stereo images, see http://www.f-lohmueller.de/pov_tut/stereo/stereo_000e.htm



The pair below is reversed, so should be viewed "cross-eyed," which is an alternative that works for some people (though the other figures in this book are *not* rendered in this way, unless you flip the screen upside down). One aid that can help fuse the images in this case is to bring a finger starting under the images at the screen, and slowly bring it towards your face while focusing on it, until the images fuse above your finger.



Other Hyperlinks and Navigating this Document

To make it easier to access information within and beyond this document, there are many hyperlinks throughout. To keep the document "pretty," the hyperlinks are not highlighted in colors or boxes by default. Some of the more obvious ones are the spelled-out URLs, like `http://steck.us`, are clickable, as are the QR codes mentioned above. Some of the less obvious ones are:

- DOI (document object identifier) codes in article citations (for locating articles online), as well as arXiv:, archive:, and JSTOR: codes for other article references.
- ISBN codes in book citations (these resolve to pages on Google Books).
- The "*op. cit.*" abbreviation in repeated footnote references (will take you to the original footnote reference).
- Section titles in the Contents.
- Page numbers in the Index.
- Chapter, section, page, and equation numbers throughout the text.

Chapter 0

Prelude: Variational Principles in Classical Mechanics

0.1 Before We Get Started

We're headed towards the study of quantum mechanics. But in order to really *understand* quantum mechanics you need to first understand *classical* mechanics.

There are a couple of reasons for this. First, it's important to be able to distinguish classical behavior from uniquely quantum behavior. This distinction is somewhat subtle in that it is possible to mean different things by ''classical behavior,'' but in particular situations this can be defined more carefully. More importantly, this distinction has historically been the source of a fair amount of confusion.

The second reason is that a fair amount of classical mechanics built into the *structure* of quantum mechanics. The most obvious example is the appearance of the Hamiltonian in the Schrödinger equation. The proper definition of a quantum Hamiltonian is rooted in the classical definition. Heuristic tricks such as writing down Hamiltonians based on the total energy have some utility, yet ultimately amount to crude shortcuts. The path-integral formulation of quantum mechanics involves the classical Lagrangian more explicitly. Semiclassical approximations to quantum mechanics are, obviously, closer yet to classical mechanics. Where things get even trickier is porting over classical constraints to quantum mechanics.

That said, it's not necessary to plow through all of this review material at once, because various parts of it are used for different quantum-mechanical purposes through the following chapters. When classical concepts are needed, there will be references back to this chapter, and so it may be best to wait until the needs arise to learn things here. Nevertheless, all the classical concepts appear together here in order to make a single, coherent presentation.

0.2 Variational Calculus

A **functional** is a function, but a particular type: one that maps functions to scalars.[1] Formally we can say that a functional is a function $F : \mathbb{F} \longrightarrow \mathbb{R}$, where $\mathbb{F}$ is a space of functions. (More generally we can say $F : \mathbb{F} \longrightarrow \mathbb{C}$; a restriction to real numbers are more appropriate in classical mechanics, but obviously complex numbers are more useful in a quantum context.)

[1] Good references on variational calculus and action principles include P. J. Morrison, ''Hamiltonian description of the ideal fluid,'' *Reviews of Modern Physics* **70**, 467 (1998) (doi: 10.1103/RevModPhys.70.467); and Robert Weinstock, *Calculus of Variations with Applications to Physics and Engineering*, (McGraw–Hill, 1952) (ISBN: 0486630692).

0.2.1 Variation

Let $x(t) \in \mathbb{F}$; then the **first variation** of the functional $F[x]$ with respect to a perturbing function $\delta x(t)$ is given by

$$\delta F[x;\delta x] := \lim_{\epsilon\to 0} \frac{F[x+\epsilon\delta x]-F[x]}{\epsilon} = \frac{d}{d\epsilon} F[x+\epsilon\delta x]\bigg|_{\epsilon=0}, \tag{0.1}$$
(first variation)

where ϵ and δx are subject to the constraint that $x+\epsilon\delta x \in \mathbb{F}$. Note that the introduction of ϵ simplifies the parameterization of the perturbation of the functional due to $\delta x(t)$.

0.2.2 Functional Derivative

The **functional derivative** $\delta F/\delta x$ such that

$$\left\langle \frac{\delta F}{\delta x}, \delta x \right\rangle := \int_{t_1}^{t_2} \frac{\delta F}{\delta x(t)}\, \delta x(t)\, dt := \delta F[x;\delta x]. \tag{0.2}$$
(first functional derivative)

The angle brackets on the left-hand side denote an inner product (i.e., dot product, see Section 1.1.2) on the functional space. We will define inner products later in Section 1.1.2, but for now the integral in the middle expression defines the inner product that we mean here. The inner product here defines the functional derivative in a way that is readily generalized, and in particular it yields a scalar value (as required to match the first variation) as a combination of the functional derivative $\delta F/\delta x(t)$ and the perturbation $\delta x(t)$, which are both functions. Note that the definition here is also a workable definition for the ordinary partial derivative of a scalar function of a vector, $\partial_\alpha F(\mathbf{x})$, where the first variation is $(\delta x^\alpha)\partial_\alpha F(\mathbf{x})$, with the repeated index summed. This is as it should be, since the functional derivative is a generalization of the vector partial derivative to a continuous ''vector index,'' where the generalization of the vector index is a function of a continuous variable. Conversely, for better intuition you can always thing of a functional derivative in terms of a countable set of partial derivative (in terms of, say, a discrete or finite-difference approximation to continuous functions, or by a Fourier-series expansion of a function; both of these procedures convert the time variable t into a discrete index).

A simple but important example is to consider the identity convolution integral

$$x(t) = \int dt\, \delta(t-t')\, x(t'). \tag{0.3}$$

In terms of a variation of $x(t)$, this becomes

$$\delta x(t) = \int dt\, \delta(t-t')\, \delta x(t'), \tag{0.4}$$

and so comparison with Eq. (0.2) allows us to identify the functional derivative

$$\frac{\delta x(t)}{\delta x(t')} = \delta(t-t'). \tag{0.5}$$

This is the continuous analogue to the Kronecker-delta relation $\partial x_\alpha/\partial x_\beta = \delta_{\alpha\beta}$.

0.2.2.1 Generalizations

The notion of the functional derivative generalizes straightforwardly in a couple of ways. For example, a functional may depend not only on $x(t)$, but also its derivatives [which we will write here as $x_t \equiv \dot{x}(t)$, $x_{tt} \equiv \ddot{x}(t)$, and so on]. Thus consider a functional of the form

$$F[x, x_t, x_{tt}, \ldots; t] = \int_{t_1}^{t_2} f(t, x, x_t, x_{tt}, \ldots)\, dt. \tag{0.6}$$

Then the first variation becomes

$$\delta F[x, x_t, x_{tt}, \ldots; t] = \int_{t_1}^{t_2} \left[\frac{\partial f}{\partial x}\delta x + \frac{\partial f}{\partial x_t}\delta x_t + \frac{\partial f}{\partial x_{tt}}\delta x_{tt} + \ldots \right] dt. \tag{0.7}$$

The functional derivative is written in terms of an integral involving $\delta x(t)$, not its derivatives; to transform this expression into a more useful form we can integrate by parts to yield

$$\delta F[x, x_t, x_{tt}, \ldots; t] = \int_{t_1}^{t_2} \left[\frac{\partial f}{\partial x} - \frac{d}{dt}\frac{\partial f}{\partial x_t} + \frac{d^2}{dt^2}\frac{\partial f}{\partial x_{tt}} + \ldots \right] \delta x\, dt + \left[\frac{\partial f}{\partial x_t}\delta x + \ldots \right]_{t_1}^{t_2}. \tag{0.8}$$

In order to ignore the boundary terms on the right-hand side, we must impose fixed-endpoint conditions on the variation

$$\delta x(t_1) = \delta x_t(t_1) = \cdots = \delta x(t_2) = \delta x_t(t_2) = \cdots = 0, \tag{0.9}$$

where only the requisite number of conditions is applied to just suppress all the boundary terms. For example, if f depends on no higher derivative than x_t, then the fixed-endpoint conditions are $\delta x(t_1) = \delta x(t_2) = 0$, with no conditions applied to the derivatives of δx. In this case of $f(t, x, x_t)$, we can identify

$$\frac{\delta F[x, x_t; t]}{\delta x} = \frac{\partial f}{\partial x} - \frac{d}{dt}\frac{\partial f}{\partial x_t} \tag{0.10}$$

(example first functional derivative)

as the first functional derivative.

Another generalization of the functional derivative is to vector functions of vector arguments. This generalization occurs happens in the natural way for the inner product:

$$\left\langle \frac{\delta F}{\delta \phi}, \delta\phi \right\rangle := \int_D \frac{\delta F}{\delta \phi_\alpha}\, \delta\phi_\alpha\, d^n x := \delta F[x; \delta x]. \tag{0.11}$$

Here the functions on which F depends are $\phi_\alpha(x^\beta)$, D is the domain of integration, and there is a summation implied over the repeated dummy index α.

A heuristic shortcut for handling functional derivative comes from treating them as ordinary derivatives via the ordinary chain rule, provided the chain terminates with the rule (0.5). This works provided that any boundary conditions can be ignored. Thus, for example, for a functional of the form (0.6),

$$\begin{aligned}
\frac{\delta F}{\delta x(t)} &= \frac{\delta}{\delta x(t)} \int_{t_1}^{t_2} f(t', x, x_{t'}, x_{t't'}, \ldots)\, dt' \\
&= \int_{t_1}^{t_2} \left[\frac{\partial f}{\partial x}\frac{\delta x(t')}{\delta x(t)} + \frac{\partial f}{\partial x_{t'}}\frac{\delta x_{t'}(t')}{\delta x(t)} + \frac{\partial f}{\partial x_{t't'}}\frac{\delta x_{t't'}(t')}{\delta x(t)} + \cdots \right] dt' \\
&= \int_{t_1}^{t_2} \left[\frac{\partial f}{\partial x}\,\delta(t'-t) + \frac{\partial f}{\partial x_{t'}}\,\delta'(t'-t) + \frac{\partial f}{\partial x_{t't'}}\,\delta''(t'-t) + \cdots \right] dt' \\
&= \frac{\partial f}{\partial x} - \frac{d}{dt}\frac{\partial f}{\partial x_t} + \frac{d^2}{dt^2}\frac{\partial f}{\partial x_{tt}} + \cdots,
\end{aligned} \tag{0.12}$$

provided $t \in (t_1, t_2)$. For a more familiar function of the form $F(\mathbf{x}) = \sum_\alpha f_\alpha(\mathbf{x})$, observe that these steps are analogous to the (pedantic) manipulations

$$\frac{\partial F}{\partial x_\beta} = \sum_{\alpha\gamma} \frac{\partial f_\alpha}{\partial x_\gamma}\frac{\partial f_\gamma}{\partial x_\beta} = \sum_{\alpha\gamma} \frac{\partial f_\alpha}{\partial x_\gamma}\delta_{\gamma\beta} = \sum_\alpha \frac{\partial f_\alpha}{\partial x_\beta}, \tag{0.13}$$

except that the functional case has additional complications due to the dependence on derivatives like x_t, which correspond to off-diagonal generalizations of the identity matrix $\delta_{\gamma\beta}$ here. The shortcut illustrated in Eqs. (0.12) also works for more general functionals as in Eq. (0.11), using the generalized rule $\delta\phi_\alpha(\mathbf{x})/\delta\phi_\beta(\mathbf{x}') = \delta_{\alpha\beta}\,\delta^n(\mathbf{x} - \mathbf{x}')$.

0.2.2.2 Second Variation

Yet another generalization to the functional differentiation that we have so far discussed is to higher derivatives. For example, by iterating the definition for the first variation, we can obtain the **second variation**

$$\begin{aligned}\delta^2 F[x;\delta x;\delta x'] &:= \lim_{\epsilon\to 0}\frac{\delta F[x+\epsilon\,\delta x;\delta x'] - \delta S[x;\delta x']}{\epsilon}\\ &= \partial_\epsilon \delta F[x+\epsilon\,\delta x;\delta x']\Big|_{\epsilon=0}\\ &= \partial_\epsilon\partial_{\epsilon'} F[x+\epsilon\,\delta x+\epsilon'\,\delta x']\Big|_{\epsilon=\epsilon'=0}.\end{aligned}$$

(second functional derivative) (0.14)

Then the definition of the functional derivative generalizes in the obvious way to the **second functional derivative** in terms of the second variation as

$$\left\langle \delta x,\ \frac{\delta^2 F}{\delta x^2}\,\delta x'\right\rangle := \int_{t_1}^{t_2} dt \int_{t_1}^{t_2} dt'\,\delta x(t)\,\frac{\delta^2 F}{\delta x(t)\,\delta x(t')}\,\delta x'(t') := \delta^2 F[x;\delta x;\delta x'].$$

(second functional derivative) (0.15)

Note the independent variations δx and $\delta x'$ here, though for simple notation we needn't make this distinction in the functional derivative itself (though the second derivative is explicitly a function of two independent variables). Also, in the inner-product expression on the left-hand side, the functional derivative $\delta^2 F/\delta x^2$ is acting as a linear operator on the function (vector) $\delta x'$; in the middle expression this operator action implies the dt' integral, while the inner product implies the dt integral. That is, Eq. (0.15) should be read as the generalization of the matrix expression $\mathbf{x}\cdot(\mathbf{A}\mathbf{x}') = x_\alpha A_{\alpha\beta} x'_\beta$ for vectors $\mathbf{x}$ and $\mathbf{x}'$ and matrix $\mathbf{A}$. Depending on the functional form of the functional, suitable endpoint conditions on the perturbation δx may be necessary. This derivative is again a generalization of a second partial derivative, in this case $\partial_\alpha\partial_\beta F(\mathbf{x})$, and the second derivative is the continuous generalization of a matrix.

For the remainder of this chapter, we won't have much use for the second derivative, but it will be useful in discussing the semiclassical form of the path integral (Section 18.3.1).

0.3 Lagrangian Mechanics

The basis of Lagrangian mechanics is the set of **generalized coordinates**, or the "q's", which parameterize the coordinate-space state of the problem. These could correspond to the ordinary Cartesian position ($\mathbf{r}$), angular coordinates (θ, ϕ), variables in general curvilinear coordinate systems, and so on. Given the generalized coordinates q^α, which act as time-dependent trajectories $q^\alpha(t)$, the next fundamental object is the **Lagrangian**, which typically has the form

$$L(\mathbf{q},\dot{\mathbf{q}};t) = T(\dot{\mathbf{q}}) - V(\mathbf{q}),$$

(typical Lagrangian form) (0.16)

where T is the kinetic-energy function and V is the potential-energy function. Although this form is typical, the Lagrangian can in principle have any form it needs to have in order to model whatever it is you need to model—this could involve mixing q^α and its time derivatives in the same term, or the Lagrangian could also depend on higher-order time derivatives of the coordinates.[2] For a particle moving in a potential, the kinetic energy is quadratic in the velocities, and thus

$$L(\mathbf{q},\dot{\mathbf{q}};t) = \frac{1}{2}m\dot{\mathbf{q}}^2 - V(\mathbf{q}),$$

(typical particle Lagrangian) (0.17)

where m is the particle mass, and we have switched to an index-free notation for the coordinate vector.

[2]Note that it may seem odd to have the Lagrangian depend on $\mathbf{q}$ and $\dot{\mathbf{q}}$ as if they are independent variables, when clearly specifying the trajectory $\mathbf{q}(t)$ clearly also specifies all of $\dot{\mathbf{q}}(t)$. However, the quantities $\mathbf{q}$ and $\dot{\mathbf{q}}$ are meant as *local* quantities at a particular time, in which case both are needed to specify the state (in the sense of an initial-value problem). See also Section 0.4.4.3 for a discussion of the manifold spanned by $\mathbf{q}$ and $\dot{\mathbf{q}}$.

0.3.1 Variational Principle

The Lagrangian comes to life in the **action functional**

$$S[L] := \int_{t_1}^{t_2} L(\mathbf{q}, \dot{\mathbf{q}}; t)\, dt. \tag{0.18}$$
(action functional)

The action functional then defines how classical mechanics works via the **action principle** $\delta S[L] = 0$, which is more specifically **Hamilton's principle**. Equivalently, the action principle is $\delta S/\delta \mathbf{q} = 0$; with the fixed-endpoint conditions $[\delta\mathbf{q}(t_1) = \delta\mathbf{q}(t_2) = 0]$, we can read off the functional derivative from Eq. (0.10) to write in components the **Euler–Lagrange equation**

$$\frac{\partial L}{\partial q^\alpha} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}^\alpha} = 0, \tag{0.19}$$
(Euler–Lagrange equation)

which is an equation of motion for the q's. In the case of a particle Lagrangian (0.17), these give the usual classical equations of motion (Newton's equations).

0.3.2 Hessian Condition

Going a bit further with Eq. (0.19), we can carry out the time derivative more explicitly using the chain rule to write

$$\frac{\partial L}{\partial q^\alpha} = \frac{\partial^2 L}{\partial \dot{q}^\alpha \partial q^\beta}\dot{q}^\beta + \frac{\partial^2 L}{\partial \dot{q}^\alpha \partial \dot{q}^\beta}\ddot{q}^\beta + \frac{\partial^2 L}{\partial \dot{q}^\alpha \partial t}. \tag{0.20}$$

This form of the Euler–Lagrange equation shows more transparently that it is a second-order differential equation in the coordinates q^α; furthermore, first derivatives only occur if there are terms in L that are mixed in q^α and $\dot{q}^\alpha$. However, there is an additional issue to consider here. For this system of equations to be well-defined, the **Hessian matrix** of second derivatives $\partial^2 L/\partial \dot{q}^\alpha \partial \dot{q}^\beta$ should be nonsingular, in which case the system of equations can be solved explicitly for the $\ddot{q}^\beta$. That is, we should have the Hessian condition

$$\det\left(\frac{\partial^2 L}{\partial \dot{q}^\alpha \partial \dot{q}^\beta}\right) \neq 0. \tag{0.21}$$

If this condition is *not* satisfied, it is a sign that the velocities are not all independent—there is a constraint built into the system. In the case of Lagrangian mechanics, the Hessian condition is typically assumed to be true. However, we will discuss how to handle this kind of situation within Hamiltonian mechanics below in Section 0.5.2.

0.4 Hamiltonian Mechanics

The Lagrangian also allows us to define the **canonically conjugate momenta**

$$p_\alpha := \frac{\partial L}{\partial \dot{q}^\alpha}. \tag{0.22}$$
(canonically conjugate momenta)

For a particle Lagrangian of the form (0.17), for example, the conjugate momentum is just the kinematic momentum, $p_\alpha = m\dot{q}^\alpha$. In terms of the momenta, the Hessian condition (0.21) may be written

$$\det\left(\frac{\partial p_\alpha}{\partial \dot{q}^\beta}\right) \neq 0. \tag{0.23}$$

Thus, the Hessian condition amounts to the requirement that the momenta p_α and velocities $\dot{q}^\beta$ are related via a valid coordinate transformation.

Once the momenta are fixed, the Hamiltonian is defined by a **Legendre transformation** of the Lagrangian,

$$H(\mathbf{q},\mathbf{p};t) := \dot{q}^\alpha p_\alpha - L(\mathbf{q},\dot{\mathbf{q}};t) \tag{0.24}$$
(Hamiltonian function)

(where a summation is implied by the repeated index α). Note that the Hamiltonian explicitly does not depend on the coordinate time-derivatives, which must be eliminated in favor of the conjugate momenta. If it isn't obvious that it is always possible to remove the dependence on $\dot{\mathbf{q}}$, consider a differential change in H due to differential changes $\delta\mathbf{q}$, $\delta\dot{\mathbf{q}}$, and δt of the arguments:

$$\begin{aligned}\delta H &= \delta\big[\dot{q}^\alpha p_\alpha - L(\mathbf{q},\dot{\mathbf{q}};t)\big] \\ &= \delta\dot{q}^\alpha p_\alpha + \dot{q}^\alpha \delta p_\alpha - \frac{\partial L}{\partial q^\alpha}\delta q^\alpha - \frac{\partial L}{\partial \dot{q}^\alpha}\delta\dot{q}^\alpha - \frac{\partial L}{\partial t}\delta t \\ &= \dot{q}^\alpha \delta p_\alpha - \frac{\partial L}{\partial q^\alpha}\delta q^\alpha - \frac{\partial L}{\partial t}\delta t.\end{aligned} \tag{0.25}$$

That is, the variation of the Hamiltonian only depends on δp_α and δq^α (and δt), not directly on $\delta\dot{q}^\alpha$ (δp_α is not an independent variation here, but rather is a function of δq^α and $\delta\dot{q}^\alpha$; the point here is that the variation only appears in the particular combination represented by δp_α). For the purposes of the upcoming variational principle, then, we don't have to worry about the presence of $\delta\dot{q}^\alpha$ in the definition here, in that we can assume that it can be eliminated in favor of momenta.

The Hamiltonian often takes the standard form $T_p(\mathbf{p})+V(\mathbf{q})$, but this is *only* the case if the Lagrangian has the form (0.16); indeed if the kinetic energy has the form $T(\dot{\mathbf{q}}) = (1/2)m\dot{\mathbf{q}}^2$, then the transformed kinetic energy is $T_p(\mathbf{p}) = \mathbf{p}^2/2m$.

0.4.1 Variational Principle

Now the **phase-space action** is

$$S[\mathbf{q},\mathbf{p}] := \int_{t_1}^{t_2} \Big[\dot{\mathbf{q}}\cdot\mathbf{p} - H(\mathbf{q},\mathbf{p};t)\Big]\,dt, \tag{0.26}$$
(phase-space action)

Note the bracketed quantity is the Lagrangian, expressed in canonical coordinates, and so the idea here will be to vary the action here in the same way as the variation of the action (0.18) in terms of the Lagrangian yielded the equations of motion. The action principle here is $\delta S[\mathbf{q},\mathbf{p}] = 0$, or equivalently the conditions $\delta S/\delta p_\alpha = 0$ and $\delta S/\delta q^\alpha = 0$. These conditions imply **Hamilton's equations**:

$$\dot{p}_\alpha = -\frac{\partial H}{\partial q^\alpha}, \qquad \dot{q}^\alpha = \frac{\partial H}{\partial p_\alpha}. \tag{0.27}$$
(Hamilton's equations)

With these solutions the action is insensitive to linear order to small perturbations of $q^\alpha(t)$ and $p_\alpha(t)$; this is subject to the condition of fixed position endpoints [$\delta\mathbf{q}(t_1) = \delta\mathbf{q}(t_2) = 0$, but now $\mathbf{p}(t_1)$ and $\mathbf{p}(t_2)$ are allowed to vary]. Note that the first Hamilton equation is equivalent to the Euler–Lagrange equation (0.19), while the second Hamilton equation is a restatement of the canonical-momentum definition (0.22).

0.4.1.1 Hamilton's Equations from Variation of the Lagrangian

An alternate derivation of the Hamilton equations starts by considering the change (0.25) in the Hamiltonian due to a small change in its arguments. Varying $H(\mathbf{q},\mathbf{p};t)$ directly gives

$$\delta H(\mathbf{q},\mathbf{p};t) = \frac{\partial H}{\partial q^\alpha}\delta q^\alpha + \frac{\partial H}{\partial p_\alpha}\delta p_\alpha + \frac{\partial H}{\partial t}\delta t, \tag{0.28}$$

and equating the coefficients of the different variations gives the set of equations

$$\frac{\partial L}{\partial q^\alpha} = -\frac{\partial H}{\partial q^\alpha}, \qquad \dot{q}^\alpha = \frac{\partial H}{\partial p_\alpha}, \qquad \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}.$$

(alternate Hamilton equations) (0.29)

The first equation here is equivalent to the first of the usual Hamilton equations (0.27) if we employ the results of the variational principle in the form of the Euler–Lagrange equation (0.19), so that the left-hand side is $(d/dt)\partial L/\partial\dot{\mathbf{q}} = (d/dt)\mathbf{p}$.

0.4.1.2 Maupertuis' Principle

While we're here, it is interesting to note one more form of the action principle for classical mechanics. If the Hamiltonian $H(\mathbf{q}, \mathbf{p})$ is not explicitly time-dependent, then its value is a constant of the motion, as we will show in the next section. That is, the energy

$$H(\mathbf{q}, \mathbf{p}) = E \tag{0.30}$$

is constant. In this case, the Hamiltonian component of the phase space action (0.26) leads to a constant, which induces no variation when $\mathbf{q}$ or $\mathbf{p}$ are varied. In this case we need only consider the reduced action

$$S[\mathbf{p}] = \int_{t_1}^{t_2} \dot{\mathbf{q}} \cdot \mathbf{p}\, dt = \int_{q_1}^{q_2} \mathbf{p} \cdot d\mathbf{q}. \tag{0.31}$$

(phase-space action)

In the latter form we can regard $\mathbf{p}$ as a function of $\mathbf{q}$. The action principle here, **Maupertuis' principle**, reads

$$\delta S[\mathbf{p}] = 0. \tag{0.32}$$

(Maupertuis' principle)

Because the time-dependence was eliminated here, Maupertuis' principle only determines the trajectory $\mathbf{p}(\mathbf{q})$ in phase space, but does not determine its time dependence. The missing time dependence can be recovered from the particular energy value E along the trajectory. That is, given the phase-space contour $\mathbf{p}(\mathbf{q})$, we can parameterize $\mathbf{q}(t)$ via a time parameter t, which determines a velocity vector $\dot{\mathbf{q}}(t)$ and a momentum $\mathbf{p} = \partial L/\partial\dot{\mathbf{q}}(t)$. This parameterization is fairly arbitrary, but the choice of time can be fixed by requiring Eq. (0.30) to be satisfied.

0.4.2 Time-Dependent Hamiltonians

In the above variational principles, we treated Hamiltonians with the possibility of explicit time-dependence, $H(\mathbf{q}, \mathbf{p}; t)$. To simplify the discussion, let's assume that the Hamiltonian has one spatial degree of freedom, so that $H(q, p; t)$. An explicitly time-dependent system of one degree of freedom system really needs a three-dimensional phase space (q, p, t), since the explicit time dependence behaves effectively as a dynamical variable. Such as system is commonly referred to as a **1½-degree-of-freedom system**. In fact, given a 1½-degree-of-freedom system $H(q, p, t)$, we can make a formal mapping to an autonomous (not explicitly time dependent), 2-degree-of-freedom system $\tilde{H}(q^1, q^2, p_1, p_2)$ as follows. Let τ be a new parameter that will become the time in the new coordinates. Then let $q^1 = q$, $p_1 = p$, $q^2 = t$, and

$$\tilde{H}(q^1, q^2, p_1, p_2) = H(q^1, p_1, q^2) + p_2.$$

Then Hamilton's equations become

$$\begin{aligned}
\frac{dq^1}{d\tau} &= \frac{\partial \tilde{H}}{\partial p_1} = \frac{\partial H}{\partial p} = \frac{dq}{dt} \\
\frac{dq^2}{d\tau} &= \frac{\partial \tilde{H}}{\partial p_2} = 1 \\
\frac{dp_1}{d\tau} &= -\frac{\partial \tilde{H}}{\partial q^1} = -\frac{\partial H}{\partial q} = \frac{dp}{dt} \\
\frac{dp_2}{d\tau} &= -\frac{\partial \tilde{H}}{\partial q^2} = -\frac{\partial H}{\partial t}.
\end{aligned}$$

The second equation says that $q^2 = \tau + \tau_0 = t$, and thus $\tau = t$ if we take $\tau_0 = 0$. The last equation says that p_2 changes in such a way as to make the value of $\tilde{H}$ constant. In fact, by taking $p_2(0) = -H(q^1, p_1, 0)$, this guarantees that the extended Hamiltonian vanishes, $\tilde{H} = 0$. The other equations for q^1 and p_1 generate the same dynamics as for the original variables q and p.

The mapping here of course applies if there are more degrees of freedom. Furthermore (Problem 0.5), a mapping such as this can also be constructed in the other direction (i.e., an autonomous system of 2 or more degrees of freedom is equivalent to an explicitly time-dependent system with one less degree of freedom).

0.4.3 Poisson Bracket

Now consider an arbitrary phase-space function $f(q, p, t)$. To find its equation of motion, we can differentiate and use the chain rule to obtain

$$\frac{df}{dt} = \frac{\partial f}{\partial q^\alpha}\frac{dq^\alpha}{dt} + \frac{\partial f}{\partial p_\alpha}\frac{dp_\alpha}{dt} + \frac{\partial f}{\partial t}. \tag{0.33}$$

Using the Hamilton equations (0.27) to eliminate the time derivatives of the coordinates,

$$\frac{df}{dt} = \frac{\partial f}{\partial q^\alpha}\frac{\partial H}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial H}{\partial q^\alpha} + \frac{\partial f}{\partial t}. \tag{0.34}$$

Now defining the **Poisson bracket**

$$[f, g]_{\text{P}} := \frac{\partial f}{\partial q^\alpha}\frac{\partial g}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial g}{\partial q^\alpha} \tag{0.35}$$

(Poisson bracket)

for arbitrary phase-space functions f and g, the equation of motion for f is given in terms of the Poisson bracket with the Hamiltonian:

$$\frac{df}{dt} = [f, H]_{\text{P}} + \frac{\partial f}{\partial t}. \tag{0.36}$$

(general equation of motion)

Because of the antisymmetry of the Poisson bracket, the bracket of any function with itself vanishes. This in turn implies that $dH/dt = \partial H/\partial t$, which means that if the Hamiltonian has no explicit time dependence ($\partial H/\partial t = 0$), then it is a constant of the motion (i.e., energy is conserved, $dH/dt = 0$).

Taking the equation of motion (0.36) with q^α and p_β as the phase-space functions, we find that Hamilton's equations (0.27) may be written as

$$\dot{q}^\alpha = [q^\alpha, H]_{\text{P}}, \qquad \dot{p}_\alpha = [p_\alpha, H]_{\text{P}}$$

(Hamilton's equations, Poisson-bracket form) (0.37)

in terms of the Poisson bracket. In canonical coordinates, we also have the Poisson brackets

$$[q, q]_{\text{P}} = [p, p]_{\text{P}} = 0, \qquad [q, p]_{\text{P}} = 1 \tag{0.38}$$

in one degree of freedom, or in multiple degrees of freedom,

$$[q^\alpha, q^\beta]_{\text{P}} = [p_\alpha, p_\beta]_{\text{P}} = 0, \qquad [q^\alpha, p_\beta]_{\text{P}} = \delta^\alpha_{\ \beta}. \tag{0.39}$$

These relations in particular are important, in that they will carry over into the quantum case.

0.4.3.1 Compact Notation

Suppose that we define again the coordinate vector z^α for an n degree-of-freedom system by $z^\alpha = q^\alpha$ and $z^{n+\alpha} = p_\alpha$ for $\alpha \in \{1, \ldots, n\}$. Then Hamilton's equations (0.27) and (0.36) take the form

$$\dot{z}^\alpha = I^{\alpha\beta} \frac{\partial H}{\partial z^\beta} = [z^\alpha, H]_{\text{P}}, \tag{0.40}$$
(Hamilton equations, compact form)

and the Poisson bracket is

$$[f, g]_{\text{P}} = \frac{\partial f}{\partial z^\alpha} I^{\alpha\beta} \frac{\partial g}{\partial z^\beta}, \tag{0.41}$$
(Poisson bracket, compact form)

where

$$(I^{\alpha\beta}) = \begin{pmatrix} 0_n & \mathcal{I}_n \\ -\mathcal{I}_n & 0_n \end{pmatrix}, \tag{0.42}$$

with $\mathcal{I}_n$ denoting the $n \times n$ identity matrix and 0_n the $n \times n$ null matrix.

0.4.3.2 Liouville's Theorem

An important result in classical Hamiltonian mechanics is **Liouville's theorem**, which says that given a volume in phase space (the space of all p's and q's), where the time evolution of classical trajectories defines a time-dependent volume $\mathscr{V}(t)$, this volume is *time-independent*. To see this, first consider in the above notation z^α for the canonical coordinates, Hamilton's equations in the generic form

$$\dot{z}^\alpha = F^\alpha(\mathbf{z}), \tag{0.43}$$

where the derivative function F^α matches the right-hand side of Eq. (0.40). The differential form of Liouville's theorem follows by computing the divergence

$$\partial_\alpha F^\alpha(\mathbf{z}) = \frac{\partial}{\partial z_\alpha} \left(I^{\alpha\beta} \frac{\partial H}{\partial z^\beta} \right) = I^{\alpha\beta} \frac{\partial^2 H}{\partial z^\alpha \partial z^\beta} = 0, \tag{0.44}$$

which vanishes owing to the antisymmetry of $I^{\alpha\beta}$. That is, the flow in the coordinates z^α is locally incompressible.

To work explicitly with the phase-space volume

$$\mathscr{V}(t) = \int_{S(t)} \prod_\alpha dz^\alpha, \tag{0.45}$$

where $S(t)$ is the (time-dependent) bounding surface of the volume, we can show that this is the same as the initial volume

$$\mathscr{V}(0) = \int_{S(0)} \prod_\alpha dz_0^\alpha, \tag{0.46}$$

where the z_0^α are the coordinates in the initial space. Since we can consider the time evolution of z_0^α into $z^\alpha(t)$ as a coordinate transformation, we can also write

$$\mathscr{V}(t) = \int_{S(0)} \mathcal{J} \prod_\alpha dz_0^\alpha, \tag{0.47}$$

where

$$\mathcal{J}(\mathbf{z}_0, t) = \det \frac{\partial \mathbf{z}}{\partial \mathbf{z}_0} \tag{0.48}$$

is the Jacobian determinant (i.e., the determinant of the matrix of all partial derivatives of z^α with respect to z_0^β, which defines the transformation of the integration volume element between coordinate systems). Now

differentiating the Jacobian,

$$\begin{aligned}
\partial_t \mathcal{J} &= \sum_\alpha \det \frac{\partial(z^1,\dots,z^{\alpha-1},\partial_t z^\alpha, z^{\alpha+1},\dots,z^{2N})}{\partial \mathbf{z}_0} \\
&= \sum_\alpha \det \frac{\partial(z^1,\dots,z^{\alpha-1},F^\alpha, z^{\alpha+1},\dots,z^{2N})}{\partial \mathbf{z}_0} \\
&= \sum_\alpha \frac{\partial F^\alpha}{\partial z^\beta} \det \frac{\partial(z^1,\dots,z^{\alpha-1},z^\beta, z^{\alpha+1},\dots,z^{2N})}{\partial \mathbf{z}_0} \\
&= \sum_\alpha \frac{\partial F^\alpha}{\partial z^\beta}\, \mathcal{J}\, \delta_\alpha{}^\beta \\
&= \mathcal{J} \sum_\alpha \frac{\partial F^\alpha}{\partial z^\alpha} = 0,
\end{aligned} \tag{0.49}$$

where we assume the Hamiltonian system to have N degrees of freedom (N generalized coordinates, with N corresponding momenta), and in the last step we used the divergence form (0.44) of Liouville's theorem. This proves Liouville's theorem, because the (partial) time derivative of Eq. (0.47) vanishes.

0.4.4 Canonical Transformations

Suppose that we have two sets of canonical coordinates (q^α, p_α) and $(\tilde{q}^\alpha, \tilde{p}_\alpha)$. Notice that the variational principle for the phase-space action must hold in either coordinate system:

$$\delta S[q,p] = \delta\left[\int_{t_1}^{t_2}\Big(\dot{q}^\alpha p_\alpha - H(\mathbf{q},\mathbf{p},t)\Big)\,dt\right] = 0 = \delta\left[\int_{t_1}^{t_2}\Big(\dot{\tilde{q}}^\alpha \tilde{p}_\alpha - \tilde{H}(\tilde{\mathbf{q}},\tilde{\mathbf{p}},t)\Big)\,dt\right] = \delta\tilde{S}[\tilde{\mathbf{q}},\tilde{\mathbf{p}}]. \tag{0.50}$$

Because of the fixed-endpoint constraint $\delta\mathbf{q}(t_1) = \delta\mathbf{q}(t_2) = 0$, the integrand can differ in the two coordinate systems, but only by at most a derivative of a free function F_1:

$$\Big(\dot{q}^\alpha p_\alpha - H(\mathbf{q},\mathbf{p};t)\Big) = \Big(\dot{\tilde{q}}^\alpha \tilde{p}_\alpha - \tilde{H}(\tilde{\mathbf{q}},\tilde{\mathbf{p}};t)\Big) + \frac{d}{dt}F_1(\mathbf{q},\tilde{\mathbf{q}},t). \tag{0.51}$$

This works because after the time integration,

$$\int_{t_1}^{t_2}\left(\frac{d}{dt}F_1(\mathbf{q},\tilde{\mathbf{q}},t)\right)dt = F_1\Big(\mathbf{q}(t_2),\tilde{\mathbf{q}}(t_2),t_2\Big) - F_1\Big(\mathbf{q}(t_1),\tilde{\mathbf{q}}(t_1),t_1\Big), \tag{0.52}$$

the variation with fixed endpoints [$\delta\mathbf{q}(t_1) = \delta\mathbf{q}(t_2) = 0$] destroys these extra surface terms. Expanding the derivative,

$$\dot{q}^\alpha p_\alpha - H(\mathbf{q},\mathbf{p};t) = \dot{\tilde{q}}^\alpha \tilde{p}_\alpha - \tilde{H}(\tilde{\mathbf{p}},\tilde{\mathbf{q}};t) + \frac{\partial F_1}{\partial t} + \frac{\partial F_1}{\partial q^\alpha}\dot{q}^\alpha + \frac{\partial F_1}{\partial \tilde{q}^\alpha}\dot{\tilde{q}}^\alpha, \tag{0.53}$$

and equating terms, we find the coordinate transformations

$$p_\alpha = \frac{\partial F_1}{\partial q^\alpha}, \qquad \tilde{p}_\alpha = -\frac{\partial F_1}{\partial \tilde{q}^\alpha}, \qquad \tilde{H} = H + \frac{\partial F_1}{\partial t} \tag{0.54}$$

(canonical transformation)

in terms of the **mixed-variable generating function** F_1. This coordinate transformation preserves the explicit Hamiltonian structure of the system, and is called a **canonical transformation**.

Other mixed-variable generating functions are possible. Consider, for example, the generating function

$$F_2(\mathbf{q},\tilde{\mathbf{p}},t) = F_1 + \tilde{q}^\alpha \tilde{p}_\alpha. \tag{0.55}$$

This function also defines a canonical transformation via the transformation relations (see Problem 0.2)

$$p_\alpha = \frac{\partial F_2}{\partial q^\alpha}, \qquad \tilde{q}_\alpha = \frac{\partial F_2}{\partial \tilde{p}^\alpha}, \qquad \tilde{H} = H + \frac{\partial F_2}{\partial t}. \tag{0.56}$$

(canonical transformation)

The idea is the same, it is just that there is a different choice for the variables for the generating function. We will consider an example of this type of generating function later in Section 1.7.6 and Problem 1.37, when we also talk about unitary transformations.

0.4.4.1 Infinitesimal Canonical Transformations

Suppose that we consider canonical transformations between "nearby" variables. That is, let

$$\tilde{q}^\alpha = q^\alpha + \delta q^\alpha, \qquad \tilde{p}_\alpha = p_\alpha + \delta p_\alpha, \tag{0.57}$$

where δq^α and δp_α are infinitesimal changes. A generating function of the form F_2 in Eq. (0.55) can accomplish this via

$$F_2(\mathbf{q}, \tilde{\mathbf{p}}, t) = q^\alpha \tilde{p}_\alpha + \epsilon G(\mathbf{q}, \tilde{\mathbf{p}}, t), \tag{0.58}$$

where ϵ is infinitesimally small, and G is the **generator** of the infinitesimal transformation. The canonical transformation equations (0.56) then give

$$p_\alpha = \tilde{p}_\alpha + \epsilon \frac{\partial G}{\partial q^\alpha}, \qquad \tilde{q}_\alpha = q^\alpha + \epsilon \frac{\partial G}{\partial \tilde{p}^\alpha}, \qquad \tilde{H} = H + \frac{\partial G}{\partial t}, \tag{0.59}$$

or in terms of infinitesimal changes,

$$\delta p_\alpha = -\epsilon \frac{\partial G}{\partial q^\alpha}, \qquad \delta q_\alpha = \epsilon \frac{\partial G}{\partial \tilde{p}^\alpha}, \qquad \delta H = \frac{\partial G}{\partial t}. \tag{0.60}$$

Since we only need to track first-order changes for infinitesimal transformations, we can drop the distinction between $\mathbf{p}$ and $\tilde{\mathbf{p}}$, which is second order in ϵ, and regard the generator $G = G(\mathbf{q}, \mathbf{p}, t)$, so that

$$\delta p_\alpha = -\epsilon \frac{\partial G}{\partial q^\alpha}, \qquad \delta q_\alpha = \epsilon \frac{\partial G}{\partial p^\alpha}, \qquad \delta H = \frac{\partial G}{\partial t}.$$

(infinitesimal canonical transformation) (0.61)

Noting the similarity to Hamilton's equations (0.27), we can use the compact coordinates defined in Section 0.4.3.1 to write

$$\delta z^\alpha = \epsilon I^{\alpha\beta} \frac{\partial G}{\partial z^\beta} = \epsilon [z^\alpha, G]_{\text{P}},$$

(infinitesimal canonical transformation) (0.62)

in analogy to the Poisson-bracket form of Hamilton's equations (0.40). More generally, for any phase-space function $f(\mathbf{z})$, the infinitesimal canonical transformation has the same form:

$$\delta f = \epsilon [f, G]_{\text{P}}. \tag{0.63}$$

(infinitesimal canonical transformation)

Comparison to the Hamilton equations (0.40) shows for example that the Hamiltonian H is the generator for infinitesimal time translations, where $\epsilon = dt$. [Similarly, for example, linear momentum generates spatial translations, position coordinates generate (negative) momentum changes, and angular momentum generates rotations.]

0.4.4.2 The Poisson Bracket Under Canonical Transformations

Now consider a time-independent coordinate change $\tilde{z}^\alpha = \tilde{z}^\alpha(z)$, with the coordinates defined again as in Section 0.4.3.1. The Hamiltonian is a scalar, so $H(z) = \tilde{H}(\tilde{z})$, and so in the new coordinate system,

$$\partial_t \tilde{z}^\mu = \frac{\partial \tilde{z}^\mu}{\partial z^\alpha} \partial_t z^\alpha = \frac{\partial \tilde{z}^\mu}{\partial z^\alpha} I^{\alpha\beta} \frac{\partial H}{\partial z^\beta} = \left[\frac{\partial \tilde{z}^\mu}{\partial z^\alpha} I^{\alpha\beta} \frac{\partial \tilde{z}^\nu}{\partial z^\beta} \right] \frac{\partial H}{\partial \tilde{z}^\nu}. \tag{0.64}$$

Thus we can define

$$J^{\mu\nu} := \frac{\partial \tilde{z}^\mu}{\partial z^\alpha} I^{\alpha\beta} \frac{\partial \tilde{z}^\nu}{\partial z^\beta}, \tag{0.65}$$

which transforms as a contravariant tensor and is called the **cosymplectic two-form** ($I^{\alpha\beta}$ is the **cosymplectic form in canonical coordinates**). Hamilton's equations in the new coordinates can be written

$$\partial_t \tilde{z}^\mu = J^{\mu\nu}\frac{\partial H}{\partial \tilde{z}^\nu} = [z^\mu, H]_{\text{P}}, \tag{0.66}$$

and the Poisson bracket is

$$[f,g]_{\text{P}} = \frac{\partial f}{\partial \tilde{z}^\mu} J^{\mu\nu}\frac{\partial g}{\partial \tilde{z}^\nu}. \tag{0.67}$$

This is a nice way to view a canonical transformation: A coordinate transformation $\tilde{z}^\alpha = \tilde{z}^\alpha(z)$ is a canonical transformation if it leaves the cosymplectic form intact, $J^{\mu\nu} = I^{\mu\nu}$, or

$$I^{\mu\nu} = \frac{\partial \tilde{z}^\mu}{\partial z^\alpha} I^{\alpha\beta}\frac{\partial \tilde{z}^\nu}{\partial z^\beta}, \tag{0.68}$$

as a more direct expression for the transformation.

0.0.4.3 Geometry of The Poisson Bracket

As a side note, the Poisson bracket defines the binary operation for a **Lie algebra** of differentiable phase-space functions, which in turn defines the flow of classical trajectories. That is, if f, g, and h are arbitrary, differentiable phase-space functions, the Poisson bracket must satisfy:

1. bilinearity: $[f+g,h]_{\text{P}} = [f,h]_{\text{P}} + [g,h]_{\text{P}}$
2. product rule: $[fg,h]_{\text{P}} = f[g,h]_{\text{P}} + g[f,h]_{\text{P}}$
3. antisymmetry: $[f,g]_{\text{P}} = -[g,f]_{\text{P}}$
4. the **Jacobi identity**: $[f,[g,h]_{\text{P}}]_{\text{P}} + [g,[h,f]_{\text{P}}]_{\text{P}} + [h,[f,g]_{\text{P}}]_{\text{P}} = 0$

To understand the significance of the Poisson bracket in this regard, we need to go a bit into vector fields on manifolds. To avoid going overboard on mathematical definitions, we will be a little vague and say that a **differential manifold** is a space that looks locally like $\mathbb{R}^n$. That is, close enough to any point on the manifold, it is possible to define a system of Cartesian coordinates associated with a neighborhood of that point; and where coordinate systems associated with different points overlap, the coordinate transformations are well-defined. Then we can define a **curve** on a differential manifold M to be a continuous, differentiable function (more specifically and more strongly, a **diffeomorphism**) $f : \mathbb{R} \longrightarrow M$, which is parameterized by $\lambda \in \mathbb{R}$. Since we have a differential manifold, we can think of f as depending on local coordinates and the parameter as $f[z^\mu(\lambda)]$. Now differentiating with respect to λ and using the chain rule,

$$\frac{df}{d\lambda} = \frac{\partial f}{\partial z^\mu}\frac{dz^\mu}{d\lambda}. \tag{0.69}$$

This relation holds for *any* function, so we need not write the function explicitly:

$$\frac{d}{d\lambda} = \left(\frac{dz^\mu}{d\lambda}\right)\frac{\partial}{\partial z^\mu}. \tag{0.70}$$

Note the analogy of this relation with the more familiar form for the displacement vector:

$$\mathbf{r} = x\hat{x} + y\hat{y} + z\hat{z} = z^\mu \hat{z}_\mu. \tag{0.71}$$

And so we can think of $d/d\lambda$ as a **vector on the manifold** or **tangent vector**, where the $\partial/\partial z^\mu$ are the **basis vectors** in the local coordinates z^μ, and the scalars $dz^\mu/d\lambda$ are the **vector components** in these coordinates.

The set of all such vectors at the point p is the **tangent vector space** at p, denoted T_pM; the tangent space has the same dimension as M. The **tangent bundle**, denoted TM, is the collection of all

tangent spaces on M, and has dimension $2n$ (we mentioned the tangent bundle before in Section 0.4). The importance of all this in dynamical systems is that the tangent bundle can be used to represent the **flow** of trajectories along the manifold. In mechanical terms, the generalized position coordinates q^α lie on a configuration-space manifold (say, still of dimension n). The velocities $\dot{q}^\alpha$ in the Lagrangian picture are associated with the tangent spaces; they are *components* of tangent vectors in the same sense as Eq. (0.69) via the time-parameterized trajectories $q^\alpha(t)$ and

$$\frac{dq^\alpha}{dt} = \frac{\partial q^\alpha}{\partial q^\beta}\frac{dq^\beta}{dt}, \tag{0.72}$$

so that

$$\frac{d}{dt} = \left(\frac{dq^\beta}{dt}\right)\frac{\partial}{\partial q^\beta}. \tag{0.73}$$

The full state space of points $(q^\alpha, \dot{q}^\alpha)$ is the tangent bundle.

The Hamiltonian picture is slightly different and complementary to the Lagrangian version. It is couched in terms of a complementary object to the tangent vector—the **differential** of a function f, which we can *define* as a linear functional mapping a vector $\mathbf{v}$ at a point p on the manifold to a scalar as

$$df(\mathbf{v}) := \mathbf{v}_p(f), \tag{0.74}$$

or if $\mathbf{v} = d/d\lambda$,

$$df\left(\frac{d}{d\lambda}\right) = \frac{df}{d\lambda} \tag{0.75}$$

with the equation here being understood to hold at the point p. This differential, or **differential form** or **one-form**, also can be expressed in terms of a coordinate basis dx^α, which satisfies

$$dx^\alpha\left(\frac{\partial}{\partial x^\beta}\right) = \frac{\partial x^\alpha}{\partial x^\beta} = \delta^\alpha{}_\beta. \tag{0.76}$$

A general one-form can be written in components as

$$\boldsymbol{\omega} = \omega_\alpha\, dx^\alpha =: \boldsymbol{\omega}\left(\frac{\partial}{\partial x^\alpha}\right)\, dx^\alpha, \tag{0.77}$$

so that the differential of a function in components is

$$df = df\left(\frac{\partial}{\partial x^\alpha}\right)\, dx^\alpha = \frac{\partial f}{\partial x^\alpha}\, dx^\alpha, \tag{0.78}$$

just as we expect from ordinary calculus. Where derivatives are vectors, one-forms are **covectors**, because vectors and covectors combine in an inner product to yield a scalar. In this sense, covectors are dual to vectors, and covectors at a point p on the manifold belong to the **cotangent space** at p, and the manifold M along with the collection of all cotangent spaces is the **cotangent bundle**, denoted T^*M.

The generalized momenta p_α lie in the cotangent space at the corresponding point q^α on the coordinate-space manifold. The combined coordinate vector z^α defined by $z^\alpha = q^\alpha$ and $z^{n+\alpha} = p_\alpha$ for $\alpha \in \{1, \ldots, n\}$ is thus a point in the $2n$-dimensional cotangent bundle, which represents the full **phase space** for a Hamiltonian system. In particular, this cotangent bundle is a **symplectic manifold**. The Lagrangian is a function mapping the tangent bundle TM to a scalar, $L : TM \longrightarrow \mathbb{R}$, and the Hamiltonian a function mapping the cotangent bundle T^*M to a scalar, $H : T^*M \longrightarrow \mathbb{R}$.

The geometry of this manifold structure is reflected in the notation with raised indices for coordinates q^α and $\dot{q}^\alpha$, but lowered indices for momenta p_α. Briefly,[3] the components of a vector (or **covariant vector**, which transform in the same way as coordinate differentials dq^α) are notated with a raised index, while a

[3]For more details, see Theodore Frankel, *The Geometry of Physics An Introduction*, 3rd ed. (Cambridge, 2012) Section 2.3c (ISBN: 9781107602601).

lowered index denotes components of a covector (or **contravariant vector**, which transforms in the way *opposite* to q^α, which is to say like $\partial/\partial q^\alpha$). Again, vectors and covectors (or covariant and contravariant vectors) are paired to form a scalar in an inner product, which is to say that one raised index and one lowered index are combined in a sum to give a scalar. The $\dot{q}^\alpha$ transform also as the components of a vector, while the momentum components $p_\alpha = \partial L/\partial \dot{q}^\alpha$, being defined through a derivative, transform contravariantly. The Lagrangian (equivalently, the Hamiltonian) thus gives extra structure to a manifold by identifying vectors with covectors, or equivalently points on TM with points on T^*M. Confusingly, it is worth remembering that basis vectors themselves are derivatives like $\partial/\partial q^\alpha$, which have lowered indices; they can be combined with raised-index vector *components* to form a component-free vector, as in Eq. (0.73). Similarly, basis covectors like dq^α have raised indices, which can be combined with lowered-index covector components to form a component-free one-form, as in Eq. (0.78). Note that in going over to quantum mechanics, this structure of a symplectic manifold underlying the Hamiltonian is lost to an operator structure, so the use of raised/lowered indices is not useful in this way in quantum mechanics.

Now back to the Poisson bracket, which was the whole point of introducing all this differential geometry. For any phase-space function $f(q,p)$, the Poisson bracket defines a canonical Hamiltonian vector field L_f by

$$L_f g := [g,f]_{\text{P}} \tag{0.79}$$

for any function g. In coordinates, the vector field is

$$L_f = I^{\mu\nu}\frac{\partial f}{\partial z^\nu}\frac{\partial}{\partial z^\mu}. \tag{0.80}$$

It turns out, for example, that (Problem 0.8)

$$[L_f, L_g] = -L_{[f,g]_{\text{P}}}, \tag{0.81}$$

where $[L_f, L_g] = L_f L_g - L_g L_f$ is the commutator; thus a vanishing Poisson bracket of two functions gives rise to a pair of commuting vector fields. This means that the transformations (flows) induced by the two vector fields can be applied in either order to obtain the same net, final transformation.

0.4.5 Hamilton–Jacobi Equation and Action–Angle Variables

One important motivation for considering canonical transformations is the following question: Is it possible to make a transformation to coordinates where the dynamics of a system are trivial, and thereby solve the equations of motion? In particular, a coordinate q^α is said to be *ignorable* if the Hamiltonian does not depend on it, so that it follows from Hamilton's equations that

$$\frac{\partial H}{\partial q^\alpha} = 0. \tag{0.82}$$

In this case, the conjugate momentum p_α is a constant of the motion, and the coordinate drifts linearly with time. Thus, if we can concoct a canonical transformation from the original variables (q^α, p_α) to new variables $(\theta^\alpha, J_\alpha)$ such that the new Hamiltonian $\tilde{H}(\mathbf{J})$ depends only on the new momenta, then all the new coordinates are ignorable and we can trivially write down the solutions to the equations of motion:

$$\dot{J}_\alpha = -\frac{\partial \tilde{H}}{\partial \theta^\alpha} = 0, \qquad \dot{\theta}^\alpha = \frac{\partial \tilde{H}}{\partial J_\alpha} =: \Omega^\alpha(\mathbf{J}). \tag{0.83}$$

Such canonical coordinates are called **action-angle variables** for the system.

How do we effect this transformation from the old Hamiltonian $H(\mathbf{q},\mathbf{p})$ to the action-angle Hamiltonian $\tilde{H}(\mathbf{J})$? First, we will only consider time-independent Hamiltonians, since a time-dependent system is equivalent to a larger autonomous (time-independent) system (Problem 0.5). Now we seek a generating function of the form $S(q,J)$, of the form of F_2 from Eq. (0.55), which gives the transformation equations

$$p_\alpha = \frac{\partial}{\partial q^\alpha}S(\mathbf{q},\mathbf{J}), \qquad \theta^\alpha = \frac{\partial}{\partial J_\alpha}S(\mathbf{q},\mathbf{J}). \tag{0.84}$$

The old and new Hamiltonians are related by

$$H\left(\mathbf{q}, \frac{\partial S}{\partial \mathbf{q}}\right) = \tilde{H}(\mathbf{J}).$$

(time-independent Hamilton–Jacobi equation) (0.85)

The new Hamiltonian may be regarded as a constant, and old momenta are replaced by derivatives with respect to q^α so that we may regard this as being a partial differential equation, in particular the **time-independent Hamilton-Jacobi equation**. This is, in general, a difficult, nonlinear partial differential equation. For example, in the case of a Hamiltonian of the form

$$H(\mathbf{q}, \mathbf{p}) = \frac{p^2}{2m} + V(\mathbf{q}), \tag{0.86}$$

and taking the constant, transformed Hamiltonian to be $\tilde{H}(\mathbf{J}) = E$, Eq. (0.85) takes the form

$$\frac{(\nabla S)^2}{2m} + V(\mathbf{q}) = E.$$

(time-independent Hamilton–Jacobi equation) (0.87)

Despite the nonlinearity, this equation is interesting as a representation of classical (particle) dynamics in terms of a wave equation. Note that the existence of a solution implies the existence of N constants of the motion (the momenta) for an N-degree-of-freedom system, and is thus only possible for classes of systems that are said to be **integrable**.

The Hamilton–Jacobi equation (0.85) is commonly written in the alternate form

$$\frac{\partial S}{\partial t} + H\left(\mathbf{q}, \frac{\partial S}{\partial \mathbf{q}}\right) = 0. \tag{0.88}$$

(Hamilton–Jacobi equation)

To see where this comes from, consider the connection of S to the alternate generating function $\tilde{S}$ via

$$S = \tilde{S} + Et, \tag{0.89}$$

where again $\tilde{H}(\mathbf{J}) = E$. Then according to the transformation rule for the Hamiltonian in Eqs. (0.56), Eq. (0.85) is satisfied in terms of $\tilde{S}$. The analogous form of Eq. (0.87) for the standard particle Hamiltonian is then

$$\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} + V(\mathbf{q}) = 0. \tag{0.90}$$

(Hamilton–Jacobi equation)

Thus, while Eq. (0.85) yields a transformation to coordinates where the Hamiltonian is constant, Eq. (0.88) yields a transformation to coordinates where the new Hamiltonian is *zero*.

0.4.5.1 One Degree of Freedom

Every (autonomous) one-degree-of-freedom system is obviously integrable because the energy is conserved, and we need only one conserved quantity for the system to be integrable. Thus, we can explicitly construct the transformation to action-angle variables. The second generating-function relation is

$$\theta = \frac{\partial}{\partial J} S(\mathbf{q}, J), \tag{0.91}$$

which we may differentiate to obtain

$$\frac{\partial \theta}{\partial q} = \frac{\partial}{\partial J} \frac{\partial S}{\partial q}. \tag{0.92}$$

We require that on one period of an orbit in action-angle variables that the position (angle) changes by exactly 2π,

$$2\pi = \oint d\theta = \frac{\partial}{\partial J} \oint \frac{\partial S}{\partial q}\, dq = \frac{\partial}{\partial J_\alpha} \oint p\, dq = \frac{\partial}{\partial J_\alpha} \oint p\, dq, \tag{0.93}$$

where the contour integral is evaluated once around the periodic orbit and the last equality follows from the other generating-function relation $p = \partial S/\partial q$. We may satisfy this constraint by defining the action variable such that

$$J = \frac{1}{2\pi} \oint p(q, \tilde{H})\, dq, \tag{0.94}$$

where the explicit dependence of p emphasizes that the contour integral is taken along a contour of constant energy in the original phase space. The corresponding generating function is given by

$$S = \int_{q_0}^{q} p(q, \tilde{H})\, dq, \tag{0.95}$$

which we can recognize from the reduced action (0.31) of Maupertuis' principle. In some sense, we must thus already know the solution to the equations of motion to construct the action-angle variables for the system. Again, the new equations of motion are trivial, though, since J is a constant of the motion and $\theta = \theta(0) + \Omega(J)t$, where $\Omega(J) = \partial \tilde{H}(J)/\partial J$.

For higher-dimensional systems, the Hamilton-Jacobi equation is only solvable for **separable** systems, systems of N degrees of freedom that decouple into N independent, one-degree-of-freedom systems.

0.4.6 Generalized Variational Principle

By this point we have already considered variational principles, but it is useful to revisit them now that we have the extra tools of infinitesimal canonical transformations, Poisson brackets, and so on. In particular, let's go back to the action functional (0.18) in terms of the Lagrantian,

$$S[L] := \int_{t_1}^{t_2} L(\mathbf{q}, \dot{\mathbf{q}}; t)\, dt, \tag{0.96}$$

where we considered a variation $\delta\mathbf{q}(t)$ to the path with fixed endpoints $\delta\mathbf{q}(t_1) = \delta\mathbf{q}(t_2) = 0$. But now let's consider a generalized variation of the action,[4] where the end times t_1 and t_2 are also allowed to vary by δt_1 and δt_2, respectively. We can think of this as an added perturbation δt to t (δt being itself a function of t, just like $\delta\mathbf{q}(t)$), where $\delta t(t_1) = \delta t_1$ and $\delta t(t_2) = \delta t_2$. Then we can write the perturbed action as

$$S + \delta S = \int_{t_1+\delta t_1}^{t_2+\delta t_2} d(t + \delta t)\, L(\mathbf{q} + \delta\mathbf{q}, \dot{\mathbf{q}} + \delta\dot{\mathbf{q}}; t + \delta t), \tag{0.97}$$

where S is still given by Eq. (0.96). To work with the integral here, the first thing is to change the integration variable back to t, via $d(t + \delta t) = dt + \delta\dot{t}\, dt = (1 + \delta\dot{t})\, dt$. Making this change also undoes the variation of the integration limits, and the result is

$$S + \delta S = \int_{t_1}^{t_2} dt\, (1 + \delta\dot{t})\, L(\mathbf{q} + \delta\mathbf{q}, \dot{\mathbf{q}} + \delta\dot{\mathbf{q}}; t + \delta t). \tag{0.98}$$

Taylor expanding and keeping terms only to first order in the variations, we have

$$\delta S = \int_{t_1}^{t_2} dt \left(\frac{\partial L}{\partial q^\alpha}\delta q^\alpha + \frac{\partial L}{\partial \dot{q}^\alpha}\delta\dot{q}^\alpha + \frac{\partial L}{\partial t}\delta t + \delta\dot{t} L \right). \tag{0.99}$$

Integration by parts to eliminate derivatives of variations, we find

$$\delta S = \int_{t_1}^{t_2} dt \left(\frac{\partial L}{\partial q^\alpha} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}^\alpha} \right) \delta q^\alpha + \Big[p_\alpha\, \delta q^\alpha \Big]_{t_1}^{t_2} + \int_{t_1}^{t_2} dt \left(\frac{\partial L}{\partial t} - \frac{dL}{dt} \right) \delta t + \Big[L\, \delta t \Big]_{t_1}^{t_2}. \tag{0.100}$$

[4] Here we are closely following (including the fancy $\oint$ notation) Paul Roman, *Advanced Quantum Theory: An Outline of the Fundamental Ideas* (Addison–Wesley, 1965) (ISBN: 0201064952), pp. 6–9. See also K. A. Milton, *Schwinger's Quantum Action Principle: From Dirac's formulation through Feynman's path integrals, the Schwinger-Keldysh method, quantum field theory, to source theory* (arXiv: 1503.08091).

The notable difference from what we did before is that we will not summarily dismiss the boundary terms—they are in fact the entire point of this exercise. Now in the boundary terms we can use the same notations $p_\alpha = \partial L/\partial \dot{q}^\alpha$ and $L = p_\alpha \dot{q}^\alpha - H$ as before from Hamiltonian mechanics, but at this point we should not think of these as definitions for p_α and H. Using these definitions, we can then write the variation as

$$\delta S = \int_{t_1}^{t_2} dt \left(\frac{\partial L}{\partial q^\alpha} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}^\alpha} \right) \delta q^\alpha + \int_{t_1}^{t_2} dt \left(\frac{\partial L}{\partial t} - \frac{dL}{dt} \right) \delta t + \Big[p_\alpha \, \not\delta q^\alpha - H \, \delta t \Big]_{t_1}^{t_2}, \tag{0.101}$$

where we have defined the *total* variation

$$\not\delta \mathbf{q}(t) := \big[\mathbf{q}(t + \delta t) + \delta \mathbf{q}(t + \delta t) \big] - \mathbf{q}(t) = \delta \mathbf{q}(t) + \dot{\mathbf{q}} \, \delta t, \tag{0.102}$$

which includes the effects of both $\delta \mathbf{q}$ and δt on $\mathbf{q}(t)$. At this point we will assume that all of our previous conclusions carry through here. That is, the system obeys the equations of motion

$$\frac{\partial L}{\partial q^\alpha} - \frac{d}{dt}\frac{\partial L}{\partial \dot{q}^\alpha} = 0, \qquad \frac{\partial L}{\partial t} = \frac{dL}{dt}, \tag{0.103}$$

which result from the fixed-endpoint variation of the same action. Then the variation becomes

$$\delta S = \Big[p_\alpha \, \not\delta q^\alpha - H \, \delta t \Big]_{t_1}^{t_2}, \tag{0.104}$$

having been reduced to only boundary terms. It is at this point that we can discuss the definitions of $\mathbf{p}$ and H—this expression can serve to *define* the conjugate variables to $\mathbf{q}$ and δt as the coefficients of their variations.

To show that the formalism here is still equivalent to the standard Hamiltonian formalism, consider the first variation of the Hamiltonian:

$$\delta H = \frac{\partial H}{\partial q^\alpha} \delta q^\alpha + \frac{\partial H}{\partial p_\alpha} \delta p_\alpha. \tag{0.105}$$

Using $H = p_\alpha \dot{q}^\alpha - L$ to evaluate the derivatives, and then the Euler–Lagrange equation in Eqs. (0.103), we find

$$\begin{aligned} \delta H &= -\frac{\partial L}{\partial q^\alpha} \delta q^\alpha + \dot{q}^\alpha \, \delta p_\alpha \\ &= -\left(\frac{d}{dt}\frac{\partial L}{\partial \dot{q}^\alpha} \right) \delta q^\alpha + \dot{q}^\alpha \, \delta p_\alpha. \end{aligned} \tag{0.106}$$

Matching up the coefficients of the independent variations in Eqs. (0.105) and (0.106) yields Hamilton's equations.

0.4.6.1 Infinitesimal Generator

The action variation (0.104) is written as a difference of boundary terms, which we can define as

$$F(t) := p_\alpha \, \not\delta q^\alpha - H \, \delta t, \tag{0.107}$$

so that the action variation is compactly

$$\delta S = F(t_2) - F(t_1). \tag{0.108}$$

The significance of the quantity defined in Eq. (0.107) is that it is a generator of an infinitesimal canonical transformation . As written here, it includes the infinitesimal part, so that for a small parameter change δs this generator is

$$F = \delta s \, G_s \tag{0.109}$$

where G_s generates a change in our previous notation (Section 0.4.4.1) of δf in a phase-space function f according to

$$\delta f = \delta s \, [f, G]_{\text{P}}, \tag{0.110}$$

in terms of the Poisson bracket.

To show that $F(t)$ is indeed the infinitesimal generator, we can consider two separate variations.

1. Consider first a variation $\delta\mathbf{q}$, with no variation of $\mathbf{p}$ or t. Then $\not\delta q = \delta q$ (because $\delta t = 0$), and the generator becomes $F = p_\alpha\,\delta q^\alpha$ (or $G_\alpha = p_\alpha$). Then the Poisson bracket of $\mathbf{q}$ with F is

$$[q^\alpha, F]_{\text{P}} = \delta q^\beta [q^\alpha, p_\beta]_{\text{P}} = \delta^\alpha_\beta \delta q^\beta = \delta q^\alpha, \tag{0.111}$$

   and similarly, $[p_\alpha, F]_{\text{P}} = 0$. Thus, G_α (i.e., F) is indeed the generator for δq^α.

2. Now consider a time variation δt, with no variation $\not\delta\mathbf{q}$ or $\not\delta\mathbf{p}$. Then $F = -H\,\delta t$ (or $G = -H$). Then we have the Poisson brackets

$$[q^\alpha, F]_{\text{P}} = -[q^\alpha, H]_{\text{P}}\delta t = -\frac{\partial H}{\partial p_\alpha}\delta t = -\dot{q}^\alpha\,\delta t \tag{0.112}$$

   and

$$[p_\alpha, F]_{\text{P}} = -[p^\alpha, H]_{\text{P}}\delta t = \frac{\partial H}{\partial q^\alpha}\delta t = -\dot{p}^\alpha\,\delta t, \tag{0.113}$$

   which generate evolution of $\mathbf{q}$ and $\mathbf{p}$. The minus signs here may seem to be a little odd; the reason for them is due to the total variation $\not\delta\mathbf{q}(t) = \delta\mathbf{q}(t) + \dot{\mathbf{q}}\,\delta t$ (and the equivalent expression for $\mathbf{p}$), with the condition $\not\delta\mathbf{q} = \not\delta\mathbf{p} = 0$, gives $\delta\mathbf{q} = -\dot{\mathbf{q}}\,\delta t$ and $\delta\mathbf{p} = -\dot{\mathbf{p}}\,\delta t$.

Thus the function $F(t)$ of Eq. (0.107) that appears in the action variation generates arbitrary evolution in terms of the generalized coordinate and of time.

0.4.6.2 Symmetries and Conserved Quantities

A useful application of the considerations above is in treating symmetries of a system. Such a symmetry occurs when a parameter change δs leaves the system invariant, in the sense that the action and the Lagrangian are unchanged:

$$\frac{\delta S}{\delta s} = 0, \qquad \frac{\partial L}{\partial s} = 0. \tag{0.114}$$

From Eq. (0.108), because the variation vanishes, $\delta S = 0$, we must have $F(t_2) = F(t_1)$. That is, $\partial F/\partial t = 0$ in differential form, and removing the infinitesimal change from the generator in the form $F = \delta s\, G_s$, we have that

$$\frac{\partial G_s}{\partial t} = 0. \tag{0.115}$$
(generator as conserved quantity)

That is, **the generator of a transformation that leaves the system invariant is a conserved quantity**. This is a statement of **Noether's theorem**,[5] and a powerful consequence of the symmetries of a system. As simple examples from the generators that we have worked out, time invariance of the Lagrangian ($\partial L/\partial t = 0$) implies that the Hamiltonian is a constant of the motion (conservation of energy). Translation invariance ($\partial L/\partial q^\alpha = 0$) implies conservation of momentum p_α. Also, angular momentum turns out to be the generator for rotations, and so rotational invariance implies conservation of angular momentum.

0.5 Constrained Dynamics

An important and useful complication that comes up in classical and quantum systems is that of a **constraint**, where the entire coordinate space is not accessible in the dynamical evolution of a system. For now suppose that we consider constraints specified in the form

$$f(\mathbf{q}, t) = 0, \tag{0.116}$$

[5] Or technically, Noether's *first* theorem, from Emmy Noether, "Invariante Variationsprobleme," *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klasse* **1918**, 235 (1918) (EuDML: 59024). English translation by M. A. Tavel: Emmy Noether, "Transport Theory and Statistical Physics," *Transport Theory and Statistical Physics* **1**, 186 (1971) (doi: 10.1080/00411457108231446) (arXiv: physics/0503066).

which depends only on the generalized coordinates and time. In the time-independent case, a relation of this form defines a constraint surface in coordinate space, and reduces the number of degrees of freedom of the system (i.e., the number of independent components of $\mathbf{q}$) from N to $N-1$. Of course, multiple constraints can be present, and unless the constraints are equivalent in some sense, each one will further reduce the number of degrees of freedom. Time-independent constraints like this don't perform any work on the system (intuitively these constraints produce situations like a bead sliding along a bent wire without friction). Of course, explicit time dependence in the function $f(\mathbf{q},t)$ corresponds to a time-varying constraint surface, which can do work on the system (imaging "flinging" a bead on a wire by an appropriate action on the wire). Of course, more general constraints are possible, but constraints of the form (0.116) are most straightforwardly incorporated into the equations of motion.

0.5.1 Lagrange Multiplier

To proceed, let's consider how to incorporate constraints into the Lagrangian formalism. Suppose we have a Lagrangian function of the form $L = T - V$, as in Eq. (0.16). Since the constraint function $f(\mathbf{q},t) = 0$ on the constrained manifold, we won't change anything if we simply add any multiple of it to the Lagrangian. Allowing for a time-dependent potential, we will take the Lagrangian to be

$$L(\mathbf{q},\dot{\mathbf{q}},t) = T(\dot{\mathbf{q}}) - V(\mathbf{q},t) - \lambda\, f(\mathbf{q},t), \qquad \text{(typical constrained Lagrangian)} \quad (0.117)$$

which, to reiterate the important part, is completely equivalent to the unconstrained Lagrangian with $\lambda = 0$, provided we stay on the surface defined by Eq. (0.116); of course, *off* the constraint surface, the Lagrangian has definitely been modified, and this is how the constraint will work. The coefficient function λ is so far an arbitrary function on the same space as the Lagrangian, but we will show momentarily how it can be fixed; it is called a **Lagrange multiplier**. Again, we are putting in a single constraint, but it is straightforward to tack on multiple constraints as additional terms, each with its own Lagrange multiplier. Note that the constraint term has the form of an added potential term $V_\lambda(\mathbf{q},t) = \lambda f(\mathbf{q},t)$; this will lead to an extra force that ensures the particle remains on the constraint surface.

Following common tradition, the argument of the Lagrange multiplier is omitted, this is because there are multiple (useful) ways to think about it. First, the Lagrange multiplier $\lambda(t)$ acts as an extra dynamical variable (generalized coordinate) that has been introduced to facilitate the implementation of the constraint. In particular, with the Lagrange multiplier, the constrained Lagrangian problem has been converted into an unconstrained problem on an extended coordinate space. In this sense, in terms of a variational principle, it varies independently of the $\mathbf{q}(t)$—although, of course, because $\dot{\lambda}$ is absent from the Lagrangian, the Euler–Lagrange equation does not lead to an equation of motion, but rather a constraint equation, namely $f(\mathbf{q},t) = 0$. However, in the final solution λ is typically fixed in terms of other coordinates $\mathbf{q}(t)$ via the constraint relation. In this case one can think of it as a function $\lambda(\mathbf{q},\dot{\mathbf{q}},t)$ on the coordinate space [see specifically Eq. (0.122) below]. In the interpretation of being a dynamical variable, this is to say that the time dependence $\lambda(t)$ may be different depending on the particular trajectory $\mathbf{q}(t)$ under consideration. However, it is important to note under an action principle involving the constrained Lagrangian (0.117), the variation of the action functional should not involve the variation of the Lagrange multipler, precisely because the result of the variation is what fixes the multiplier's value.

0.5.1.1 Constraint Force

With the modified Lagrangian, the action functional (0.18) is defined in the same way as before, and Hamilton's principle leads to the same Euler–Lagrange equation (0.19); in the case of the constrained Lagrangian (0.117) this becomes the set of equations of motion

$$\frac{d}{dt}\frac{\partial T}{\partial \dot{q}^\alpha} = -\frac{\partial V}{\partial q^\alpha} - \lambda\frac{\partial f}{\partial q^\alpha}. \quad (0.118)$$

Note that any term involving a derivative of λ—arising either from a variation with respect to the independent variable λ, or from thinking of λ as a function $\lambda(\mathbf{q},\dot{\mathbf{q}},t)$—is suppressed due to the condition $f = 0$. For a

particle Lagrangian with $T = m\dot{\mathbf{q}}^2$, the left-hand side is $m\ddot{\mathbf{q}}$, expressed in components; the total quantity on the right-hand side is a generalized force. Writing this case out in coordinate-independent form, we have

$$m\ddot{\mathbf{q}} = -\nabla V - \lambda \nabla f =: -\nabla V(\mathbf{q}, t) + \mathbf{C}(\mathbf{q}, t). \tag{0.119}$$

(constrained equation of motion)

Here,

$$\mathbf{C}(\mathbf{q}, t) := -\lambda \nabla f(\mathbf{q}, t) \tag{0.120}$$

(constraint force)

is the **constraint force** corresponding to the constraint (0.116). Because the constraint function $f(\mathbf{q}, t)$ is constant on the constraint surface owing to its definition in Eq. (0.116), the constraint force must be normal to the constraint surface. This matches the intuition that the constraint forces should not do any work on the particle in the case where $f(\mathbf{q}, t)$ is time-indepenent. However, we have an additional unknown parameter λ. This is in principle determined, because in the case of N degrees of freedom, we have N components of the evolution equation (0.119) plus the constraint equation (0.116), for a total of $N + 1$ conditions (not to mention the $2N$ initial conditions on $\mathbf{q}$ and $\dot{\mathbf{q}}$); this matches the $N + 1$ unknown quantities: the N components of $\mathbf{q}(t)$ plus λ.

Phrased differently and more precisely, let $\boldsymbol{\tau}$ be a vector (field) tangent to the constraint surface,

$$\boldsymbol{\tau} \cdot \nabla f = 0. \tag{0.121}$$

Thus also $\boldsymbol{\tau} \cdot \mathbf{C} = 0$, so the tangent vector is normal to the constraint force. Then Eq. (0.119) becomes

$$\boldsymbol{\tau} \cdot \Big[m\ddot{\mathbf{q}} + \nabla V \Big] = 0. \tag{0.122}$$

Since τ is arbitrary, there are $N - 1$ independent possible tangent vectors, and so Eq. (0.122) amounts to $N - 1$ independent equations of motion on the constraint surface. The constraint equation (0.116) gives the Nth condition needed to fix the full N components of $\mathbf{q}(t)$—the conditions (0.122) are only sufficient to fix the location of $\mathbf{q}(t)$ on the constraint manifold. The analogous condition

$$\mathbf{n} \cdot \Big[m\ddot{\mathbf{q}} + \nabla V \Big] = -\mathbf{n} \cdot \lambda \nabla f, \tag{0.123}$$

where $\mathbf{n}$ is a vector (field) normal to the constraint surface, gives one extra condition that determines λ, since $\mathbf{q}$ is by this time already determined, and thus so is everything else in this equation. But this shows why we needed to introduce the Lagrange multiplier λ: The gradient ∇f is (by definition) always normal to the constraint surface, and thus is always parallel to the required constraint force; however, there is some arbitrariness to how the constraint function can be defined, such that the magnitude of ∇f is not uniquely defined, and thus λ gives the required correction to the magnitude to produce the correct constraint force in the modified Lagrangian (0.117). Note that this correction differs in general depending on the point $\mathbf{q}$ on the constraint surface, as well as on the velocity $\dot{\mathbf{q}}$ and time (all of which are needed to determine the $\ddot{\mathbf{q}}$ that appears in the normal-force equation). It is in this constraint expression (0.123) that the Lagrange multiplier is ''demoted'' from a dynamical variable to a function of the other dynamical variables.

0.5.1.2 Energy Conservation

Let's talk briefly about energy conservation under the constraint. Taking the dot product of Eq. (0.119) with $\dot{\mathbf{q}}$ gives

$$m\dot{\mathbf{q}} \cdot \ddot{\mathbf{q}} = -\dot{\mathbf{q}} \cdot \nabla V - \lambda \dot{\mathbf{q}} \cdot \nabla f. \tag{0.124}$$

Now we will use the derivatives

$$\frac{d}{dt}\left(\frac{1}{2} m\dot{\mathbf{q}}^2\right) = m\dot{\mathbf{q}} \cdot \ddot{\mathbf{q}}, \qquad \frac{dV}{dt} = (\nabla V) \cdot \dot{\mathbf{q}} + \frac{\partial V}{\partial t}, \qquad \frac{df}{dt} = (\nabla f) \cdot \dot{\mathbf{q}} + \frac{\partial f}{\partial t} = 0, \tag{0.125}$$

where in the last case we use that $f = 0$, and thus $df/dt = 0$. Using these with Eq. (0.124), we can compute the derivative of the total energy as

$$\frac{dE}{dt} = \frac{d}{dt}\left[\frac{1}{2}m\dot{\mathbf{q}}^2 + V(\mathbf{q})\right] = \frac{\partial V}{\partial t} + \lambda\frac{\partial f}{\partial t}. \tag{0.126}$$

That is, energy is constant unless there is explicit time-dependence in either the potential function or the constraint function. The constraint function obviously affects the energy via the term $-\lambda\dot{\mathbf{q}}\cdot\nabla f$ in Eq. (0.124). Remember that ∇f is normal to the constraint surface, and so in the time-dependent case where $\dot{\mathbf{q}}$ is tangent to the constraint surface, this term must vanish. But in the case of a time-dependent constraint, $\dot{\mathbf{q}}$ need no longer be tangent to the surface, and this allows the constraint force $-\lambda\nabla f$ to perform work on the system (or, strictly speaking, the *rate* at which the constraint performs work on the particle may be nonzero).

0.5.1.3 Holonomic Constraints

Now to discuss a bit further the form $f(\mathbf{q}, t) = 0$ of the constraint (0.116). First, of all, we have seen the off-manifold behavior of the constraint—in particular, the gradient ∇f at the constraint surface—is important in determining the constraint force. Thus, the constraint should not have a vanishing gradient on the surface. For example, if $f(\mathbf{q}, t) = 0$ is a good constraint in this sense, then $f^2 = 0$ is *not* a good constraint, because $\nabla f^2 = 2f\nabla f = 0$ on the constraint surface.

A constraint of the form $f(\mathbf{q}, t) = 0$, with a nonvanishing gradient on the constraint surface, is called a **holonomic constraint**. Note that mechanical Lagrangians depend on $\dot{\mathbf{q}}$ as well as on $\mathbf{q}$, and we can imagine that a more general constraint could have the form

$$g(\mathbf{q}, \dot{\mathbf{q}}, t) = 0. \tag{0.127}$$

In the case of a holonomic constraint $f = 0$, it also follows that $df/dt = 0$, and thus

$$\frac{df}{dt} = (\nabla f)\cdot\dot{\mathbf{q}} + \frac{\partial f}{\partial t} = 0, \tag{0.128}$$

which amounts to a constraint on the velocities. If the constraint (0.127) can be placed into this form then it is a holonomic constraint. More generally, though, it is not holonomic.

The problem with a velocity-dependent constraint (0.127) that can't be integrated into a holonomic constraint comes from the generalization of Eq. (0.129) for the Euler–Lagrange equation including the constraint, which becomes

$$\frac{d}{dt}\frac{\partial T}{\partial\dot{q}^\alpha} + \frac{d}{dt}\left[\lambda\frac{\partial g}{\partial\dot{q}^\alpha}\right] = -\frac{\partial V}{\partial q^\alpha} + \lambda\frac{\partial g}{\partial q^\alpha}. \tag{0.129}$$

In this case, our above argument for how λ may be determined—purely as a function of the trajectories $\mathbf{q}(t)$—breaks down, because this equation now amounts to a first-order differential equation for λ. The system of equations then requires an initial value for λ in order to be well-defined. This is somewhat problematic, as it requires the initial constraint force to be specified, or equivalently a specification for $\ddot{\mathbf{q}}$.

In general, constraints that cannot be put in the holonomic form $f(\mathbf{q}, t) = 0$ are called **nonholonomic constraints**. These could also refer, for example, to constraints involving an inequality.

0.5.1.4 Example: Particle Constrained to a Circle

As a simple example of a Lagrangian constraint, suppose that we have a particle moving in a 2D potential, constrained to a circle of radius ℓ. Before the constraint, the particle Lagrangian is

$$L = \frac{1}{2}m\big(\dot{x}^2 + \dot{y}^2\big) - V(x, y, t), \tag{0.130}$$

and the constraint to implement is $r^2 = \ell^2$ (in order to avoid a square root), so that the constraint function is

$$f(x, y) = x^2 + y^2 - \ell^2 = 0. \tag{0.131}$$

Note that the gradient of f is nonvanishing at $r = \ell$. Implementing the constraint with a Lagrange multiplier, the constrained Lagrangian is

$$L = \frac{1}{2}m\big(\dot{x}^2 + \dot{y}^2\big) - V(x, y, t) - \lambda f(x, y). \tag{0.132}$$

The Euler–Lagrange equation leads to an equation of motion as in Eq. (0.119), which in this case becomes

$$m\ddot{\mathbf{r}} = -\nabla V(x, y, t) + \lambda \nabla f(x, y) = -\nabla V(x, y, t) - 2\lambda \mathbf{r}. \tag{0.133}$$

It is obviously more natural to be in cylindrical coordinates (r, θ), so we will need the time derivatives

$$\begin{aligned}
\dot{\mathbf{r}} &= \dot{r}\hat{r} + r\dot{\theta}\hat{\theta} \\
\ddot{\mathbf{r}} &= \ddot{r}\hat{r} + \dot{r}\dot{\hat{r}} + \dot{r}\dot{\theta}\hat{\theta} + r\ddot{\theta}\hat{\theta} + r\dot{\theta}\dot{\hat{\theta}} \\
&= \ddot{r}\hat{r} + 2\dot{r}\dot{\theta}\hat{\theta} + r\ddot{\theta}\hat{\theta} - r\dot{\theta}^2\hat{r} \\
&= \big(\ddot{r} - r\dot{\theta}^2\big)\hat{r} + \big(2\dot{r}\dot{\theta} + r\ddot{\theta}\big)\hat{\theta}.
\end{aligned} \tag{0.134}$$

The tangential $(\hat{\theta})$ component of Eq. (0.133) then gives the equation of motion

$$m\big(r\ddot{\theta} + 2\dot{r}\dot{\theta}\big) = -\hat{\theta} \cdot \nabla V(x, y, t) = -\frac{1}{r}\frac{\partial V}{\partial \theta}, \tag{0.135}$$

and then setting $r = \ell$ gives the usual equation of motion

$$m\ell^2\ddot{\theta} = -\frac{\partial V}{\partial \theta} \tag{0.136}$$

that applies, for example to a pendulum of inertial moment $m\ell^2$. The normal $(\hat{r})$ component of Eq. (0.133) is

$$m\big(\ddot{r} - r\dot{\theta}^2\big) = -\hat{r} \cdot \nabla V(x, y, t) - 2\lambda r = 0, \tag{0.137}$$

which, with $r = \ell$, becomes

$$2\ell\lambda = r\dot{\theta}^2 - \hat{r} \cdot \nabla V(x, y, t) \tag{0.138}$$

and thus determines λ. Alternately, we can express this as the constraint force

$$\mathbf{C}(\theta, t) = \hat{r}\left(-\ell\dot{\theta}^2 + \frac{\partial V(r, \theta, t)}{\partial r}\right) \tag{0.139}$$

on the constraint surface $r = \ell$. This force has two components; the first is the centripetal force needed to keep the particle on the circle, while the second component exactly cancels any radial force due to the potential $V(x, y, t)$.

0.5.2 Dirac's Theory of Hamiltonian Constraints

In Hamiltonian mechanics, the philosophy behind constraints is slightly different than in Lagrangian mechanics. In the Lagrangian, constraints are *added* via constraint functions and Lagrange multipliers. In Hamiltonian mechanics, the Dirac[6] or Dirac–Bergmann[7] theory of constraints shows how to deal with constraints that *already exist*. This approach is useful in dealing with classical systems that involve **gauge**

[6]The canonical reference is Paul A. M. Dirac, *Lectures on Quantum Mechanics* (Belfer Graduate School of Science, 1964) (ISBN: 1607964325); other good references are Marc Henneaux and Claudio Teitelboim, *Quantization of Gauge Systems* (Princeton, 1992) (ISBN: 069108775X); Andrew Hanson, Tullio Regge, and Claudio Teitelboim, *Constrained Hamiltonian Systems* (Accademia Nazionale dei Lincei, 1976) (ISBN: 8821803120); and Vladimir I. Arnold, Valery V. Kozlov, and Anatoly I. Neishtadt, *Mathematical Aspects of Classical and Celestial Mechanics*, 3rd ed. (Springer, 2000) (ISBN: 3-540-28246-7), Section 1.5, p. 48.

[7]After Peter Bergmann; for a historical overview see D. C. Salisbury, ''Peter Bergmann and the Invention of Constrained Hamiltonian Dynamics,'' in *Einstein and the Changing Worldviews of Physics*, Christoph Lehner, Jürgen Renn, and Matthias Schemmel, Eds. (Birkhäuser, 2012) (ISBN: 9780817649401) (doi: 10.1007/978-0-8176-4940-1_11), p. 247 (arXiv: physics/0608067).

freedom—different sets of coordinate values that correspond to the same physical state. Once these are handled in classical mechanics, there is then a route to handling the quantization of gauge systems.

The origin of constraints in Hamiltonian systems goes back to the Hessian condition (0.21). Recall that when recast in the form (0.23),

$$\det\left(\frac{\partial p_\alpha}{\partial \dot{q}^\beta}\right) \neq 0, \tag{0.140}$$

there is a valid transformation between the velocities and conjugate momenta. But problematic cases where this determinant vanishes can arise in a number of ways. One important case is where a particular component $\dot{q}^j$ of the velocity does not appear at all in the Lagrangian; in this case the canonical momentum $p_j = \partial L/\partial \dot{q}^j = 0$, in which case there is clearly no mapping from this velocity component to its corresponding momentum. We have already seen this in the case of Lagrange multipliers, as in the constrained Lagrangian (0.117). If $\lambda(t)$ is regarded as one of the generalized coordinates, then because $\dot{\lambda}$ does not appear in the Lagrangian, the corresponding Euler-Lagrange equation just yields the constraint equation $f = 0$. Thus, any constraints introduced via Lagrange multipliers in the Lagrangian carry naturally over to the Hamiltonian formalism, provided care is taken to identify them and treat them appropriately, as we will show below.

To see slightly more broadly how problematic coordinates can crop up, consider a Lagrangian of the form

$$L(\mathbf{q}, \dot{\mathbf{q}}; t) = T_2(\dot{\mathbf{q}}) + T_1(\dot{\mathbf{q}}) + T_0(\dot{\mathbf{q}}) - V(\mathbf{q}), \tag{0.141}$$

where $T_n(\dot{\mathbf{q}})$ is Euler homogeneous of degree n, which means that for any scalar α,

$$T_n(\alpha\dot{\mathbf{q}}) = \alpha^n T_n(\dot{\mathbf{q}}). \tag{0.142}$$

That is, T_2 includes "normal" (quadratic) kinetic energies, T_1 includes linear functions, and T_0 includes constant functions. By differentiating with respect to λ and then setting $\lambda = 1$, these functions satisfy the important relation

$$\dot{\mathbf{q}} \cdot \frac{\partial T_n}{\partial \dot{\mathbf{q}}} = n T_n(\dot{\mathbf{q}}). \tag{0.143}$$

Then using this relation, we can write down the corresponding Hamiltonian as

$$\begin{aligned} H(\mathbf{q}, \mathbf{p}; t) &= \dot{\mathbf{q}} \cdot \mathbf{p} - L \\ &= \dot{\mathbf{q}} \cdot \left(\frac{\partial T_2}{\partial \dot{\mathbf{q}}} + \frac{\partial T_1}{\partial \dot{\mathbf{q}}} + \frac{\partial T_0}{\partial \dot{\mathbf{q}}}\right) - T_2(\dot{\mathbf{q}}) - T_1(\dot{\mathbf{q}}) - T_0(\dot{\mathbf{q}}) + V(\mathbf{q}) \\ &= T_2(\dot{\mathbf{q}}) - T_0(\dot{\mathbf{q}}) + V(\mathbf{q}), \end{aligned} \tag{0.144}$$

where of course the velocities should still be replaced by momenta. But consider the case where a particular velocity component $\dot{q}^j$ *only* appears in T_1, something that will lead to a vanishing Hessian determinant. In this case the corresponding momentum is absent from the Hamiltonian.

An analogous situation (though not problematic as far as the Hessian condition is concerned) is a Lagrangian independent of a particular coordinate q^j—that is, there a translational symmetry in this direction. In this case the corresponding momentum is conserved, amounting to a constraint equation for the momentum, and the coordinate is said to be an **ignorable coordinate**.

0.5.2.1 Primary Constraints

Thus we see that in the case where the Hessian condition fails,

$$\det\left(\frac{\partial \mathbf{p}}{\partial \dot{\mathbf{q}}}\right) = 0, \tag{0.145}$$

the coordinate transformation from velocities to momenta is ill-defined, because the momenta are not all independent. That is, there must be constraint relations among the canonical variables of the form

$$\phi(\mathbf{q}, \mathbf{p}) = 0, \tag{0.146}$$

in the case of an autonomous Hamiltonian system $\partial H/\partial t = 0$ (which results in no loss of generality, as we noted before). A constraint of this type—arising directly from a failure to use the full set of momenta as dynamical variables—is called a **primary constraint**. Of course, there can be multiple such constraints, and the generalization to multiple constraints from a single constraint will be reasonably obvious. Note that the constraint here is more general than the holonomic constraint (0.116), in the sense that it effectively includes constraints on the velocities.

Since the constraint function ϕ vanishes on the constraint surface, the Hamiltonian is unchanged if we modify it by adding on the constraint function along with a Lagrange multiplier in essentially the same way as before, as in

$$\tilde{H}(\mathbf{q},\mathbf{p}) = H(\mathbf{q},\mathbf{p}) + \lambda\,\phi(\mathbf{q},\mathbf{p}).$$

(Hamiltonian with Lagrange multiplier) (0.147)

That is this modification of the Hamiltonian is irrelevant as far as the physical trajectories are concerned. Here, the multiplier λ has the same interpretation as in the Lagrangian case; it can act as a dynamical variable, or it can act as a function of the phase-space variables. If we regard λ as a generalized coordinate, the Hamilton equation $\dot{p}_\alpha = -\partial H/\partial q^\alpha$ yields the constraint equation $\phi(\mathbf{q},\mathbf{p}) = 0$. Because $\dot{\lambda}$ does not appear in the corresponding Lagrangian, the conjugate momentum $p_\alpha = \partial L/\partial \dot{q}^\alpha$ ends up just being $p_\lambda = 0$. This was one of the possible symptoms of a constraint associated with a singular Lagrangian that we alluded to above.

As we will see, the distinction between relations valid only on the constraint manifold vs. valid throughout phase space. Dirac's notation to distinguish these cases is "$\approx$" to mean "weak equality," or equivalence only on the constraint surface, whereas the normal equality applies throughout phase space. In this notation, Eq. (0.146) is

$$\phi(\mathbf{q},\mathbf{p}) \approx 0, \tag{0.148}$$

and Eq. (0.147) becomes

$$\tilde{H}(\mathbf{q},\mathbf{p}) \approx H(\mathbf{q},\mathbf{p}), \tag{0.149}$$

which is the mathematical version of the statement that the modified Hamiltonian is unchanged, so far as the physical trajectories are concerned. However, the off-constraint-manifold modifications are important. As we saw in the Lagrangian case, these led to the constraint forces that ultimately maintain the constraint. Correspondingly, we now have a modified set of Hamilton equations in place of the original Hamilton equations (0.27),

$$\begin{aligned}
\dot{p}_\alpha &\approx [p_\alpha, \tilde{H}]_{\text{P}} = -\frac{\partial \tilde{H}}{\partial q^\alpha} = -\frac{\partial H}{\partial q^\alpha} - \lambda\frac{\partial \phi}{\partial q^\alpha} \\
\dot{q}^\alpha &\approx [q^\alpha, \tilde{H}]_{\text{P}} = \frac{\partial \tilde{H}}{\partial p_\alpha} = \frac{\partial H}{\partial p_\alpha} + \lambda\frac{\partial \phi}{\partial p_\alpha}.
\end{aligned}$$

(constrained Hamilton equations) (0.150)

Additionally, by applying the first Hamilton equation in Eqs. (0.29),

$$\frac{\partial L}{\partial q^\alpha} \approx -\frac{\partial \tilde{H}}{\partial q^\alpha} = -\frac{\partial H}{\partial q^\alpha} - \lambda\frac{\partial \phi}{\partial q^\alpha}, \tag{0.151}$$

which is really just an alternative to the first of Eqs. (0.150). Note that in the weak equalities, the terms involving derivatives of g vanish due to the constraint relation (0.148). Also, the weak equalities symbols here are often omitted, because by definition the equations of motion only make sense on the constraint manifold. Now we have a set of constrained equations of motion, but the problem is that we still have an undetermined function λ to deal with.

Now suppose that we return to the variation of H in Eqs. (0.25),

$$\begin{aligned}
\delta H &= \delta\big[\dot{q}^\alpha p_\alpha - L(\mathbf{q},\dot{\mathbf{q}};t)\big] \\
&= \dot{q}^\alpha \delta p_\alpha - \frac{\partial L}{\partial q^\alpha}\delta q^\alpha.
\end{aligned} \tag{0.152}$$

Computing δH directly in terms of δp_α and δq^α, and equating the result with the above result, we obtain

$$\left(\frac{\partial H}{\partial p_\alpha} - \dot{q}^\alpha\right)\delta p_\alpha + \left(\frac{\partial H}{\partial q^\alpha} + \frac{\partial L}{\partial q^\alpha}\right)\delta q^\alpha = 0. \tag{0.153}$$

Using the second of Eqs. (0.150) and Eq. (0.151), this equation becomes

$$\lambda\left(\frac{\partial \phi}{\partial p_\alpha}\delta p_\alpha + \frac{\partial \phi}{\partial q^\alpha}\delta q^\alpha\right) \approx 0. \tag{0.154}$$

Since the physical variations of $\mathbf{p}$ and $\mathbf{q}$ are tangent to the constraint surface, we see that the phase-space gradient of the constraint function ϕ is orthogonal to the variations, as required. This is the statement analogous to Eq. (0.121) in the Lagrangian case.

0.5.2.2 Consistency and Secondary Constraints

We already noted in Eqs. (0.150) that the equations of motion for the canonical variables can still be written in terms of the Poisson bracket with the effective Hamiltonian (0.147). In fact, this holds for a general phase-space function $g(\mathbf{q}, \mathbf{p})$, as

$$\dot{g} \approx [g, \tilde{H}]_{\text{P}} = [g, H]_{\text{P}} + \lambda[g, \phi]_{\text{P}}. \tag{0.155}$$
(constrained equation of motion)

Again, any term of the form $[g, \lambda]_{\text{P}}\phi$ that may appear in the last expression is suppressed because of the constraint condition $\phi \approx 0$ (thinking of λ as an extra dynamical variable, the Poisson bracket is not even well-defined in terms of the original canonical variables). There is an important point here: The action of the Poisson bracket, which governs the flow in phase space, must be determined *globally* in the phase space, not just on the constraint manifold. Only *after* the action of the Poisson brackets is defined can any constraint relations be implemented. This was in fact Dirac's[8] motivation for introducing the "$\approx$" notation, as a reminder of this order of calculations when handling constraints.

At this point it is important to ensure consistency of the constraints. Since $\phi \approx 0$, it should be the case that $\dot{\phi} \approx 0$, according to the equation of motion (0.155). Thus, in the case of a single constraint relation, we should have

$$[\phi, H]_{\text{P}} \approx 0, \tag{0.156}$$
(consistency for single constraint)

since $[\phi, \phi]_{\text{P}} = 0$. More generally, there will be multiple constraints, $\phi_\alpha(\mathbf{q}, \mathbf{p}) = 0$, in which case the effective Hamiltonian (0.147) becomes

$$\tilde{H}(\mathbf{q}, \mathbf{p}) = H(\mathbf{q}, \mathbf{p}) + \lambda^\alpha \phi_\alpha(\mathbf{q}, \mathbf{p}).$$
(Hamiltonian with multiple Lagrange multipliers) (0.157)

In this case the consistency relations among the constraints are

$$[\phi_\alpha, H]_{\text{P}} + \lambda^\beta[\phi_\alpha, \phi_\beta]_{\text{P}} \approx 0. \tag{0.158}$$
(consistency for multiple constraints)

When these consistency conditions are worked out for a particular system, there are several possible outcomes for a consistency relation:

1. The consistency condition reduces to something manifestly inconsistent, like $1 = 0$. This indicates an ill-posed mathematical problem, so we will assume this possibility doesn't occur in well-posed physical model.

2. The consistency condition could reduce to something manifestly *consistent*, like $0 = 0$, in which case the condition is obviously fine. This is saying that as long as the initial condition is on the constraint manifold, the dynamical evolution will maintain the constraint automatically.

[8] P. A. M. Dirac, *op. cit.*, p. 12.

3. The condition could reduce to something of the form

$$\chi(\mathbf{q}, \mathbf{p}) = 0, \tag{0.159}$$

which is independent of the Lagrange multipliers. Assuming this is independent of the original set of constraints, this has the form of a *new* constraint, called a **secondary constraint**. New constraints found are subject to the same consistency conditions with each other and the primary constraints; that is,

$$[\chi, H]_{\text{P}} + \lambda^{\beta}[\chi, \phi_{\beta}]_{\text{P}} \approx 0. \tag{0.160}$$

(consistency condition for secondary constraint)

these can be added to the Hamiltonian with new Lagrange multipliers, and the consistency process can be iterated until all the constraints are apparent. For practical purposes, other than how they are found, secondary constraints are the same as primary constraints, and can be lumped together in the set of ϕ_{α}.

4. The condition could reduce to a constraint equation involving the Lagrange multipliers. This amounts to a constraint *on* the Lagrange multipliers, an important case that we will discuss further below.

At this point, we will assume all secondary constraints have been found, and incorporated into the effective Hamiltonian (0.158).

0.5.2.3 First-Class Constraints

The distinction between primary and secondary constraints is somewhat superficial—it only reflects how a given constraint was found, but a secondary constraint is as effective as a primary constraint in defining the constraint manifold. In fact, a particular constraint for some system could end up being primary or secondary, depending on the setup of the Lagrangian. However, there is another classification of the constraints that is crucial to the structure of constrained Hamiltonian systems. Consider a general phase-space function $g(\mathbf{q}, \mathbf{p})$. Then g is said to be **first class** if its Poisson bracket with *all* constraints is zero on the constraint manifold,

$$[g, \phi_{\alpha}]_{\text{P}} \approx 0 \quad (\forall_{\alpha}). \tag{0.161}$$

(first-class consition)

Otherwise, if the Poisson bracket is nonzero on the manifold for one or more constraints, then g is said to be **second class**. Since g could be a constraint function, this classification carries over to the constraints. From the consistency condition (0.158), we can see that first-class constraints lead to constraint equations not involving Lagrange multipliers, (or trivially consistent equations), whereas secondary constraints lead to constraint equations *with* Lagrange multipliers. Again, any of the first- or second-class constraints may be either primary or secondary. Clearly, linear combinations of first-class constraints are also first-class constraints, while linear combinations of second-class constraints are also second-class. However, a linear combination of first- and second-class constraints is second class. In the following, we will assume that the second-class constraints form an irreducible set: that is, there is no linear transformation among the constraints that will make more independent first-class constraints at the expense of reducing the number of second-class constraints.

To get an intuitive idea of what is going on with these classes of constraints, recall from Section 0.4.4.3 that Poisson brackets induce vector fields that represent flows on a manifold. In this case, a Poisson bracket with a constraint function represents a flow on the constraint manifold. Since for two first-class constraints we have

$$[\phi_{\alpha}, \phi_{\beta}]_{\text{P}} \approx 0, \tag{0.162}$$

and so Eq. (0.81) says that the vector fields (flows) induced by these constraint functions commute. For first-class constraints we also have that

$$[\phi_{\alpha}, H]_{\text{P}} \approx 0, \tag{0.163}$$

which says that the constraint vector fields commute with the Hamiltonian flow. This is essentially saying that the Hamiltonian flow naturally respects first-class constraints: the Hamiltonian flow maps points on the

constraint manifold to other points on the constraint manifold. For second-class constraints, the Lagrange multipliers are needed to help keep the Hamiltonian flow on the constraint manifold.

0.5.2.4 Second-Class Constraints

Now let's consider separately the second-class constraints. Since the distinction here is important, we will continue to use ϕ_α to denote first-class constraints, but switch to using φ_α for the second-class constraints. Considering the antisymmetric matrix $[\varphi_\alpha, \varphi_\beta]_{\text{P}}$ of Poisson brackets of second-class constraints, we can define the inverse matrix $C^{\alpha\beta}$ such that

$$C^{\alpha\beta}[\varphi_\beta, \varphi_\gamma]_{\text{P}} = \delta^\alpha{}_\gamma. \tag{0.164}$$

That $C^{\alpha\beta}$ exists amounts to the above assumption that we have a minimal set of second-class constraints, having reduced as many as possible to first-class constraints.[9] Since the determinant of an odd-dimensioned, antisymmetric matrix necessarily vanishes, the number of second-class constraints must be even. Roughly speaking, second-class constraints occur in pairs because they correspond to redundant degrees of freedom in the Hamiltonian; they will be explicitly eliminated in the following treatment.

The effective Hamiltonian (0.157) becomes

$$\tilde{H}(\mathbf{q}, \mathbf{p}) = H(\mathbf{q}, \mathbf{p}) + \lambda^\alpha \phi_\alpha + \mu^\alpha \varphi_\alpha,$$

(Hamiltonian with first- and second-class constraints) (0.165)

after separating the constraints by class. The second-class constraints are still subject to the consistency conditions (0.158)

$$[\varphi_\alpha, H]_{\text{P}} + \mu^\beta [\varphi_\alpha, \varphi_\beta]_{\text{P}} \approx 0, \tag{0.166}$$

and solving this weak equation for the Lagrange multipliers gives

$$\mu^\alpha \approx -C^{\alpha\beta}[\varphi_\beta, \tilde{H}]_{\text{P}} = -[H, \varphi_\beta]_{\text{P}} C^{\beta\alpha} \tag{0.167}$$

on the constraint manifold. In this way, since we only care about the Hamiltonian on the constraint manifold, we can eliminate the Lagrange multipliers μ^α for the second-class constraints to write

$$\tilde{H}(\mathbf{q}, \mathbf{p}) = H(\mathbf{q}, \mathbf{p}) + \lambda^\alpha \phi_\alpha - [H, \varphi_\alpha]_{\text{P}} C^{\alpha\beta} \varphi_\beta, \tag{0.168}$$

(extended Hamiltonian)

so that only the Lagrange multipliers for the first-class constraints are left over. Dirac referred to this form as the **extended Hamiltonian** or the **total Hamiltonian**.[10]

Let's explore the combination of second-class constraints that appears in the effective Hamiltonian (0.168). Consider a general phase-space function $g(\mathbf{q}, \mathbf{p})$. In general, it will happen that $[g, \varphi_\alpha]_{\text{P}} \not\approx 0$ for some second-class constraint φ_α. As a motivation for what follows, suppose that we define a modified version of g, designed to have vanishing brackets with second-class constraints:

$$\tilde{g} := g - [g, \varphi_\alpha]_{\text{P}} C^{\alpha\beta} \varphi_\beta.$$

(modification for second-class constraints) (0.169)

The "correction" of course, has the same form as in the effective Hamiltonian (0.168), and of course $\tilde{g} \approx g$ (for the purposes of this discussion, the weak equality refers only to the second-class constraints). It is easy to verify that this modified function has a vanishing Poisson bracket with any of the second-class constraints:

$$\begin{aligned}
[\tilde{g}, \varphi_\gamma]_{\text{P}} &= [g, \varphi_\gamma]_{\text{P}} - [g, \varphi_\alpha]_{\text{P}} C^{\alpha\beta} [\varphi_\beta, \varphi_\gamma]_{\text{P}} - \left[[g, \varphi_\alpha]_{\text{P}} C^{\alpha\beta}, \varphi_\gamma \right]_{\text{P}} \varphi_\beta \\
&= [g, \varphi_\gamma]_{\text{P}} - [g, \varphi_\alpha]_{\text{P}} \delta^\alpha{}_\gamma - \left[[g, \varphi_\alpha]_{\text{P}} C^{\alpha\beta}, \varphi_\gamma \right]_{\text{P}} \varphi_\beta \\
&= -\left[[g, \varphi_\alpha]_{\text{P}} C^{\alpha\beta}, \varphi_\gamma \right]_{\text{P}} \varphi_\beta \\
&\approx 0.
\end{aligned} \tag{0.170}$$

[9] Dirac, *op. cit.* discusses more formally the proof of the existence of $C^{\alpha\beta}$; see the discussion starting on p. 39.

[10] Dirac distinguished between the extended and total Hamiltonian. The *total* Hamiltonian is the one obtained by adding on primary first-class constraints with arbitrary multipliers, and any second-class constraints (with their multipliers fixed in terms of Poisson brackets). The *extended* Hamiltonian has the *secondary* first-class constraints also added on with arbitrary multipliers. Since it doesn't seem very useful to distinguish between primary and secondary constraints for the purposes of gauge freedom, we will just refer to the extended Hamiltonian and lump both primary and secondary gauge freedoms together.

However, $\tilde{g}$ is not first class in general because we haven't said anything about the first-class constraints ϕ_α. The effective Hamiltonian (0.168) has these same terms that cause brackets with second-class constraints to vanish. The Hamiltonian already had a (weakly) vanishing Poisson bracket with the first-class constraints from Eq. (0.163); thus, $\tilde{H}$ is *first class*.

0.5.2.5 Dirac Bracket

The above discussion motivates the definition of an alternative to the Poisson bracket. For two phase-space functions f and g, we want to define the **Dirac bracket** such that

$$[f,g]_{\text{D}} \approx [\tilde{f},\tilde{g}]_{\text{P}} \approx [\tilde{f},g]_{\text{P}} \approx [f,\tilde{g}]_{\text{P}}, \tag{0.171}$$

with the twiddled variables still defined as in Eq. (0.169), and the equalities follow from Eqs. (0.169) and (0.170). Note that while $\tilde{f} \approx f$ and $\tilde{g} \approx g$, it is *not* true in general that $[\tilde{f},\tilde{g}]_{\text{P}} \approx [f,g]_{\text{P}}$, because the bracket includes information off the constraint manifold. Defining the Dirac bracket as

$$[f,g]_{\text{D}} := [f,g]_{\text{P}} - [f,\varphi_\alpha]_{\text{P}} C^{\alpha\beta} [\varphi_\beta, g]_{\text{P}}, \tag{0.172}$$
(Dirac bracket)

Eqs. (0.171) are satisfied. The idea behind the Dirac bracket is to adopt it as the classical bracket *in place of* the Poisson bracket, whenever second-class constraints occur. As it turns out, the Dirac bracket satisfies the same properties as the Poisson bracket, as required to define a Lie algebra (Section 0.4.4.3). For example the Jacobi identity is satisfied weakly because $[f,[g,h]_{\text{D}}]_{\text{D}} \approx [\tilde{f},[\tilde{g},\tilde{h}]_{\text{P}}]_{\text{P}}$; however, it can be shown that the Jacobi identity also holds *globally*.

Now for the general phase-space function $g(\mathbf{q},\mathbf{p})$, notice that

$$[g,\tilde{H}]_{\text{D}} \approx [g,\tilde{H}]_{\text{P}}, \tag{0.173}$$

because we already noted that $\tilde{H}$ is first class, and so the bracket $[\varphi_\beta,\tilde{H}]_{\text{P}} \approx 0$, making the constraint term in the Dirac bracket (0.172) vanish weakly. Thus, the Poisson-bracket equation of motion (0.36) is equally valid in terms of the Dirac bracket:

$$\dot{g} \approx [g,\tilde{H}]_{\text{D}}. \tag{0.174}$$
(evolution using Dirac bracket)

Also for the Dirac bracket with a constraint, we have

$$\begin{aligned} [g,\varphi_\gamma]_{\text{D}} &= [g,\varphi_\gamma]_{\text{P}} - [g,\varphi_\alpha]_{\text{P}}\, C^{\alpha\beta}[\varphi_\beta,\varphi_\gamma]_{\text{P}} \\ &= [g,\varphi_\gamma]_{\text{P}} - [g,\varphi_\alpha]_{\text{P}}\, \delta^\alpha{}_\gamma \\ &= 0. \end{aligned} \tag{0.175}$$

Note that the equality here is *global*, not weak, unlike the similar calculation in Eq. (0.170). Unlike the Poisson-bracket version (0.161) of this relation, where we needed to compute the bracket *before* setting $\varphi_\alpha \approx 0$, it is still valid to compute the Dirac bracket *after* fixing second-class constraints via the global equality $\varphi_\alpha = 0$. In particular, this means that the second-class constraint functions in the extended Hamiltonian $\tilde{H}$ can be discarded when using the Dirac bracket, so that we may rewrite Eq. (0.174) equivalently as

$$\dot{g} = [g,H]_{\text{D}}. \tag{0.176}$$
(evolution using Dirac bracket)

The second-class constraint terms in the extended Hamiltonian (0.168) only serve to maintain the constraints according to Poisson-bracket dynamics.

Therein lies the advantage of using the Dirac bracket as a replacement for the Poisson bracket, in conjunction with the extended Hamiltonian (0.168). The second-class constraints have effectively been removed from the problem, with the equations $\varphi_\alpha = 0$ acting as identities relating the canonical variables, rather than as constraint equations. The remaining constraints to deal with are all first class, $\phi_\alpha \approx 0$. This also implies that second-class constraints $\varphi_\alpha = 0$ do not generate further secondary constraints via the consistency condition $\dot{\varphi}_\alpha = [\varphi,\tilde{H}]_{\text{D}} = 0$ after adopting the Dirac bracket.

0.5.2.6 Toy Model for Eliminating Second-Class Constraints

As a simple example[11] of what happens here to second-class constraints, consider a system of N canonical degrees of freedom, with the first degree of freedom set to zero: $q^1 = p_1 = 0$. Thus, we have a pair of constraints

$$\varphi_1 = q^1, \qquad \varphi_2 = p_1, \tag{0.177}$$

with $\varphi_1 \approx 0$ and $\varphi_2 \approx 0$. Because

$$[\varphi_1, \varphi_2]_{\mathrm{P}} = [q^1, p_1]_{\mathrm{P}} = 1 \not\approx 0, \tag{0.178}$$

it follows that the constraints are second class. In fact the matrix of Poisson brackets of the constraints is simply

$$[\varphi_\alpha, \varphi_\beta]_{\mathrm{P}} = \epsilon_{\alpha\beta}, \tag{0.179}$$

where $\epsilon_{\alpha\beta}$ is the Levi-Civita symbol with two indices (i.e., $\epsilon_{12} = 1$, $\epsilon_{21} = -1$, $\epsilon_{\alpha\alpha} = 0$). The bracket matrix is the transpose of its inverse:

$$C^{\alpha\beta} = \epsilon^{\beta\alpha} = -\epsilon^{\alpha\beta}. \tag{0.180}$$

The Poisson bracket is defined in Eq. (0.35) as

$$[f, g]_{\mathrm{P}} := \frac{\partial f}{\partial q^\alpha}\frac{\partial g}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial g}{\partial q^\alpha}, \tag{0.181}$$

and so now we can work out the Dirac bracket (0.172):

$$\begin{aligned}
[f, g]_{\mathrm{D}} &= [f, g]_{\mathrm{P}} + [f, \varphi_\alpha]_{\mathrm{P}} \epsilon^{\alpha\beta} [\varphi_\beta, g]_{\mathrm{P}} \\
&= [f, g]_{\mathrm{P}} + [f, q^1]_{\mathrm{P}} [p_1, g]_{\mathrm{P}} - [f, p_1]_{\mathrm{P}} [q^1, g]_{\mathrm{P}} \\
&= \frac{\partial f}{\partial q^\alpha}\frac{\partial g}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial g}{\partial q^\alpha} + \frac{\partial f}{\partial p_1}\frac{\partial g}{\partial q^1} - \frac{\partial f}{\partial q^1}\frac{\partial g}{\partial p_1} \\
&= \sum_{\alpha=2}^{N} \left(\frac{\partial f}{\partial q^\alpha}\frac{\partial g}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha}\frac{\partial g}{\partial q^\alpha} \right).
\end{aligned} \tag{0.182}$$

That is, the Dirac bracket is just the Poisson bracket with the first degree of freedom omitted. After adopting the Dirac bracket in place of the Poisson bracket, the constraints become the strong equations $q^1 = p_1 = 0$, which simply eliminate the first degree of freedom completely from the problem. The other degrees of freedom are, sensibly, unaffected.

0.5.2.7 Gauge Freedom

Now the extended Hamiltonian (0.168), reproduced here,

$$\tilde{H}(\mathbf{q}, \mathbf{p}) = H(\mathbf{q}, \mathbf{p}) + \lambda^\alpha \, \phi_\alpha - [H, \varphi_\alpha]_{\mathrm{P}} \, C^{\alpha\beta} \, \varphi_\beta, \tag{0.183}$$

may have had some of its Lagrange multipliers eliminated, due to the presence of the final term. The first-class constraints and the associated multipliers are still present, however. Since the multipliers are arbitrary, these represent some arbitrariness of the system: some configurations of the canonical coordinates are redundant.

So see how this works out, consider an arbitrary canonical coordinate $z(t)$, and its change over a small time interval δt:

$$\begin{aligned}
\delta z(t) &:= z(t + \delta t) - z(t) \\
&= \dot{z}(t) \, \delta t \\
&= [z, \tilde{H}]_{\mathrm{P}} \, \delta t \\
&= [z, H']_{\mathrm{P}} \, \delta t + \lambda^\alpha [z, \phi_\alpha]_{\mathrm{P}} \, \delta t.
\end{aligned} \tag{0.184}$$

[11] Example from Henneaux and Teitelboim, *op. cit.*, p. 22.

Here we used the equation of motion (0.40), with the extended Hamiltonian (0.168), which is again equivalent to H on the constraint manifold; and we are using H' to denote the original Hamiltonian with the second-class constraints:

$$H' := H - [H, \varphi_\alpha]_{\text{P}}\, C^{\alpha\beta}\, \varphi_\beta. \tag{0.185}$$

Since the Lagrange multipliers are arbitrary, we can consider the evolution under a different set of values λ'^α:

$$\delta z'(t) = [z, H']_{\text{P}}\, \delta t + \lambda'^\alpha [z, \phi_\alpha]_{\text{P}}\, \delta t. \tag{0.186}$$

The difference between the two evolutions is

$$\Delta z(t) := \delta z(t) - \delta z'(t) = \big(\lambda^\alpha - \lambda'^\alpha\big)[z, \phi_\alpha]_{\text{P}}\, \delta t. \tag{0.187}$$

Comparing to Eq. (0.62), we can see that this difference has the form of an infinitesimal canonical transformation, with generators ϕ_α and increments $\epsilon^\alpha = (\lambda^\alpha - \lambda'^\alpha)\, \delta t =: \Delta\lambda^\alpha\, \delta t$. Thus, the first-class constraints ϕ_α are generators of canonical transformations between configurations that correspond to the *same physical state*. These transformations (0.187), which map a physical state to itself, are called **gauge transformations**, parameterized by the λ^α. The first-class constraints are not the only generators of gauge transformations; as it turns out, Poisson brackets of two first-class constraints $[\phi_\alpha, \phi_\beta]_{\text{P}}$, as well as Poisson brackets of first-class constraints with the Hamiltonian $[\phi_\alpha, H']_{\text{P}}$, can also generate gauge transformations.

0.5.2.8 Redux: Particle Constrained to a Circle

Let's return to the example from Section 0.5.2.8 of the particle constrained to a circle, to see how it works out in the Hamiltonian case. As a starting point, we can take the Lagrangian (0.130) before the constraint is added:

$$L = \frac{1}{2} m\big(\dot{x}^2 + \dot{y}^2\big) - V(x, y, t). \tag{0.188}$$

Here, the constraint is

$$\varphi_1(x, y) = x^2 + y^2 - \ell^2 = 0. \tag{0.189}$$

Note that we are already using the notation for a second-class constraint, with associated Lagrange multiplier μ^1. Intuitively, we should expect this constraint to be second class: An unconstrained particle wants to move in a straight line, not around a circle, and second-class constraints are the kind that aren't naturally respected by Hamiltonian evolution. (We should thus generically expect holonomic constraints in the Lagrangian formalism to be second-class constraints for the corresponding Hamiltonian.) Since second-class constraints occur in pairs, we still need to find the other one, but first let's set up the canonical momenta and the Hamiltonian.

There are two coordinates here, x and y; the corresponding momenta are

$$p_x = \frac{\partial L}{\partial \dot{x}} = m\dot{x}, \qquad p_y = \frac{\partial L}{\partial \dot{y}} = m\dot{y}, \tag{0.190}$$

as usual. The canonical Hamiltonian is simply

$$H = \frac{p_x^2 + p_y^2}{2m} + V, \tag{0.191}$$

where the Hamiltonian should be generalized to include the constraint function and a Lagrange multiplier; however, since second-class constraints are involved, we will defer this procedure until we have checked their consistency. Thus we will want the Poisson bracket

$$[\varphi_1, H]_{\text{P}} = \frac{2}{m}(x p_x + y p_y). \tag{0.192}$$

Since we so far have only one constraint, the consistency condition (0.156) generates a second constraint,

$$\varphi_2 = x p_x + y p_y = \mathbf{r} \cdot \mathbf{p} \approx 0. \tag{0.193}$$

With φ_1, this constraint is saying that the radial component of the momentum vanishes, which is sensible. This will also intuitively be a second-class constraint, but we still need to check the Poisson brackets:

$$[\varphi_2, H]_{\text{P}} = \frac{p_x^2 + p_y^2}{m} - x\partial_x V - y\partial_y V = \frac{p^2}{m} - \mathbf{r}\cdot\nabla V, \qquad [\varphi_1, \varphi_2]_{\text{P}} = 2\big(x^2 + y^2\big) = 2r^2. \tag{0.194}$$

So clearly φ_1 and φ_1 are second class. The consistency condition (0.158) is a relation that fixes the Lagrange multiplier μ^1 for φ_1:

$$\mu^1 \approx \frac{[\varphi_2, H]_{\text{P}}}{[\varphi_1, \varphi_2]_{\text{P}}} = \frac{p^2}{2mr^2} - \frac{\hat{r}}{r}\cdot\nabla V. \tag{0.195}$$

This quantity still corresponds to the centripetal force in Eq. (0.139). However, in this form it is not completely intuitive; note that with a factor of r^3, it is basically the form of the Runge–Lenz vector (see Section 8.4.6) appropriate to this problem.

Now we have a 2×2 Poisson-bracket matrix

$$[\varphi_\alpha, \varphi_\beta]_{\text{P}} = 2r^2\epsilon_{\alpha\beta}, \tag{0.196}$$

with inverse

$$C^{\alpha\beta} = -\frac{1}{2r^2}\epsilon^{\alpha\beta}. \tag{0.197}$$

Thus, we can work out the extended Hamiltonian (0.168),

$$\begin{aligned}\tilde{H} &= H + \frac{1}{mr^2}\varphi_2 - \left(\frac{p^2}{2mr^2} - \frac{\hat{r}}{r}\cdot\nabla V\right)\varphi_1 \\ &= \frac{p^2}{2m} + V + \frac{1}{mr}\,\hat{r}\cdot\mathbf{p} + \left(\frac{p^2}{2mr^2} - \frac{\hat{r}}{r}\cdot\nabla V\right)\big(\ell^2 - r^2\big).\end{aligned} \tag{0.198}$$

This again generates the proper dynamical evolution via the Poisson bracket. The constraint force from the Lagrangian analysis is present here in the last term, but the previous term also appears here.

The Dirac bracket (0.172) in this case is

$$\begin{aligned}[f,g]_{\text{D}} &= [f,g]_{\text{P}} + \frac{1}{2r^2}[f,r^2]_{\text{P}}[\mathbf{r}\cdot\mathbf{p},g]_{\text{P}} - \frac{1}{2r^2}[f,\mathbf{r}\cdot\mathbf{p}]_{\text{P}}[r^2,g]_{\text{P}} \\ &= [f,g]_{\text{P}} - \frac{1}{r^2}\mathbf{r}\cdot(\nabla_p f)\,(\mathbf{p}\cdot\nabla_p g - \mathbf{r}\cdot\nabla g) + \frac{1}{r^2}\,(\mathbf{p}\cdot\nabla_p f - \mathbf{r}\cdot\nabla f)\,\mathbf{r}\cdot(\nabla_p g) \\ &= [f,g]_{\text{P}} - \Big[(\hat{r}\cdot\nabla f)(\hat{r}\cdot\nabla_p g) - (\hat{r}\cdot\nabla_p f)(\hat{r}\cdot\nabla g)\Big] - \frac{1}{r}\Big[(\hat{r}\cdot\nabla_p f)(\mathbf{p}\cdot\nabla_p g) - (\mathbf{p}\cdot\nabla_p f)(\hat{r}\cdot\nabla_p g)\Big].\end{aligned} \tag{0.199}$$

The middle term subtracts away the radial components of the Poisson bracket; the last term is less obvious, but is important in enforcing the constraints. To see this, we can work out the constrained Hamilton equations on the circle, using the general equation of motion (0.176). The position evolves according to

$$\dot{\mathbf{r}} = [\mathbf{r}, H]_{\text{D}} = \frac{1}{m}\big[\mathbf{p} - \hat{r}(\hat{r}\cdot\mathbf{p})\big] \approx \frac{\mathbf{p}}{m}. \tag{0.200}$$

We have written a weak inequality here in the last step to emphasize that in the algebra, we are implementing a constraint (here, that there is no radial component to the momentum, $\hat{r}\cdot\mathbf{p} = 0$). However, it is worth reiterating that equations of motion only make sense on the constraint manifold, so the weak equality can

just as well be written as a strong equality. Moving on to the evolution equation for momentum,

$$\begin{aligned}\dot{\mathbf{p}} &= [\mathbf{p}, \tilde{H}]_{\text{D}} \\ &= -\nabla V + \hat{r}(\hat{r}\cdot\nabla V) - \frac{1}{r}\hat{r}\frac{p^2}{m} + \frac{1}{r}\mathbf{p}\left(\hat{r}\cdot\frac{\mathbf{p}}{m}\right) \\ &= \mathbf{F} - \hat{r}(\hat{r}\cdot\mathbf{F}) - \frac{1}{r}\hat{r}\frac{p^2}{m} + \frac{1}{r}\mathbf{p}\left(\hat{r}\cdot\frac{\mathbf{p}}{m}\right) \\ &\approx \mathbf{F} - \hat{r}(\hat{r}\cdot\mathbf{F}) - \frac{p^2}{mr}\hat{r} \\ &\approx \mathbf{F} - \hat{r}(\hat{r}\cdot\mathbf{F}) - \frac{1}{m}\mathbf{p}\cdot[(\mathbf{p}\cdot\nabla)\hat{r}]\hat{r},\end{aligned} \tag{0.201}$$

where $\mathbf{F} := -\nabla V$. In the last step, we transformed the last term using

$$\mathbf{p}\cdot[(\mathbf{p}\cdot\nabla)\hat{r}]\hat{r} = \frac{1}{r}p_\alpha p_\beta(\delta_{\alpha\beta} - \hat{r}_\alpha\hat{r}_\beta)\hat{r} = \frac{1}{r}[p^2 - (\hat{r}\cdot\mathbf{p})^2]\hat{r} \approx \frac{p^2}{r}, \tag{0.202}$$

where we used the derivative $\partial_\alpha\hat{r}_\beta = \partial_\alpha(\mathbf{r}_\beta/r) = \delta_{\alpha\beta}/r - r_\alpha r_\beta/r^3 = (\delta_{\alpha\beta} - \hat{r}_\alpha\hat{r}_\beta)/r$. In Eqs. (0.201), the middle term eliminates the radial component of the external force, while the last term maintains the constraint [the last term here comes from the last term in the Dirac bracket (0.199)]. Combining the generalized Hamilton equations (0.200) and (0.201) and eliminating the momentum, we can write

$$\begin{aligned}m\ddot{\mathbf{r}} &= \mathbf{F} - \hat{r}(\hat{r}\cdot\mathbf{F}) - m\dot{\mathbf{r}}\cdot[(\dot{\mathbf{r}}\cdot\nabla)\hat{r}]\hat{r} \\ &= \mathbf{F} - \hat{r}(\hat{r}\cdot\mathbf{F}) - m\big(\dot{\mathbf{r}}\cdot\dot{\hat{r}}\big)\hat{r},\end{aligned} \tag{0.203}$$

so that the net force is the tangential external force plus a centripetal part. With the identifications

$$\dot{\hat{r}} = \dot{\theta}\hat{\theta}, \qquad \nabla V \approx \hat{r}\frac{\partial V}{\partial r} + \frac{\hat{\theta}}{\ell}\frac{\partial V}{\partial\theta} \tag{0.204}$$

and the expressions (0.134) for $\dot{\mathbf{r}}$ and $\ddot{\mathbf{r}}$, the equation of motion (0.203) reduces to the equation of motion (0.136) that we derived in the Lagrangian formalism.

0.5.3 Relativistic Particle

An interesting example of a constrained system is the relativistic particle in flat space-time. The action principle is given in terms of the proper time τ of the space-time path (or worldline),

$$S = -mc^2\int_{\tau_0}^{\tau_1} d\tau \tag{0.205}$$

(relativistic-particle action)

where the proper time is defined through its increment $d\tau$ by

$$c^2 d\tau^2 = c^2 dt^2 - dx^2 - dy^2 - dz^2. \tag{0.206}$$

There is obviously a large mathematical apparatus for handling relativistic systems, but to parallel other systems in classical mechanics, we are intentionally avoiding relativistic notation here. Then the action can be written

$$S = \int_{\tau_0}^{\tau_1} d\tau\, L(\mathbf{r}, t, \dot{\mathbf{r}}, \dot{t}) \tag{0.207}$$

where the dots denote differentiation with respect to τ, and the Lagrangian is

$$L(\mathbf{r}, t, \dot{\mathbf{r}}, \dot{t}) = -mc\sqrt{c^2\dot{t}^2 - \dot{x}^2 - \dot{y}^2 - \dot{z}^2}. \tag{0.208}$$

(relativistic-particle Lagrangian)

Note that the square root here is essentially c times the derivative $d\tau/d\tau = 1$, so the Lagrangian has fixed value $-mc^2$. This action principle is invariant invariant under (monotonic) reparameterizations $\tau \longrightarrow \tau'(\tau)$, but we will wait a bit before discussing this invariance in detail.

The canonical momenta are given as usual by the derivatives

$$\begin{aligned} \mathbf{p} &= \frac{\partial L}{\partial \dot{\mathbf{r}}} = m\dot{\mathbf{r}} \\ p_t &= \frac{\partial L}{\partial \dot{t}} = -mc^2\dot{t}. \end{aligned} \tag{0.209}$$

Here we can already see that the Lagrangian is singular according to the Hessian criterion (0.21), because the diagonal second derivatives all vanish, $\partial^2 L/\partial r_\alpha^2 = 0$ and $\partial^2 L/\partial t^2 = 0$, and so the Hessian determinant vanishes. This is also reflected in the Hamiltonian, which is

$$\begin{aligned} H(\mathbf{r}, t, \mathbf{p}, p_t) &= \mathbf{p}\cdot\dot{\mathbf{r}} + p_t\dot{t} - L(\mathbf{r}, t, \dot{\mathbf{r}}, \dot{t}) \\ &= \mathbf{p}\cdot\dot{\mathbf{r}} + p_t\dot{t} + mc\sqrt{c^2\dot{t}^2 - \dot{r}^2} \\ &= \frac{p^2}{m} - \frac{p_t^2}{mc^2} + c\sqrt{\frac{p_t^2}{c^2} - p^2}. \end{aligned} \tag{0.210}$$

However, if we look at the momentum combination

$$\frac{p_t^2}{c^2} - p^2 = m^2\left(c^2\dot{t}^2 - \dot{r}^2\right) = \frac{L^2}{c^2} = m^2c^2, \tag{0.211}$$

then we can see the Hamiltonian is really of the form $H = m - m$ or

$$H(\mathbf{r}, t, \mathbf{p}, p_t) = 0. \tag{0.212}$$

(relativistic-particle Hamiltonian)

We already knew to expect a vanishing Hamiltonian from Eq. (0.144) because the Lagrangian is Euler homogeneous of degree 1 in the velocities. In fact Eq. (0.211) is a constraint equation, the **mass-shell constraint**:

$$p_t^2 = p^2c^2 + m^2c^4. \tag{0.213}$$

(mass-shell constraint)

Typically p_t is identified as the relativistic "energy," in which case this constraint has the familiar form

$$E^2 = p^2c^2 + m^2c^4. \tag{0.214}$$

We will discuss the identification of p_t with the relativistic energy E further below.

Thus, we have a single first-class constraint

$$\phi = p^2c^2 - p_t^2 + m^2c^4 \approx 0, \tag{0.215}$$

because it is the only constraint, and its Poisson bracket with the Hamiltonian obviously vanishes (weakly). Then the extended Hamiltonian (0.168) is

$$\tilde{H} = H + \lambda\phi = \lambda(\tau)\left(p^2 - \frac{p_t^2}{c^2} + m^2c^2\right). \tag{0.216}$$

The extended Hamilton's equations give the equations of motion

$$\begin{aligned} \dot{\mathbf{p}} &= -\frac{\partial \tilde{H}}{\partial \mathbf{r}} = 0 \\ \dot{p}_t &= -\frac{\partial \tilde{H}}{\partial t} = 0 \\ \dot{\mathbf{r}} &= \frac{\partial \tilde{H}}{\partial \mathbf{p}} = 2\lambda\mathbf{p} \\ \dot{t} &= \frac{\partial \tilde{H}}{\partial p_t} = -\frac{2\lambda p_t}{c^2}. \end{aligned} \tag{0.217}$$

The first two say that all the momenta are conserved quantities, as we expect for a translation-invariant action. The second two can be rewritten

$$\begin{aligned} \dot{\mathbf{r}} &= 2\lambda m \dot{\mathbf{r}} \\ \dot{t} &= 2\lambda m \dot{t}, \end{aligned} \tag{0.218}$$

in which case the Lagrange multiplier must be fixed to

$$\lambda = \frac{1}{2m} \tag{0.219}$$

for self-consistency. Then the extended Hamiltonian has the quadratic form

$$\tilde{H} = \frac{p^2}{2m} - \frac{p_t^2}{2mc^2} + \frac{1}{2}mc^2,$$

(extended Hamiltonian of relativistic particle) (0.220)

which has a term like the free-particle Hamiltonian, along with a temporal kinetic energy and half the rest-mass energy. Of course, this Hamiltonian still vanishes on the constraint surface.

0.5.3.1 Reparameterization Invariance

Suppose that instead of the proper time, we had used another variable τ' to parameterize the action (0.207), with $\tau'(\tau)$ a monotonic and increasing function. In this case the action becomes

$$S = \int_{\tau_0'}^{\tau_1'} d\tau' \, L(\mathbf{r}, t, \dot{\mathbf{r}}, \dot{t}) \tag{0.221}$$

where now the dots denote differentiation with respect to τ'. Now the Lagrangian has the value $-mc^2\dot{\tau}$ (with $\dot{\tau} > 0$) instead of just $-mc^2$. Furthermore, the canonical momenta (0.209) are modified to read

$$\begin{aligned} \mathbf{p} &= \frac{\partial L}{\partial \dot{\mathbf{r}}} = \frac{m\dot{\mathbf{r}}}{\dot{\tau}} \\ p_t &= \frac{\partial L}{\partial \dot{t}} = -\frac{mc^2\dot{t}}{\dot{\tau}} \end{aligned} \tag{0.222}$$

Note that now the momenta are not uniquely defined due to the reparameterization invariance, but they must nevertheless satisfy the same mass-shell constraint (0.213). The Hamiltonian is extended in the same way as before, and the last two of the extended Hamilton equations (0.218) would then be replaced by

$$\begin{aligned} \dot{\mathbf{r}} &= 2\lambda \mathbf{p} = \frac{2\lambda m \dot{\mathbf{r}}}{\dot{\tau}} \\ \dot{t} &= -\frac{2\lambda p_t}{c^2} = \frac{2\lambda m \dot{t}}{\dot{\tau}}. \end{aligned} \tag{0.223}$$

This means that the Lagrange multiplier is instead fixed to

$$\lambda = \frac{\dot{\tau}}{2m}, \tag{0.224}$$

in which case the extended Hamiltonian (0.220) becomes

$$\tilde{H} = \dot{\tau}\left(\frac{p^2}{2m} - \frac{p_t^2}{2mc^2} + \frac{1}{2}mc^2\right).$$

(extended Hamiltonian of relativistic particle) (0.225)

In this version, there is an arbitrary function $\dot{\tau}$ left over because there is still a gauge freedom due to the reparameterization invariance that we have not yet handled.

0.5.3.2 Reparameterization Invariance as Gauge Freedom

Now suppose that we explicitly constrain the reparameterization invariance in the Hamiltonian (0.225). We began by essentially ignoring the independence by setting $\tau' = \tau$ as one example of a fixed gauge. As another example, consider the case where we parameterize by the local time, $\tau' = t$. Then with the existing constraint (0.215)

$$\begin{aligned}\varphi_1 &= p^2c^2 - p_t^2 + m^2c^4 \approx 0\\ \varphi_2 &= t - \tau' \approx 0,\end{aligned} \tag{0.226}$$

where the previous constraint has now become second class, because the two constraints have a nonvanishing Poisson bracket. In fact,

$$[\varphi_1, \varphi_2]_{\text{P}} = -[t, p_t^2]_{\text{P}} = -2p_t, \tag{0.227}$$

so that

$$[\varphi_\alpha, \varphi_\beta]_{\text{P}} = -2p_t\epsilon_{\alpha\beta}, \tag{0.228}$$

and thus the inverse matrix is

$$C^{\alpha\beta} = \frac{1}{2p_t}\epsilon^{\alpha\beta}. \tag{0.229}$$

The Dirac bracket (0.172) in this case is

$$[f, g]_{\text{D}} = [f, g]_{\text{P}} + \frac{1}{2p_t}[f, p^2c^2 - p_t^2]_{\text{P}}[t, g]_{\text{P}} - \frac{1}{2p_t}[f, t]_{\text{P}}[p^2c^2 - p_t^2, g]_{\text{P}}. \tag{0.230}$$

For most combinations of canonical variables, the Dirac bracket remains the same as the Poisson bracket, for example

$$[r^\alpha, p^\beta]_{\text{D}} = \delta^{\alpha\beta}, \qquad [r^\alpha, r^\beta]_{\text{D}} = [p^\alpha, p^\beta]_{\text{D}} = 0, \tag{0.231}$$

but the major exception is that t and p_t lose their canonical character:

$$[t, p_t]_{\text{D}} = 0. \tag{0.232}$$

Now to compute the extended Hamiltonian (0.168). Using the Hamiltonian in the form (0.210),

$$H(\mathbf{r}, t, \mathbf{p}, p_t) = \frac{p^2}{m} - \frac{p_t^2}{mc^2} + \sqrt{\frac{p_t^2}{c^2} - p^2}, \tag{0.233}$$

we should be careful to evaluate the Poisson brackets before implementing the constraint equations, with the result

$$\begin{aligned}\tilde{H} &= H - [H, \varphi_\alpha]_{\text{P}}\, C^{\alpha\beta}\, \varphi_\beta\\ &= \frac{1}{2p_t}[H, t]_{\text{P}}\left(p^2c^2 - p_t^2 + m^2c^4\right)\\ &= \frac{1}{2p_t}\left[\frac{2p_t}{mc^2} - \frac{p_t/c}{\sqrt{p_t^2/c^2 - p^2}}\right]\left(p^2c^2 - p_t^2 + m^2c^4\right)\\ &= \frac{1}{2mc^2}\left(p^2c^2 - p_t^2 + m^2c^4\right).\end{aligned} \tag{0.234}$$

This Hamiltonian has the same form of the extended Hamiltonian (0.220), without the free function $\dot{\tau}$ of Eq. (0.225); and of course this Hamiltonian still vanishes on the constraint surface.

To understand better what is going on, we can refer back to the discussion in Section 0.4.2 and Problem 0.5, where a Hamiltonian system with explicit time dependence is equivalent to an autonomous Hamiltonian system with one additional degree of freedom. We will need to exploit this equivalence in the reverse direction, where we reduce the system to three degrees of freedom, identifying t as the new time parameter and p_t as the new Hamiltonian. Then from the mass-shell constraint (0.213), the replacement Hamiltonian is

$$H(\mathbf{r}, \mathbf{p}) = p_t = \sqrt{p^2c^2 + m^2c^4}, \tag{0.235}$$

(Hamiltonian in local time)

which is the usual expression for the relativistic energy. Hamilton's equations are equivalent to the original Hamilton equations. In particular, note that the Dirac bracket (0.230) generates the appropriate equations of motion in terms of this new Hamiltonian:

$$\begin{aligned}\frac{d\mathbf{r}}{dt} &= [\mathbf{r}, \tilde{H}]_{\text{D}} = [\mathbf{r}, \tilde{H}]_{\text{P}} = \frac{\mathbf{p}c^2}{p_t} = \frac{\mathbf{p}c^2}{\sqrt{p^2c^2 + m^2c^4}} \\ \frac{d\mathbf{p}}{dt} &= [\mathbf{p}, \tilde{H}]_{\text{D}} = [\mathbf{p}, \tilde{H}]_{\text{P}} = 0\end{aligned} \tag{0.236}$$

Writing the relativistic energy as the value of the new Hamiltonian, $E = \sqrt{p^2c^2 + m^2c^4}$, the first Hamilton equation becomes

$$\mathbf{v}(t) := \frac{d\mathbf{r}}{dt} = \frac{\mathbf{p}c^2}{\sqrt{p^2c^2 + m^2c^4}}. \tag{0.237}$$

This is the well-known relativistic equation

$$\frac{\mathbf{v}}{c} = \frac{\mathbf{p}c}{E}, \tag{0.238}$$

which can be rearranged to give

$$\mathbf{p} = \frac{m\mathbf{v}}{\sqrt{1 - v^2/c^2}}, \tag{0.239}$$

which is the usual expression for the relativistic momentum in terms of the velocity.

0.5.3.3 Alternate Action Principle

Now let's return to the quadratic Hamiltonian (0.225), which we can rewrite as just some Hamiltonian,

$$H = e(\tau)\left(\frac{p^2}{2m} - \frac{p_t^2}{2mc^2} + \frac{1}{2}mc^2\right), \tag{alternate Hamiltonian of relativistic particle} \quad (0.240)$$

where we are using τ to parameterize the proper time, and we have replaced the undetermined function $\dot{\tau}$ by the explicit free function $e(\tau)$. For technical reasons, $e(\tau)$ is often called an **einbein**, in its resemblance to a vierbein in general relativity (in this case, it has the form of a metric acting only in the time direction). The einbein, which we already know functions as a Lagrange multiplier, can in some sense function here as an extra generalized coordinate, but to study it we will first transform back to the equivalent Lagrangian.

Hamilton's equations give in this case

$$\begin{aligned}\dot{\mathbf{r}} &= \frac{e\mathbf{p}}{m} \\ \dot{t} &= -\frac{ep_t}{mc^2} \\ \dot{\mathbf{p}} &= \dot{p}_t = 0,\end{aligned} \tag{0.241}$$

and thus we may derive the Lagrangian via

$$L = \mathbf{p} \cdot \dot{\mathbf{r}} + p_t\dot{t} - H, \tag{0.242}$$

with the result

$$L(\mathbf{r}, t, e, \dot{\mathbf{r}}, \dot{t}) = \frac{m}{2e}\dot{r}^2 - \frac{mc^2}{2e}\dot{t}^2 - \frac{e}{2}mc^2. \tag{alternate Lagrangian of relativistic particle} \quad (0.243)$$

Now the modified action

$$S = \int_{\tau_0}^{\tau_1} d\tau\, L(\mathbf{r}, t, e, \dot{\mathbf{r}}, \dot{t}) \tag{0.244}$$

should be stationary with respect to the usual coordinates in addition to the einbein. (The presence of the einbein here without its velocity signals a constraint is coming.) Stationarity with respect to variation of e gives

$$\frac{\delta S}{\delta e} = \frac{\partial L}{\partial e} = -\frac{m}{2e^2}\dot{r}^2 + \frac{mc^2}{2e^2}\dot{t}^2 - \frac{1}{2}mc^2 = 0. \tag{0.245}$$

This condition is just the mass-shell constraint (0.213),

$$p_t^2 = p^2c^2 + m^2c^4. \tag{0.246}$$

(mass-shell constraint)

Of course the other stationarity conditions reproduce the Hamilton equations, and the function $e(\tau)$ acts as a gauge freedom as before for invariance under reparameterization. We've already shown how this can be left free or fixed to a particular gauge choice.

From the point of view of the Hamiltonian (0.240), the conjugate momentum to e is $p_e = 0$, which is a primary constraint. This also happened in the discussion of the Lagrange multiplier around Eq. (0.147), so this outcome is expected. Then in this line of thinking, the requirement that the Poisson bracket of the primary-constraint function p_e with the Hamiltonian must also vanish leads to the mass-shell constraint, which now appears as a secondary constraint. Then the constraint function p_e is evidently second class, while the mass-shell constraint is still first class. Note that the Hamiltonian itself also must vanish, and so it acts as a second class constraint function as well. The mass-shell constraint is first class unless a parameterization is fixed, and this leads to a Lagrange-multiplier term as before, which signifies that $e(\tau)$ can be modified arbitrarily.

0.5.4 Schrödinger Field

A cornerstone of quantum mechanics is the Schrödinger wave equation

$$i\hbar\psi_t = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi, \tag{0.247}$$

where here we will use the subscript-t notation to represent a partial time derivative (to make the notation a little more manageable and to parallel the notation of Section 0.2.2.1). However, for the moment we will think of this as a *classical* wave equation, for the classical wave function $\psi(\mathbf{r}, t)$, which is classical in the same sense as, say, the electric field. Here we will examine the classical Hamiltonian structure of this wave equation. We will summarize the highlights of the analysis, leaving the derivations of the results as an exercise (Problem 0.9).

The Schrödinger equation (0.247) is derivable from the action functional

$$S = \int d^3r \int dt \left[i\hbar\psi^*\psi_t - \frac{\hbar^2}{2m}\nabla\psi^* \cdot \nabla\psi - \psi^* V(x,t)\psi \right],$$

(Schrödinger-field action) (0.248)

which has the general form

$$S = \int dt\, L(\psi, \psi^*, \psi_t, \nabla\psi, \nabla\psi^*; t), \tag{0.249}$$

where L is the Lagrangian, and ψ^* is treated as a variable independent of ψ. The canonical momenta follow from differentiation of the full Lagrangian,

$$\pi(\mathbf{r}, t) = \frac{\delta}{\delta\psi_t}L = i\hbar\psi^*, \qquad \tilde{\pi}(\mathbf{r}, t) = \frac{\delta}{\delta\psi_t^*}L = 0,$$

(Schrödinger-field canonical momenta) (0.250)

which in this case means a generalization of Hamilton's equations to functional differentiation. The vanishing canonical momentum $\tilde{\pi}$ here is an obvious constraint, but so is the first momentum equation $\pi = i\hbar\psi^*$. Now

the Hamiltonian density[12] is given by transforming the Lagrangian density in the usual way, minding the volume integral, with the result

$$H = \int d^3r \left[\frac{\hbar}{2mi} \nabla\pi\nabla\psi + \frac{1}{i\hbar}\pi V(x,t)\psi \right]. \quad \text{(Schrödinger-field Hamiltonian)} \tag{0.251}$$

Hamilton's equations also appear in terms of the full Hamiltonian as

$$\pi_t = -\frac{\delta}{\delta\psi}H, \qquad \psi_t = \frac{\delta}{\delta\pi}H \tag{0.252}$$

and the resulting equations of motion are

$$\pi_t = -\frac{i\hbar}{2m}\nabla^2\pi + \frac{i}{\hbar}V(x,t)\pi, \qquad \psi_t = \frac{i\hbar}{2m}\nabla^2\psi + \frac{i}{\hbar}V(x,t)\psi. \tag{0.253}$$

At this point, ψ satisfies the Schrödinger equation, while π satisfies the complex-conjugate equation. The other variables ψ^* and $\tilde{\pi}$ do not even appear, so they are ignorable variables. In this case we could proceed by continuing to ignore them, since they are determined in terms of the ''active'' variables by Eqs. (0.250). However, it is instructive to see how to handle them within Dirac's formalism.

Now from Eqs. (0.250), we have the constraint functions[13]

$$\varphi_1 = \pi - i\hbar\psi^* \approx 0, \qquad \varphi_2 = \tilde{\pi} \approx 0, \tag{0.254}$$

which form a pair of second-class constraints. The Poisson bracket here has the generalized form

$$[f(\mathbf{r}), g(\mathbf{r}')]_{\text{P}} := \int d^3r'' \left[\frac{\delta f(\mathbf{r})}{\delta\psi^\alpha(\mathbf{r}'')}\frac{\delta g(\mathbf{r}')}{\delta\pi_\alpha(\mathbf{r}'')} - \frac{\delta f(\mathbf{r})}{\delta\pi_\alpha(\mathbf{r}'')}\frac{\delta g(\mathbf{r}')}{\delta\psi^\alpha(\mathbf{r}'')} \right] \tag{0.255}$$

in terms of functional derivatives, and in particular the constraint-bracket matrix turns out to be

$$[\varphi_\alpha(\mathbf{r}), \varphi_\beta(\mathbf{r}')]_{\text{P}} = -i\hbar\epsilon_{\alpha\beta}\delta^3(\mathbf{r}-\mathbf{r}'), \tag{0.256}$$

showing that the constraints are indeed second class. With these constraints, the extended Hamiltonian is

$$\tilde{H} = \int d^3r \left[\frac{\hbar}{2mi}\nabla\pi\nabla\left(\psi + \frac{i}{\hbar}\tilde{\pi}\right) + \frac{1}{i\hbar}\pi V(x,t)\left(\psi + \frac{i}{\hbar}\tilde{\pi}\right) \right]. \tag{0.257}$$

The form here is more complicated than the original Hamiltonian, but the canonical transformation

$$\Pi = \pi, \qquad \tilde{\Pi} = \varphi_2 = \tilde{\pi}, \qquad \Psi = \psi + \frac{i}{\hbar}\tilde{\pi}, \qquad \Psi^* = \frac{i}{\hbar}\varphi_1 = \psi^* + \frac{i}{\hbar}\pi \tag{0.258}$$

yields the simpler extended Hamiltonian

$$\tilde{H} = \int d^3r \left[\frac{\hbar}{2mi}\nabla\Pi\nabla\Psi + \frac{1}{i\hbar}\Pi V(x,t)\Psi \right], \tag{0.259}$$

which has the same form as the original Hamiltonian (0.251).

The Dirac bracket corresponding to the Hamiltonian (0.257) is the somewhat unwieldy

$$[f(\mathbf{r}), g(\mathbf{r}')]_{\text{D}} = \int d^3r'' \left[\frac{\delta f(\mathbf{r})}{\delta\psi(\mathbf{r}'')}\frac{\delta g(\mathbf{r}')}{\delta\pi(\mathbf{r}'')} - \frac{\delta f(\mathbf{r})}{\delta\pi(\mathbf{r}'')}\frac{\delta g(\mathbf{r}')}{\delta\psi(\mathbf{r}'')} \right] - \frac{i}{\hbar}\int d^3r'' \left[\frac{\delta f(\mathbf{r})}{\delta\psi(\mathbf{r}'')}\frac{\delta g(\mathbf{r}')}{\delta\psi^*(\mathbf{r}'')} - \frac{\delta f(\mathbf{r})}{\delta\psi^*(\mathbf{r}'')}\frac{\delta g(\mathbf{r}')}{\delta\psi(\mathbf{r}'')} \right]. \tag{0.260}$$

[12] For another treatment this Hamiltonian, see Leonard L. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw–Hill, 1968) (ISBN: 0070856435), p. 499.

[13] A variation of this constrained problem is treated by László Á. Gergely, ''On Hamiltonian Formulations of the Schrödinger System,'' *Annals of Physics* **298**. 394 (2002) (doi: 10.1006/aphy.2002.6262) (arXiv: hep-th/0301052).

The first term on the right-hand side is the Poisson bracket on the canonical pair (ψ, π) that remains in the Hamiltonian. The second term is evidently related to the enforcement of the constraint φ_1 constraint, which "slaves" ψ^* to π. This bracket is simplified by the alternate canonical transformation

$$\Pi = \pi + i\hbar\psi^*, \qquad \tilde{\Pi} = \tilde{\pi} + i\hbar\psi, \qquad \Psi = \psi, \qquad \Psi^* = \psi^*, \tag{0.261}$$

and in the new coordinates the bracket is

$$[f(\mathbf{r}), g(\mathbf{r}')]_{\text{D}} = \int d^3r'' \left[\frac{\delta f(\mathbf{r})}{\delta\Psi(\mathbf{r}'')} \frac{\delta g(\mathbf{r}')}{\delta\Pi(\mathbf{r}'')} - \frac{\delta f(\mathbf{r})}{\delta\Pi(\mathbf{r}'')} \frac{\delta g(\mathbf{r}')}{\delta\Psi(\mathbf{r}'')} \right], \tag{0.262}$$

which has the same form as the original Poisson bracket (0.255).

In principle, we should have also checked for secondary constraints by setting $\partial_t\varphi_\alpha \approx 0$, but there are none, because by this point the second-class constraints have been eliminated by adopting the Dirac bracket (see the comment at the end of Section 0.5.2.5).

0.5.5 Electromagnetic Field

Of course, *the* canonical example of gauge freedom is electromagnetism, which follows from the Lagrangian

$$L(\mathscr{A}, \phi, \mathscr{A}_t, \phi_t) = \frac{\epsilon_0}{2} \int d^3r \left[(\nabla\phi + \mathscr{A}_t)^2 - c^2(\nabla \times \mathscr{A})^2 - \rho\phi + \mathbf{j} \cdot \mathscr{A} \right].$$

(electromagnetic Lagrangian) (0.263)

The Lagrangian is written in terms of the vector potential $\mathscr{A}(\mathbf{r}, t)$ and the scalar potential $\phi(\mathbf{r}, t)$; in terms of the potentials, the electric and magnetic fields are defined via derivatives:

$$\begin{aligned} \mathscr{E} &:= -\nabla\phi - \mathscr{A}_t \\ \mathscr{B} &:= \nabla \times \mathscr{A}. \end{aligned} \tag{0.264}$$

(electromagnetic fields)

The Lagrangian here includes coupling to source charge density $\rho(\mathbf{r}, t)$ and current density $\mathbf{j}(\mathbf{r}, t)$, but otherwise assumes no media that interact with the field. Stationarity of the action integral of this Lagrangian reproduces Maxwell's equations; this is covered later in Section 7.4.4.1, while here we will focus on the Hamiltonian structure of electromagnetism. Again, while it is common to work with the electromagnetic field in relativistic notation as an antisymmetric tensor, we will intentionally avoid relativistic notation here.

To find the canonical momenta, we differentiate the Lagrangian appropriately, with the result

$$\mathbf{\Pi}(\mathbf{r}, t) = \frac{\delta}{\delta\mathscr{A}_t} L = \epsilon_0(\nabla\phi + \mathscr{A}_t) = -\epsilon_0\mathscr{E}, \qquad \pi(\mathbf{r}, t) = \frac{\delta}{\delta\phi_t} L = 0.$$

(electromagnetic canonical momenta) (0.265)

Note that the momentum conjugate to $\mathscr{A}$ is the electric displacement field $\mathscr{D} = \epsilon_0\mathscr{E}$, up to a minus sign. We have already found our first (primary) constraint, $\pi \approx 0$, which we will discuss further once we have the Poisson bracket. The Hamiltonian is the usual transform of the Lagrangian,

$$H(\mathscr{A}, \phi, \mathbf{\Pi}, \pi) = \int d^3r \left[\mathbf{\Pi} \cdot \mathscr{A}_t + \pi\phi_t \right] - L(\mathscr{A}, \phi, \mathscr{A}_t, \phi_t), \tag{0.266}$$

and the resulting expression is

$$H(\mathscr{A}, \phi, \mathbf{\Pi}, \pi) = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 - \mathbf{\Pi} \cdot \nabla\phi + \frac{1}{2}\epsilon_0 c^2(\nabla \times \mathscr{A})^2 + \rho\phi - \mathbf{j} \cdot \mathscr{A} \right].$$

(electromagnetic Hamiltonian) (0.267)

Let's take a minute to interpret this expression. The last two terms are linear coupling terms to the sources; in the absence of these, we expect the Hamiltonian to act as a total energy, something like the volume

integral of $\epsilon_0\mathscr{E}^2 + \mathscr{B}^2/\mu_0$, where $\epsilon_0\mu_0 = 1/c^2$. The $(\nabla \times \mathscr{A})^2$ term clearly plays the role of $\mathscr{B}^2/\mu_0$, while the Π^2 term clearly plays the role of $\epsilon_0\mathscr{E}^2$. So what about the $\mathbf{\Pi} \cdot \nabla\phi$ term? Roughly speaking, the electric field has two components: a radiative component and a static component. The static component is nonzero in the derivative $\nabla \cdot \boldsymbol{\mathscr{E}}$, while the radiative component is nonzero under the derivative $\nabla \times \boldsymbol{\mathscr{E}}$ (more precisely, these are the longitudinal and transverse parts of the electric field). The function of this term is to remove the static part of the electric field from the Π^2 term, leaving only the radiative electric field. (The magnetic field is already radiative in this sense, so there is not corresponding magnetic term.) Observe, for a field with $\nabla \cdot \mathbf{\Pi} = 0$, that $\mathbf{\Pi}$ could be written as the curl of another field, and the $\mathbf{\Pi} \cdot \nabla\phi$ term would then vanish after integration by parts.

Now to work out Hamilton's equations for the electromagnetic field. These are given by the derivatives

$$\begin{aligned}
\mathscr{A}_t &= \frac{\delta}{\delta \mathbf{\Pi}} H = \frac{1}{\epsilon_0}\mathbf{\Pi} - \nabla\phi \\
\phi_t &= \frac{\delta}{\delta \pi} H = 0 \\
\mathbf{\Pi}_t &= -\frac{\delta}{\delta \mathscr{A}} H = -\epsilon_0 c^2 \nabla \times \nabla \times \mathscr{A} + \mathbf{j} \\
\pi_t &= -\frac{\delta}{\delta \phi} H = -\nabla \cdot \mathbf{\Pi} - \rho \approx 0.
\end{aligned}$$

(electromagnetic Hamilton equations) (0.268)

The first two equations are the most straightforward functional derivatives. The third equation must be handled a little more carefully in order to put the first variation in the correct form to extract the functional derivative; it relies on the vector identity $\nabla \cdot (\mathbf{A} \times \mathbf{B}) = \mathbf{B} \cdot (\nabla \times \mathbf{A}) - \mathbf{A} \cdot (\nabla \times \mathbf{B})$, which becomes $\nabla \cdot (\mathscr{A} \times \nabla \times \mathscr{A}) = (\nabla \times \mathscr{A})^2 - \mathscr{A} \cdot (\nabla \times \nabla \times \mathbf{A})$ on setting $\mathbf{A} = \mathscr{A}$ and $\mathbf{B} = \nabla \times \mathscr{A}$. This gives a particular form of integration by parts; discarding the surface term then produces the $\nabla \times \nabla \times \mathscr{A}$ term. The fourth equation also requires integration by parts, via the vector identity $\nabla \cdot (\phi\mathbf{A}) = \mathbf{A} \cdot \nabla\phi + \phi\nabla \cdot \mathbf{A}$.

To interpret the Hamilton equations (0.268), let's consider them one by one. The first one contains no new information, as it is equivalent to the definition of the electric field in Eqs. (0.264). The second equation is a constraint $\phi_t = 0$, but this is basically the same as the constraint $\pi = 0$, because we expect π to generate the evolution of ϕ. The third equation is the same as Ampère's law,

$$\nabla \times \boldsymbol{\mathscr{B}} = \frac{1}{c^2}\boldsymbol{\mathscr{E}}_t + \mu_0\mathbf{j}. \tag{0.269}$$

The fourth equation is a new constraint (the equation vanishes because of the constraint $\pi \approx 0$), and it is equivalent to Gauss' law:

$$\nabla \cdot \boldsymbol{\mathscr{E}} = \frac{\rho}{\epsilon_0}. \tag{0.270}$$

Thus, the Hamilton equations produce directly two out of the four Maxwell equations. The remaining two are the monopole law

$$\nabla \cdot \boldsymbol{\mathscr{B}} = 0, \tag{0.271}$$

and Faraday's law,

$$\nabla \times \boldsymbol{\mathscr{E}} = -\nabla \times \mathscr{A}_t = -\boldsymbol{\mathscr{B}}_t. \tag{0.272}$$

Both of these follow from the definitions of the fields in terms of the gauge potentials.

0.5.5.1 Constraints

Now to summarize, we have the constraints[14]

$$\phi_1 = \pi \approx 0, \qquad \phi_2 = \nabla \cdot \mathbf{\Pi} + \rho \approx 0. \tag{0.273}$$

[14]For good related discussions of constraints in electromagnetism, including Coulomb gauge, see Andrew Hanson *et al.*, *op. cit.*, Chapter 5; and Steven Weinberg, *Lectures on Quantum Mechanics* (Cambridge, 2013) (ISBN: 9781107028722) (doi: 10.1017/CBO9781316276105), Chapter 11.

The ϕ_1 constraint arose from finding the canonical momenta, and is thus a primary constraint. The ϕ_2 constraint came from the Hamilton equations of motion (and from the primary constraint), and it is thus a secondary constraint. Remember that consistency demands that we check the Poisson bracket of the primary constraint $\phi_1 = \pi$ with the Hamiltonian, and demand that it vanish; but this is precisely what we calculated in computing π_t.

To see this more explicitly, we can consider the Poisson bracket

$$[f(\mathbf{r}), g(\mathbf{r}')]_{\text{P}} = \int d^3r'' \left[\frac{\delta f(\mathbf{r})}{\delta \mathscr{A}^\alpha(\mathbf{r}'')} \frac{\delta g(\mathbf{r}')}{\delta \Pi_\alpha(\mathbf{r}'')} - \frac{\delta f(\mathbf{r})}{\delta \Pi_\alpha(\mathbf{r}'')} \frac{\delta g(\mathbf{r}')}{\delta \mathscr{A}^\alpha(\mathbf{r}'')} \right], \tag{0.274}$$

where for the purposes of summation over the repeated α index, we are using the shorthand $(\mathscr{E}^\alpha) = (\phi, \mathscr{E}^x, \mathscr{E}^y, \mathscr{E}^z)$ and $(\Pi_\alpha) = (\phi, \Pi_x, \Pi_y, \Pi_z)$. Then the Poisson bracket of the primary constraint ϕ_1 with the Hamiltonian must vanish weakly,

$$[\phi_1, H]_{\text{P}} = [\pi, H]_{\text{P}} = \pi_t = -\nabla \cdot \mathbf{\Pi} - \rho = -\phi_2 \approx 0, \tag{0.275}$$

leading to the secondary constraint. Because the two constraints involve only different degrees of freedom, $[\phi_1, \phi_2]_{\text{P}} = 0$, and thus these constraints are first class.

From Eq. (0.274) we can also write down the canonical Poisson bracket

$$[\mathscr{A}^\alpha(\mathbf{r}, t), \Pi_\beta(\mathbf{r}', t)]_{\text{P}} = \delta^\alpha{}_\beta \, \delta^3(\mathbf{r} - \mathbf{r}'), \tag{0.276}$$
(canonical Poisson bracket)

which is the generalization of $[q^\alpha, p_\beta]_{\text{P}} = \delta^\alpha{}_\beta$. Note that despite the four-vector notation for compactness, there are no tricky sign conventions ($\delta^\alpha{}_\beta$ is no different from $\delta_{\alpha\beta}$ despite the raised index). This Poisson bracket shows that the constraint equations (0.273) should indeed be thought of as weak equalities, because they are not in general consistent with the canonical bracket—that is substituting $\pi = 0$ into the canonical bracket leads to $[\phi, \pi]_{\text{P}} = 0$ instead of a delta function, so these constraint equations do not hold off the constraint manifold.

For completeness, we ought to check for more constraints by differentiating ϕ_1 and ϕ_2. Setting $\partial_t \phi_1 \approx 0$ is something we already did in the last of Eqs. (0.268), so this gives nothing new. However, setting $\partial_t \phi_2 \approx 0$ gives

$$\nabla \cdot \mathbf{\Pi}_t + \rho_t = 0, \tag{0.277}$$

and then using Ampère's law (0.269) gives

$$\rho_t = -\nabla \cdot \mathbf{j}, \tag{0.278}$$
(continuity equation)

which is the continuity equation for the sources. Here we see that source continuity is in some sense a manifestation of Gauss' law.

0.5.5.2 Gauge Freedom

Because there are no second-class constraints, the Dirac bracket and the Poisson bracket are identical. The extended Hamiltonian has two Lagrange multipliers for the two constraints:

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0} \Pi^2 - \mathbf{\Pi} \cdot \nabla \phi + \frac{1}{2} \epsilon_0 c^2 (\nabla \times \mathscr{A})^2 + \rho\phi - \mathbf{j} \cdot \mathscr{A} + \lambda^1 \pi + \lambda^2 \big(\nabla \cdot \mathbf{\Pi} + \rho \big) \right]. \tag{0.279}$$

That is, we have introduced Lagrange-multiplier fields $\lambda^{1,2}(\mathbf{r}, t)$ to pull in the gauge freedoms. Integrating by parts an discarding the surface term gives

$$\int d^3r \, \mathbf{\Pi} \cdot \nabla \phi = -\int d^3r \, \phi \nabla \cdot \mathbf{\Pi}, \tag{0.280}$$

so that

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0} \Pi^2 + \frac{1}{2} \epsilon_0 c^2 (\nabla \times \mathscr{A})^2 - \mathbf{j} \cdot \mathscr{A} + \lambda^1 \pi + (\lambda^2 + \phi) \Big(\nabla \cdot \mathbf{\Pi} + \rho \Big) \right]. \tag{0.281}$$

Now the multiplier λ^2 can be seen to make ϕ arbitrary. The additional gauge freedom from λ^1 is not really independent, as we can see by looking at the evolution under this new Hamiltonian.

Hamilton's equations under the extended Hamiltonian are

$$\begin{aligned}
\mathscr{A}_t &= \frac{\delta}{\delta \mathbf{\Pi}}\tilde{H} = \frac{1}{\epsilon_0}\mathbf{\Pi} - \nabla\phi - \nabla\lambda^2 \\
\phi_t &= \frac{\delta}{\delta \pi}\tilde{H} = \lambda^1 \\
\mathbf{\Pi}_t &= -\frac{\delta}{\delta \mathscr{A}}\tilde{H} = -\epsilon_0 c^2 \nabla\times\nabla\times\mathscr{A} + \mathbf{j} \\
\pi_t &= -\frac{\delta}{\delta \phi}\tilde{H} = -\nabla\cdot\mathbf{\Pi} - \rho \approx 0.
\end{aligned} \tag{0.282}$$

These equations show more clearly the effects of the Lagrange multipliers. First, the identification $\lambda^1 = \phi_t$ shows that ϕ is an arbitrary function. Also the first Hamilton equation suggests that λ^2 is associated with an arbitrariness of ϕ. Note that it is useful to preserve the form of $\mathbf{\Pi}$ in Eq. (0.265), because $\mathbf{\Pi}$, being proportional to the electric field, is physically measurable and should therefore be gauge-invariant (suggesting that in fact we want $\lambda^2 = 0$). This is an observation outside of the strict Hamiltonian formalism, however. Nonetheless, it seems undesirable to have λ^2 in the first Hamilton equation. We can attempt to get rid of it by making a translation $\phi \longrightarrow \phi - \lambda^2$; for such a transformation to be canonical we must make the combined transformation (see Problem 0.12, and also Problem 1.37 for an analogous transformation)

$$\phi \longrightarrow \phi - \lambda^2, \qquad \pi \longrightarrow \pi - (\lambda^2)_t, \qquad H \longrightarrow H + \int d^3r \Big[-\phi(\lambda^2)_{tt} + \pi(\lambda^2)_t - (\lambda^2_t)^2\Big]. \tag{0.283}$$

Under this transformation the extended Hamiltonian (0.281) becomes

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 + \frac{1}{2}\epsilon_0 c^2(\nabla\times\mathscr{A})^2 - \mathbf{j}\cdot\mathscr{A} + \big(\lambda^1 + \lambda^2_t\big)\big(\pi - \lambda^2_t\big) + \phi\big(\nabla\cdot\mathbf{\Pi} + \rho - \lambda^2_{tt}\big)\right], \tag{0.284}$$

and the dynamical equations that change from Eqs. (0.282) become

$$\begin{aligned}
\mathscr{A}_t &= \frac{1}{\epsilon_0}\mathbf{\Pi} - \nabla\phi \\
\phi_t &= \lambda^1 + \lambda^2_t \\
\pi_t &= -\nabla\cdot\mathbf{\Pi} - \rho + \lambda^2_{tt} \approx \lambda^2_{tt}.
\end{aligned} \tag{0.285}$$

Thus, in these coordinates, $\mathbf{\Pi}$ maintains its gauge-invariant form, both Lagrange multipliers are associated with the arbitrariness of ϕ, and λ^2 in particular is associated with an arbitrariness of the scalar momentum π. Note that the effect of λ^2 on π_t does not upset Gauss' law, because we also applied the canonical transformation to the primary constraint $\pi \approx 0$ in order to obtain the shifted constraint $\pi \approx \lambda^2_t$. The effect of λ^2 on ϕ may be absorbed into λ^1; formally making the replacement $\lambda^1 \longrightarrow \lambda^1 - \lambda^2_t$ leads to the extended Hamiltonian

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 + \frac{1}{2}\epsilon_0 c^2(\nabla\times\mathscr{A})^2 - \mathbf{j}\cdot\mathscr{A} + \lambda^1\big(\pi - \lambda^2_t\big) + \phi\big(\nabla\cdot\mathbf{\Pi} + \rho - \lambda^2_{tt}\big)\right], \tag{0.286}$$

(total electromagnetic Hamiltonian)

and the only dynamical equation that changes form from Eqs. (0.285) is

$$\phi_t = \lambda^1. \tag{0.287}$$

At this point, the effect of λ^2 is restricted to the variable π, which we don't particularly care about, and only the λ^1 multiplier is associated with the arbitrariness of ϕ.

To connect to the standard view of gauge freedom in classical electromagnetism, note that π is uninteresting as a dynamical variable, and in the most recent coordinates only λ^2 affects it. Therefore we may as well fix that gauge freedom, to better focus on the more important one. Thus fixing $\lambda^2 = 0$ (or only $\lambda_t^2 = 0$ is really necessary), the resulting extended Hamiltonian is

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 + \frac{1}{2}\epsilon_0 c^2 (\nabla \times \mathscr{A})^2 + \phi\rho - \mathbf{j}\cdot\mathscr{A} + \pi\chi_t - \mathbf{\Pi}\nabla\chi \right],$$

(total electromagnetic Hamiltonian, $\lambda^2 = 0$) (0.288)

after renaming the remaining Lagrange multiplier via

$$\chi = \int_0^t dt' \lambda^1(t'), \tag{0.289}$$

and integrating the $\phi\nabla\cdot\mathbf{\Pi}$ term by parts before setting $\phi = \chi$ according to Eq. (0.287).

Focusing on the last two terms in the extended Hamiltonian (0.288), which have the combined form

$$H_{\text{gauge}} = \int d^3r \left[\pi\chi_t - \mathbf{\Pi}\nabla\chi \right], \tag{0.290}$$

we can see that the Poisson brackets associated with the gauge part of the Hamiltonian are

$$[\phi, H_{\text{gauge}}]_{\text{P}} = \frac{\delta}{\delta\pi} H_{\text{gauge}} = \chi_t \tag{0.291}$$

for the scalar potential, and

$$[\mathscr{A}, H_{\text{gauge}}]_{\text{P}} = \frac{\delta}{\delta\mathbf{\Pi}} H_{\text{gauge}} = -\nabla\chi \tag{0.292}$$

for the vector potential, with $[\pi, H_{\text{gauge}}]_{\text{P}} = [\mathbf{\Pi}, H_{\text{gauge}}]_{\text{P}} = 0$. That is, the gauge Hamiltonian (0.290) acts as the generator of an infinitesimal gauge transformation [cf. Eq. (0.62)]. The conventional way to express the finite form of this gauge transformation is the simultaneous transformation

$$\begin{aligned} \mathscr{A} &\longrightarrow \mathscr{A} - \nabla\chi \\ \phi &\longrightarrow \phi + \chi_t. \end{aligned} \tag{0.293}$$

(gauge transformation)

Under these transformations, both the electric and magnetic fields are left unchanged. The extended Hamiltonian is also unchanged; however, the invariance of the source terms relies on the continuity constraint and consideration of the time integral in the action functional (Problem 0.11). The gauge invariance expressed by χ is exactly the same gauge freedom possessed by the Lagrangian (0.263). The Hamiltonian form introduced a *second* gauge freedom (the Lagrange multiplier λ_2), associated with the arbitrariness of the new canonical variable π.[15]

[15] The presence of a second gauge freedom in the electromagnetic Hamiltonian has been the root of some consternation. See J. Brian Pitts, ''A first class constraint generates not a gauge transformation, but a bad physical change: The case of electromagnetism,'' *Annals of Physics* **351** 382 (2014) (doi: 10.1016/j.aop.2014.08.014) (arXiv: 1310.2756), who argues that this indicates that the point of view that first-class constraints generate gauge freedoms is flawed. This point can be seen by reviewing the modification (0.187) in the evolution due to a variation in the Lagrange multiplier. In electromagnetism the problem can be seen in the evolution equations (0.282), because a variation in λ^2 induces a change in the evolution of $\mathscr{A}$, while a variation in λ^1 induces a (separate) variation in the evolution of ϕ. However, it seems only physical for this to work out in the particular combination (0.293) of Lagrange-multiplier variations. After the canonical transformation (0.283), the effects of varying the Lagrange parameters has of course changes, as reflected in the new equations of motion (0.284). In the new coordinates, varying Lagrange multipliers only impacts the evolutions of ϕ and π, which we thus regard as arbitrary functions. Any effect on ϕ is counterbalanced by the appropriate effect on $\mathscr{A}$, so that $\mathbf{\Pi}$ is explicitly gauge-invariant. The confusing effect of the two gauge freedoms in the original coordinates can be attributed to having some of the arbitrariness of π mixed into that of ϕ, which of course would not be compensated in the same arbitrariness of $\mathscr{A}$.

0.5.5.3 Coulomb Gauge

To finish up this treatment of gauge freedom in the electromagnetic-field Hamiltonian, let's consider an example of fixing a particular gauge. An important example is the **Coulomb gauge**, which is specified by the condition

$$\nabla \cdot \mathscr{A} = 0. \tag{0.294}$$
(Coulomb-gauge condition)

We can implement this in the Hamiltonian (0.288) by making a gauge transformation of the form

$$\nabla \cdot \mathscr{A} \longrightarrow \nabla \cdot \mathscr{A} - \nabla^2 \chi = 0, \tag{0.295}$$

where χ satisfies

$$\nabla \cdot \mathscr{A} = \nabla^2 \chi. \tag{0.296}$$

Under the gauge condition (0.294), Gauss' law (0.270) becomes

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_0}, \tag{0.297}$$

which now has the form of a constraint equation that determines ϕ solely in terms of the charge density. In fact, we know from the study of electrostatics that the solution to Eq. (0.297) is

$$\phi(\mathbf{r}, t) = \frac{1}{4\pi\epsilon_0} \int d^3r' \, \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \tag{0.298}$$

Thus, in this gauge, the scalar potential appears as an instantaneous response to the charge density; to detractors, this is a major downer. However, this is actually convenient in atom-field interactions, since the scalar potential generates the binding potential for the electron to the nucleus, a potential that doesn't need a time delay.

To summarize, we now have four total constraints, including the former two constraints (0.273):

$$\varphi_1 = \pi \approx 0, \qquad \varphi_2 = \nabla \cdot \mathbf{\Pi} + \rho \approx 0, \qquad \varphi_3 = \nabla \cdot \mathscr{A} \approx 0, \qquad \varphi_4 = \phi - \frac{1}{4\pi\epsilon_0} \int d^3r' \, \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \approx 0. \tag{0.299}$$

Note that in the case where $\rho = 0$ (such that the only source is $\mathbf{j}$, where $\nabla \cdot \mathbf{j} = 0$), the last constraint function could be replaced by $\varphi_4 = \phi \approx 0$

As in the relativistic-particle problem, when fixing the gauge freedom the constraints go from first to second class. To see the second-class nature of the constraints, we can examine the Poisson brackets of the constraint functions. One nonvanishing bracket is

$$[\varphi_1(\mathbf{r}), \varphi_4(\mathbf{r}')]_{\text{P}} = [\pi(\mathbf{r}), \phi(\mathbf{r}')]_{\text{P}} = -\delta(\mathbf{r} - \mathbf{r}') \tag{0.300}$$

while the other is

$$[\varphi_2(\mathbf{r}), \varphi_3(\mathbf{r}')]_{\text{P}} = [\nabla \cdot \mathbf{\Pi}(\mathbf{r}), \nabla \cdot \mathscr{A}(\mathbf{r}')]_{\text{P}} = -\int d^3\mathbf{r}'' \left[\nabla\delta^3(\mathbf{r} - \mathbf{r}'')\right]\left[\nabla\delta^3(\mathbf{r}' - \mathbf{r}'')\right] = \nabla^2\delta^3(\mathbf{r} - \mathbf{r}'). \tag{0.301}$$

Putting together the matrix of Poisson brackets, we have

$$\Big[[\varphi_\alpha(\mathbf{r}), \varphi_\beta(\mathbf{r}')]_{\text{P}}\Big] = \begin{bmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & \nabla^2 & 0 \\ 0 & -\nabla^2 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \delta^3(\mathbf{r} - \mathbf{r}'). \tag{0.302}$$

We will need to invert this matrix, using the generalization of (0.164),

$$\int d^3\mathbf{r}'' \, C^{\alpha\beta}(\mathbf{r}, \mathbf{r}'') \, [\varphi_\beta(\mathbf{r}''), \varphi_\gamma(\mathbf{r}')]_{\text{P}} = \delta^\alpha{}_\gamma \, \delta^3(\mathbf{r} - \mathbf{r}'). \tag{0.303}$$

Formally, we can write the inverse matrix as

$$\left[C^{\alpha\beta}(\mathbf{r},\mathbf{r}')\right] = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -\nabla^{-2} & 0 \\ 0 & \nabla^{-2} & 0 & 0 \\ -1 & 0 & 0 & 0 \end{bmatrix} \delta^3(\mathbf{r}-\mathbf{r}'), \tag{0.304}$$

where we will work out the details of the inverse operator ∇^{-2} to ∇^2 below. Then the general Dirac bracket (0.172) under the present constraints is

$$[f(\mathbf{r}),g(\mathbf{r}')]_{\text{D}} = [f(\mathbf{r}),g(\mathbf{r}')]_{\text{P}} - \int d^3\mathbf{r}'' \int d^3\mathbf{r}''' \, [f(\mathbf{r}),\varphi_\alpha(\mathbf{r}'')]_{\text{P}} C^{\alpha\beta}(\mathbf{r}'',\mathbf{r}''')[\varphi_\beta(\mathbf{r}'''),g(\mathbf{r}')]_{\text{P}}. \tag{0.305}$$

Specifically, we have the canonical Dirac bracket

$$[\phi(\mathbf{r}),\pi(\mathbf{r}')]_{\text{D}} = \delta(\mathbf{r}-\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}') = 0 \tag{0.306}$$

for the scalar degree of freedom, which is now inactive (with both variables having been constrained to the source or to zero). Working through the summation for the canonical bracket for the vector degrees of freedom yields

$$[\mathscr{A}^\alpha(\mathbf{r},t),\Pi_\beta(\mathbf{r}',t)]_{\text{D}} = \delta^\alpha{}_\beta \, \delta^3(\mathbf{r}-\mathbf{r}') - \partial_\alpha\partial_\beta \frac{1}{\nabla^2}\delta^3(\mathbf{r}-\mathbf{r}'). \tag{0.307}$$

The combination on the right-hand side is special, and it is called the **transverse projector** or **transverse delta function**, which we can define by

$$\delta^\perp_{\alpha\beta}(\mathbf{r}) := \left(\delta_{\alpha\beta} - \frac{\partial_\alpha\partial_\beta}{\nabla^2}\right)\delta^3(\mathbf{r}). \tag{0.308}$$

(transverse delta function)

Here we have made use of the fact that the derivatives ∂_α commute with ∇^{-2} (to be shown below), so that the ordering does not matter. Then the canonical bracket (0.307) may be written

$$[\mathscr{A}^\alpha(\mathbf{r},t),\Pi_\beta(\mathbf{r}',t)]_{\text{D}} = \delta^\perp_{\alpha\beta}(\mathbf{r}-\mathbf{r}') \tag{0.309}$$

(canonical bracket, Coulomb gauge)

This differs from the canonical bracket (0.276) before fixing the gauge, which was just an ordinary delta function. This modified bracket reflects the absence of any **longitudinal** or **irrotational** component of $\mathscr{A}$ (i.e., a part of $\mathscr{A}^\parallel$ where $\nabla\cdot\mathscr{A}^\parallel \neq 0$). In general, a vector field can be decomposed into longitudinal and transverse parts (or irrotational and solenoidal parts), $\mathscr{A} = \mathscr{A}^\parallel + \mathscr{A}^\perp$, such that $\nabla\times\mathscr{A}^\parallel = 0$ and $\nabla\cdot\mathscr{A}^\perp = 0$. This decomposition is called the **Helmholtz decomposition**. Here, this means that in the Coulomb gauge, only the transverse part of the vector potential contributes in the extended Hamiltonian.

To gain some more insight into the significance of the transverse projector, we can work out an explicit expression for the operator ∇^{-2}, and in particular an expression for its action on the delta function. We can do this by setting $\rho(\mathbf{r}) = \epsilon_0\delta^3(\mathbf{r})$ in Eqs. (0.297) and (0.298), to obtain the relations

$$\nabla^2\phi(\mathbf{r}) = -\delta^3(\mathbf{r}), \qquad \phi(\mathbf{r},t) = \frac{1}{4\pi}\int d^3r' \, \frac{\delta^3(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \frac{1}{4\pi|\mathbf{r}|}. \tag{0.310}$$

Eliminating ϕ gives the important relation

$$\nabla^2\frac{1}{|\mathbf{r}|} = -4\pi\delta^3(\mathbf{r}), \tag{0.311}$$

which basically says that $1/4\pi r$ is the Green-function solution to the Poisson equation. Note that elsewhere [Eq. (13.57)] we compute the energy-space Green function for the Schrödinger equation, which reduces to the same $1/4\pi r$ if we take $E = \hbar = 2m = 1$. Reversing the logic here, this could be taken as a derivation

of the solution (0.298) to Gauss' law. For our present purposes the more useful form of this equation comes from applying the inverse-Laplacian operator:

$$\frac{1}{\nabla^2}\delta^3(\mathbf{r}) = -\frac{1}{4\pi|\mathbf{r}|}. \tag{0.312}$$

This is the explicit expression that we seek. That the derivative ∂_α commutes with ∇^{-2} follows from applying it to Eqs. (0.311) and (0.312) and comparing the results. With Eq. (0.312), the transverse delta function (0.308) becomes

$$\delta^\perp_{\alpha\beta}(\mathbf{r}) := \delta_{\alpha\beta}\delta^3(\mathbf{r}) + \partial_\alpha\partial_\beta\frac{1}{4\pi r}. \tag{0.313}$$

(transverse delta function)

This expression is interesting in that it shows that the transverse projector is a *nonlocal* operator. Thus, while the gauge-free Poisson bracket (0.276) is local, the gauge-fixed version (0.309) is nonlocal in space, as a consequence of having eliminated any static-Coulomb component.

After adopting the Dirac bracket (0.309) in place of the Poisson bracket, we can freely implement the constraints (0.299) in the extended Hamiltonian (0.288), with the result

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 + \frac{1}{2}\epsilon_0 c^2(\nabla\times\mathscr{A})^2 - \mathbf{j}\cdot\mathscr{A}\right].$$

(Coulomb-gauge Hamiltonian) (0.314)

Observe that the scalar canonical pair (ϕ,π) has been constrained away, and they are now completely decoupled from the vector degree of freedom (along with the source field ρ). The scalar potential ϕ is determined by Eq. (0.298), while $\pi = 0$. Thus, the Hamiltonian only really refers to two degrees of freedom, corresponding to the two independent components of $\mathscr{A}^\perp$.

The equations of motion following from the constrained Hamiltonian (0.314) follow from the canonical Dirac bracket (0.309). To apply the canonical bracket to the more complicated functionals of $\mathbf{\Pi}$ and $\mathscr{A}$, we will need a product rule for the Dirac bracket. Because of the definition (0.172) of the Dirac bracket in terms of the Poisson bracket, the Dirac bracket (like the Poisson bracket) satisfies the product rule $[A,BC]_{\text{D}} = B[A,C]_{\text{D}} + [A,B]_{\text{D}}C$. (The properties of the Poisson bracket are given on p. 84.) For fields here, this product rule generalizes to

$$\left[A, \int d^3r\, B(\mathbf{r})\, C(\mathbf{r})\right]_{\text{D}} = \int d^3r\, B(\mathbf{r})\left[A, C(\mathbf{r})\right]_{\text{D}} + \int d^3r\left[A, B(\mathbf{r})\right]_{\text{D}} C(\mathbf{r}). \tag{0.315}$$

Applying this to the canonical equations of motion, we find

$$\begin{aligned}
\mathscr{A}_t &= [\mathscr{A}, H]_{\text{D}} = \frac{1}{\epsilon_0}\mathbf{\Pi}^\perp \\
\mathbf{\Pi}_t &= [\mathbf{\Pi}, H]_{\text{D}} = -\epsilon_0 c^2 \nabla\times\nabla\times\mathscr{A} + \mathbf{j}^\perp = \epsilon_0 c^2\nabla^2\mathscr{A}^\perp + \mathbf{j}^\perp,
\end{aligned}$$

(electromagnetic evolution equations, Coulomb gauge) (0.316)

where we have used

$$\mathbf{\Pi}^\perp(\mathbf{r}) = \int d^3r\, \delta^\perp_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\,\mathbf{\Pi}(\mathbf{r}'), \tag{0.317}$$

with a similar expression for $\mathbf{j}^\perp$. In both cases $\nabla\cdot\mathbf{\Pi}^\perp = 0$ and $\nabla\cdot\mathbf{j}^\perp = 0$. (Note that we are leaving some statements unjustified here to keep the discussion from going on way too long.) That is, the effect of the canonical bracket is to ensure that the fields couple only to the transverse parts of the conjugate fields and of the source, in order to maintain the Coulomb constraint. This constraint is automatic in the term $\nabla\times\nabla\times\mathscr{A}$, because the curl knocks out any longitudinal part and thus $\nabla\times\nabla\times\mathscr{A} = \nabla\times\nabla\times\mathscr{A}^\perp$. Thus we were able to use the vector identity $\nabla\times\nabla\times\mathbf{A} = \nabla(\nabla\cdot\mathbf{A}) - \nabla^2\mathbf{A}$ applied to only the transverse potential $\mathscr{A}^\perp$. In this sense Eqs. (0.316) can also be regarded as equations of motion for the nonvanishing parts $\mathscr{A}^\perp$ and $\mathbf{\Pi}^\perp$ of the full fields. They maintain what could be regarded as initial conditions $\nabla\cdot\mathscr{A} = \nabla\cdot\mathbf{\Pi} = 0$.

0.6 Exercises

Problem 0.1

Show that the shortest distance between two points p_1 and p_2 is a straight line. That is, consider the length functional ℓ for the curve $y(x)$,

$$\ell[y] = \int_{x_1}^{x_2} \sqrt{1 + y_x^2}\, dx, \tag{0.318}$$

and show that the condition $\delta\ell/\delta y = 0$ (with fixed endpoints) implies that $y(x)$ is a straight line.

Problem 0.2

Recall that a mixed-variable generating function for a (classical) canonical transformation arises from equating the actions in two coordinate systems.

Review the steps leading to the generating function $F_1(q, \tilde{q}; t)$, and define the alternate generating function

$$F_2(q^\alpha, \tilde{p}_\alpha; t) := F_1 + \tilde{q}^\alpha \tilde{p}_\alpha. \tag{0.319}$$

Writing out the differential dF_2 in two ways (corresponding to the two sides of this equation), equate terms to derive the coordinate transformations

$$p_\alpha = \frac{\partial F_2}{\partial q^\alpha}, \qquad \tilde{q}_\alpha = \frac{\partial F_2}{\partial \tilde{p}^\alpha}, \qquad \tilde{H} = H + \frac{\partial F_2}{\partial t}. \tag{0.320}$$

Problem 0.3

Show that infinitesimal time translation, $z^\alpha(t) \longrightarrow z^\alpha(t + dt)$, is a canonical transformation.

Problem 0.4

Prove **Poisson's theorem**: the Poisson bracket of two constants of the motion is itself a constant of the motion.

Problem 0.5

Beginning with an autonomous, 2-degree-of-freedom Hamiltonian $H(q^1, q^2, p_1, p_2)$, the point of this problem is to show that this system can be mapped to a $1\frac{1}{2}$-degree-of-freedom system $\tilde{H}(q, p, t)$. The key is to use one of the generalized coordinates as a time variable.

Since the Hamiltonian $H(q^1, q^2, p_1, p_2)$ is constant, we can write

$$H(q^1, q^2, p_1, p_2) = E \tag{0.321}$$

for some constant E. Thinking of this as a constraint on the four coordinates, we can eliminate p_2 as an independent coordinate,

$$p_2 = p_2(q^1, q^2, p_1, E). \tag{0.322}$$

We will then regard $q^2 = t$ as the new time coordinate (the old time coordinate for $H(q^1, q^2, p_1, p_2)$ is τ). Then we can take p_2 to be the new Hamiltonian (and taking E to be fixed):

$$\tilde{H}(q, p, t) = p_2(q^1, q^2, p_1, E), \tag{0.323}$$

with $q = q^1$, $p = p_1$, and again $t = q^2$.

Verify that the new, reduced Hamiltonian generates the same evolution as the original.

Problem 0.6

For any phase-space function $f(q,p)$, the Poisson bracket defines a canonical Hamiltonian vector field L_f by

$$L_f g = [g,f]_{\rm P} \tag{0.324}$$

for any function g. In coordinates, the vector field is

$$L_f = I^{\mu\nu}\frac{\partial f}{\partial z^\nu}\frac{\partial}{\partial z^\mu}. \tag{0.325}$$

Show that the commutator of two vector fields satisfies

$$[L_f, L_g] = L_{[f,g]_{\rm P}} \tag{0.326}$$

for any two phase-space functions f and g.

Any two first integrals I_α and I_β are said to be **in involution** if $[I_\alpha, I_\beta]_{\rm P} = 0$. Thus, invariants in involution define commuting vector fields.

Problem 0.7

Find the transformation to action-angle variables for the reduced Kepler Hamiltonian,

$$H = \frac{p^2}{2\mu} - \frac{k}{x} + \frac{\ell^2}{x^2}. \tag{0.327}$$

Do this by noting that the action can be written as

$$J = \frac{\sqrt{2\mu}}{2\pi}\oint \sqrt{E - V(x)}\,dx, \tag{0.328}$$

where $E < 0$ for the Kepler potential above. Then extend $V(x)$ into the complex plane with a branch cut that extends between the two turning points $x_{1,2}$ defined by $E = V(x_{1,2})$. Then use Cauchy's theorem to evaluate the integral on a contour that loops around the branch cut.

(*Hint*: the action turns out to be $J = k\sqrt{\mu/2|E|} + \ell\sqrt{2\mu}$.)

Problem 0.8

Show that the commutator of two vector fields, as defined in Section 0.4.4.3, satisfies

$$[L_f, L_g] = -L_{[f,g]_{\rm P}} \tag{0.329}$$

for any two phase-space functions f and g.

Problem 0.9

(a) Compute the functional derivative of

$$S = \int d^3r \int dt\, \left[i\hbar\psi^*\psi_t - \frac{\hbar^2}{2m}\nabla\psi^*\cdot\nabla\psi - \psi^* V(\mathbf{r},t)\psi \right], \tag{0.330}$$

with respect to the fields $\psi^*(\mathbf{r},t)$ and $\psi(\mathbf{r},t)$, ignoring surface terms. Work out the equations of motion obtained from the action principles $\delta S/\delta\psi = 0$ and $\delta S/\delta\psi^* = 0$, and then compute the canonically conjugate momentum fields π to the coordiante ψ, and $\tilde{\pi}$ to the coordinate ψ^*.

(b) The integrand in Eq. (0.330) acts as a Lagrangian density L; the Lagrangian is then the volume integral of the density L. Write down the corresponding Hamiltonian density H, eliminating the

variables $\tilde{\psi}$ and ϕ^*, and work out the Hamilton equations of motion for ψ and ϕ. (Working with the densities here is not quite correct, but will save a lot of writing volume integrals over and over.)

Note that there are constraints in this problem, but at this point they are already handled, because there are two ignorable coordinates. Thus, we are done. The rest of this problem is to see how the constraints work out in Dirac's theory, in a simple case where we know how they should work out.

(c) In deriving the Hamiltonian density, you should have found two constraint equations. Check the consistency of the corresponding constraint functions, and show that both constraints are second class. Write down the total Hamiltonian density, using the specific forms of the constraint functions.

(d) The Poisson brackets with the total Hamiltonian should yield equations of motion for the canonical variables on the full phase space $(\phi, \phi^*, \pi, \tilde{\pi})$ that respect the constraints. In particular, they should match the results from Hamilton's equations in part (b). To show this, consider the transformation

$$\Pi = \pi, \qquad \tilde{\Pi} = \varphi_2 = \tilde{\pi}, \qquad \Psi = \psi + \frac{i}{\hbar}\tilde{\pi}, \qquad \Psi^* = \frac{i}{\hbar}\varphi_1 = \psi^* + \frac{i}{\hbar}\pi. \tag{0.331}$$

Show that this is a canonical transformation by finding the appropriate generating function F_2 (see Problem 0.2). After making this transformation, you should be able to argue that the constraints are respected by the Poisson-bracket evolution without explicitly computing them.

(e) Write out the Dirac bracket in the phase space $(\psi, \psi^*, \pi, \tilde{\pi})$, and find a canonical transformation that reduces it to the Poisson bracket on a single canonical pair (Ψ, Π).

Problem 0.10

Consider a particle with Hamiltonian[16]

$$H = \frac{p^2}{2m} + V(\mathbf{r}), \tag{0.332}$$

constrained to a surface

$$f(\mathbf{r}) = 0. \tag{0.333}$$

(a) Show that this constraint is second class, and work out the other second-class constraint.

(b) Derive the expressions for the Dirac brackets

$$\begin{aligned} [x_\alpha, x_\beta]_{\text{D}} &= 0 \\ [x_\alpha, p_\beta]_{\text{D}} &= \delta_{\alpha\beta} - \hat{n}_\alpha \hat{n}_\beta \\ [p_\alpha, p_\beta]_{\text{D}} &= \hat{n}_\beta \big(\mathbf{p}\cdot\nabla\big)\hat{n}_\alpha - \hat{n}_\alpha \big(\mathbf{p}\cdot\nabla\big)\hat{n}_\beta. \end{aligned} \tag{0.334}$$

(c) Work out the Dirac brackets $[\mathbf{r}, H]_{\text{D}}$ and $[\mathbf{p}, H]_{\text{D}}$ to derive the constrained equations of motion

$$\begin{aligned} \dot{\mathbf{r}} &= \frac{1}{m}\Big[\mathbf{p} - \hat{n}(\hat{n}\cdot\mathbf{p})\Big] \approx \frac{\mathbf{p}}{m} \\ \dot{\mathbf{p}} &\approx \mathbf{F} - \hat{n}(\hat{n}\cdot\mathbf{F}) - \frac{1}{m}\mathbf{p}\cdot[(\mathbf{p}\cdot\nabla)\hat{n}]\hat{n}, \end{aligned} \tag{0.335}$$

where $\hat{n}(\mathbf{r}) := \nabla f/|\nabla f|$ is the unit normal vector to the constraint surface, and $\mathbf{F} := -\nabla V$ is the external force.

(d) From the results of part (c), show that

$$m\ddot{\mathbf{r}} = \mathbf{F} - \hat{n}(\hat{n}\cdot\mathbf{F}) - m\big(\dot{\mathbf{n}}\cdot\dot{\hat{m}}\big)\hat{n}. \tag{0.336}$$

[16] Sonnet Nguyen and Łukasz A. Turski, "Examples of the Dirac approach to dynamics of systems with constraints," *Physica A* **290**, 431 (2001) (doi: 10.1016/S0378-4371(00)00449-0).

That is, the net force is the tangential part of the external force, plus a (normal) constraint component. These results generalize those of the plane pendulum from Section 0.5.2.8.

Problem 0.11

Isolating the source-coupling part of the electromagnetic Lagrangian (0.263), and writing this as an action, gives

$$S_{\text{source}} = \int dt \int d^3r \Big[-\rho\phi + \mathbf{j}\cdot\mathscr{A} \Big]. \tag{0.337}$$

Show that gauge invariance for this piece of the action implies continuity of the sources.

Problem 0.12

For the total electromagnetic Hamiltonian (0.281)

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 + \frac{1}{2}\epsilon_0 c^2 (\nabla\times\mathscr{A})^2 - \mathbf{j}\cdot\mathscr{A} + \lambda^1\pi + (\lambda^2+\phi)\Big(\nabla\cdot\mathbf{\Pi}+\rho\Big)\right], \tag{0.338}$$

show that the canonical transformation

$$\phi \longrightarrow \phi - \lambda^2, \qquad \pi \longrightarrow \pi - (\lambda^2)_t, \qquad H \longrightarrow H + \int d^3r \Big[-\phi(\lambda^2)_{tt} + \pi(\lambda^2)_t - (\lambda_t^2)^2 \Big] \tag{0.339}$$

is induced by the generating function

$$F_2(\phi,\pi';t) = \int d^3r \Big[\pi'\phi - \phi(\lambda^2)_t + \pi'\lambda^2\Big] - \int d^3r \int_0^t dt' \left[\lambda^2(t')(\lambda^2)_{t't'} + \big[(\lambda^2)_{t'}\big]^2\right], \tag{0.340}$$

according to the transformation rules (0.56)

$$\pi = \frac{\delta F_2}{\delta\phi}, \qquad \phi' = \frac{\delta F_2}{\delta\pi'}, \qquad H' = H + \frac{\partial F_2}{\partial t}, \tag{0.341}$$

where the primes denote transformed variables.

Then verify that the form of the total Hamiltonian is (0.284)

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0}\Pi^2 + \frac{1}{2}\epsilon_0 c^2 (\nabla\times\mathscr{A})^2 - \mathbf{j}\cdot\mathscr{A} + \big(\lambda^1+\lambda_t^2\big)\big(\pi-\lambda_t^2\big) + \phi\big(\nabla\cdot\mathbf{\Pi}+\rho-\lambda_{tt}^2\big)\right] \tag{0.342}$$

after this canonical transformation (after dropping primes on the transformed quantities).

Chapter 1

Axiomatic Structure of Quantum Mechanics

The goal here is to make explicit the assumptions underlying quantum mechanics *before* we take it for a test drive and do some calculations. Since quantum mechanics is fundamentally a theory of linear systems, some mathematical background will help to get started. However, the goal is *not* to write down a rigorous set of axioms: The axioms we will use to start off with for quantum mechanics are sloppy (but mostly okay for finite-dimensional situations) and redundant. They are nevertheless useful as a starting point for discussion, and we will return to fix up their deficiencies to some extent in later chapters. It can be a useful approach to let yourself get into a bit of trouble, and then learn from how you save the situation, and that's how we will approach things in this text.

1.1 Mathematical Preliminaries

As we are headed toward the fundamental objects of quantum mechanics, vectors in Hilbert spaces and their transformations, let's step back for a bit and define the underlying concepts.

1.1.1 Vector Space

First, a **vector space** V is a set of elements (vectors) with *closed* operations $+$ and $\cdot$ (**closed operations** are functions that map vectors in V back to vectors in V) that satisfy the following axioms:

1. $x + (y + z) = (x + y) + z \quad \forall_{x,y,z \in V}$
2. $\exists_{e \in V} \ (x + e = x)$
3. $\forall_{x \in V} \ \exists_{x^{-1} \in V} \ (x + x^{-1} = e)$
4. $x + y = y + x \quad \forall_{x,y \in V}$
5. $a \cdot (x + y) = (a \cdot x) + (a \cdot y) \quad \forall_{a \in \mathbb{C}, x, y \in V}$
6. $(a + b) \cdot x = (a \cdot x) + (b \cdot x) \quad \forall_{a,b \in \mathbb{C}, x \in V}$
7. $(ab) \cdot x = a \cdot (b \cdot x) \quad \forall_{a,b \in \mathbb{C}, x \in V}$
8. $1 \cdot x = x \quad \forall_{x \in V}$

(Quick test-drive: Is the set $\{0\}$ a vector space? What about the set $\mathbb{Q}$ of all rational numbers? The set $\mathbb{I}$ of all irrational numbers?) All of these properties make intuitive sense for the ''usual'' finite-dimensional vectors in $\mathbb{C}^n$, but the point is that more general objects such as functions and derivative operators can live in vector spaces as well. Note that as we have quantum mechanics in mind, we are referring to the set $\mathbb{C}$ of complex numbers as the allowable scalars.

1.1.2 Inner-Product Space

A **inner-product space** is a vector space V, along with an **inner product** (or **scalar product**), which we will write as function $\langle\cdot,\cdot\rangle : V \times V \longrightarrow \mathbb{C}$, that satisfies the following axioms:[1]

1. $\langle x, x\rangle \geq 0$, with $\langle x, x\rangle = 0$ if and only if $x = 0$ (or "$x = e$" in the notation of the vector-space axioms above), $\quad \forall_{x\in V}$
2. $\langle y, x\rangle = \langle x, y\rangle^* \quad \forall_{x,y\in V}$
3. $\langle x + y, z\rangle = \langle x, z\rangle + \langle y, z\rangle \quad \forall_{x,y,z\in V}$
4. $\langle x, ay\rangle = a\langle x, y\rangle \quad \forall_{x\in V, a\in\mathbb{C}}$

Note that the second and fourth axioms together imply that $(ax, y) = a^*(x, y)$. Also, note that we are defining the inner product (or **scalar product**) such that we choose vectors for both "slots" from the same vector space, but it can be useful to choose them from *different* spaces (more on this later). Finally, from the first axiom, it is natural to define a **norm** via

$$\|x\|^2 := \langle x, x\rangle, \tag{1.1}$$

because the self-inner-product is nonnegative. This also allows us to define a *distance* between vectors as the norm of the difference vector ($\|x - y\|$). Thus, an inner-product space, as we have defined it, is also a metric space.

Good examples of inner-product spaces are: the set of complex-valued, finite-dimensional vectors ("x_n"), where the inner product is defined as

$$\langle x, y\rangle = x_1^* y_1 + x_2^* y_2 + \cdots x_n^* y_n; \tag{1.2}$$

and the set of bounded, complex-valued functions, where the inner product is

$$\langle f, g\rangle = \int f^*(x)\, g(x)\, dx, \tag{1.3}$$

though in the latter case there need to be extra constraints on either the functions allowed in the vector space or on the integration domain to guarantee that the integral converges.

1.1.3 Cauchy–Schwarz Inequality

This is a good point to take a short break from defining stuff, to prove a useful result involving inner products, the **Cauchy–Schwarz inequality**, which we can write as

$$\langle x, x\rangle\langle y, y\rangle \geq \left|\langle x, y\rangle\right|^2 \tag{1.4}$$
(Cauchy–Schwarz inequality)

for any vectors $|x\rangle$ and $|y\rangle$. To prove this, we will start by defining an auxiliary vector

$$z := y - \frac{\langle x, y\rangle}{\langle x, x\rangle} x, \tag{1.5}$$

under the assumption $x \neq 0$. Then the first inner-product axiom says that $(z, z) \geq 0$. Multiplying this all out gives (after a bit of algebra, make sure to fill in the steps!)

$$\begin{aligned}\langle z, z\rangle &= \langle y, y\rangle - \frac{\langle x, y\rangle}{\langle x, x\rangle}\langle y, x\rangle - \frac{\langle x, y\rangle^*}{\langle x, x\rangle^*}\langle x, y\rangle + \frac{\langle x, y\rangle^*\langle x, y\rangle}{\langle x, x\rangle^*\langle x, x\rangle}\langle x, x\rangle \\ &= \langle y, y\rangle - \frac{|\langle x, y\rangle|^2}{\langle x, x\rangle} \geq 0\end{aligned} \tag{1.6}$$

[1] As a function, the inner product $\langle\cdot,\cdot\rangle$ satisfying these axioms is called a **Hermitian form**. Relaxing the conjugation axiom by the condition $\langle ax, y\rangle = a^*\langle x, y\rangle$ gives a more general function called a **sesquilinear form**. The **anti-Hermitian form**, which satisfies $\langle y, x\rangle = -\langle x, y\rangle^*$, is an example of a sesquilinear form that is not Hermitian.

Since $\langle x, x\rangle > 0$ by assumption, we can multiply through on the last inequality to obtain

$$\langle x, x\rangle\langle y, y\rangle - |\langle x, y\rangle|^2 \geq 0, \tag{1.7}$$

which gives the desired inequality. In the case where $x = 0$, this argument is invalid; if $y \neq 0$ then the argument will carry through by interchanging x and y, otherwise $x = y = 0$, in which case the Cauchy–Schwarz inequality is equivalent to $0 \geq 0$, which is certainly true.

1.1.4 Linear Transformation

Before getting to quantum mechanics itself, it's useful to define one more concept. A **linear transformation** L of a vector space V into another vector space W is a function $L : V \longrightarrow W$ such that:

1. $L(x + y) = L(x) + L(y) \quad \forall_{x,y\in V}$
2. $L(ax) = aL(x) \quad \forall_{a\in\mathbb{C},x\in V}$

It's useful to note that *any* linear transformation between finite-dimensional vector spaces can be represented by a matrix (see Problem 1.1). In quantum mechanics, it is common to use infinite-dimensional generalizations of vectors and matrices, however.

Additionally, if V is an inner product space, then the linear transformation $L^\dagger$ is the **Hermitian conjugate** or **adjoint** of the linear transformation L provided

$$\big\langle x, L(y)\big\rangle = \big\langle L^\dagger(x), y\big\rangle \qquad \forall_{x,y\in V}. \tag{1.8}$$

Furthermore, a linear transformation L is **Hermitian** or **self-adjoint**[2] if $L = L^\dagger$.

1.2 Mechanics in Hilbert Space

Now we have most of the concepts needed to define the world in which quantum mechanics exists. This world is a **Hilbert space** $\mathscr{H}$, which is an inner-product space (also called a **pre-Hilbert space**) that is both normed and complete (to be defined).

We have already commented that the inner product itself induces a natural norm on the space. The second condition of completeness is a bit more technical. To define this, we need the concept of a **Cauchy sequence** in $\mathscr{H}$, which is a sequence (x_n) of vectors such that

$$\lim_{n,n'\to\infty} \|x_n - x_{n'}\| = 0. \tag{1.9}$$

That is, the vectors must get arbitrarily close as the sequence progresses. (To read the above statement formally, we could say that for every $\epsilon > 0$ there is a positive integer N such that for every pair $n, n' > N$, that $\|x_n - x_{n'}\| < \epsilon$.) Then a normed vector space is **complete** if the limit of every Cauchy sequence exists (in the same vector space).

The main consequence of completeness of Hilbert spaces is the **Riesz representation theorem**. Roughly speaking, suppose that we define inner products $\langle x, y\rangle$ in a more general, asymmetric way, where we pick the right-hand vector from the Hilbert space, $y \in \mathscr{H}$, while the left-hand vector is chosen from a **dual Hilbert space** $\mathscr{H}^*$, i.e., $x \in \mathscr{H}^*$. Then $\mathscr{H}^*$ is isomorphic to $\mathscr{H}$ (isomorphic here meaning mathemetically equivalent, in the sense that a vector in either space can be uniquely identified with a **form** in the other space). More formally, the dual space $\mathscr{H}^*$ is defined as the set of all linear functionals on $\mathscr{H}$ (i.e., the set of all linear functions of vectors in $\mathscr{H}$ that yield a complex scalar); then the elements of $\mathscr{H}^*$ (forms) can be associated uniquely with an inner product $\langle x, y\rangle$. That is, $y \in \mathscr{H}$ is the Hilbert-space vector and $\langle x, \cdot\rangle \in \mathscr{H}^*$ is the form; the Riesz theorem says that we are allowed to think of the elements in $\mathscr{H}^*$ as inner products like this. More colloquially, then we can think of $x \in \mathscr{H}^*$, where we combine elements of $\mathscr{H}^*$ and $\mathscr{H}$ in inner products.

[2] These terms are really only synonymous in finite-dimensional vector spaces, and the distinction can be important. We will return to this in Section 21.1.

Completeness of Hilbert space has useful consequences in addition to the Riesz theorem.[3] Hilbert spaces always have orthonormal bases, any two orthonormal bases of the same Hilbert space must be isomorphic (i.e., must have the same cardinality), and any two Hilbert spaces with isomorphic bases must themselves be isomorphic. We will, however, defer these properties until the measurement axiom below, where we can more conveniently deduce these properties from the association of Hilbert-space vectors with probabilities. (We are working with an overcomplete set of axioms, which suits our purposes just fine.)

So, completeness requirement is something of a technical detail as far as grinding out calculations is concerned. Nevertheless, it is useful to be conscious of what spaces are allowable as Hilbert spaces. For example, the space of continuous, square-integrable functions (those for which $\int |f(x)|^2\,dx < \infty$) is *not* a Hilbert space, because it is possible to construct a sequence of continuous functions whose limit is discontinuous. (Can you think of an example sequence?) On the other hand, the space of square-integrable functions *is* a Hilbert space. (But something to think about: It is possible to construct a sequence of normalized Gaussian functions of width $\sim 1/n$, which "converges" to a delta function, but a delta function is not allowed in this Hilbert space. What gives? For a more precise setup of this statement, see Problem 1.4.)

There are a few examples of Hilbert spaces that are of primary importance. The set of all complex-valued N-tuples $x = (x_1, x_2, \ldots, x_N)$ is a Hilbert space. The set l^2, which is the set of all complex-valued sequences that are square-summable:

$$l^2 := \left\{ x = \{x_n\}_{n=1}^{\infty} : \sum_{n=1}^{\infty} |x_n|^2 < \infty \right\}. \tag{1.10}$$

On the finite, continuous domain $[0, 1]$, the set of all square-integrable functions, denoted $L^2([0, 1])$, or that is,

$$L^2([0,1]) = \left\{ f : [0,1] \longrightarrow \mathbb{C} : \int_0^1 |f(x)|^2\,dx < \infty \right\}, \tag{1.11}$$

is a Hilbert space. Similarly, $L^2(\mathbb{R})$, the set of all square-integrable functions on the whole real line, is a Hilbert space. This space includes many functions that may not be nice, with discontinuities, kinks, slowly decaying tails, and so on.

1.3 First Axiom: States in Hilbert Space

Now that we have defined the concept of a Hilbert space, the first axiom of quantum mechanics is easy to state: Every physical state is represented by a vector in a (quantum-mechanical) Hilbert space $\mathscr{H}$. As to what we mean by "physical state," for the moment at least we will be vague about this; it's not easy to say anything that won't quickly devolve into fisticuffs and crying—or worse yet, workshops. For now let's say that quantum mechanics uses Hilbert-space vectors to represent whatever there is to represent about the physical system we're trying to model. We'll come back to this point later in Chapter 10, since the state of a quantum system is often better represented in terms of a more general object that can be defined in terms of vectors.

In Dirac notation, a vector in Hilbert space is represented (abstractly) by a **ket** $|\psi\rangle \in \mathscr{H}$. When this is combined as an inner product with another vector $|\phi\rangle$, the vector in the left-hand "slot" is written as a **bra** (reversed ket), so that the inner product looks like $\langle\phi|\psi\rangle$. (The bra and ket are, colloquially, each half of a "bracket," where the "c" has sadly gone astray.) In terms of the Riesz theorem above, bras come from the dual space, $\langle\phi| \in \mathscr{H}^*$, which yields a scalar via $\langle\phi|\psi\rangle$, but because the spaces $\mathscr{H}$ and $\mathscr{H}^*$ are equivalent, we don't really need to worry too muchabout the distinction.

The rest of the axiom is that we will typically assume that vectors $|\psi\rangle$ in Hilbert space corresponding to physical states are normalized:

$$\langle\psi|\psi\rangle = 1. \tag{1.12}$$
(normalization condition for state vectors)

[3] Yvonne Choquet-Bruhat, Cécile DeWitt-Morette, and Margaret Dillard-Bleick, *Analysis, Manifolds, and Physics*, revised ed. (Elsevier, 1982) (ISBN: 0444860177).

It is occasionally useful to have unnormalized vectors, however, and of course every complex scalar multiple of a vector must also be in the same vector space. So really we should think of all vectors that are the same up to a (nonzero) scalar multiple as an equivalence class of vectors corresponding to the same physical state. The normalization condition (1.12) can be tricky for certain cases (delta functions, extended states on unbounded domains), a topic that we will return to later (see, for example, Section 1.7.2 and Chapter 21).

Since the Hilbert-space vector is synonymous with the state of a physical system, the vector itself is called a **state vector**, and the vector itself is colloquially referred to as ''the state'' itself, although it is technically a representation or specification of the state.

Given two states in Hilbert space, there are necessarily many other states, because from the axioms of vector spaces, any linear combinations of vectors is also a vector. One important caveat is that not every possible vector in Hilbert space may correspond to a physical state. A common example is that the state $|\text{boson}\rangle$, representing the existence of a boson, and the state $|\text{fermion}\rangle$, representing the existence of a fermion, are both valid states. However, superpositions of these states are not allowed: a particle is either a boson or a fermion, with certainty.

1.4 Second Axiom: Operators and Observables

The second axiom of quantum mechanics is also relatively simple to state: Every physical observable is represented by a linear, Hermitian operator on the Hilbert space.[4] In terms of what we have defined, a linear, Hermitian operator is just a linear transformation on $\mathscr{H}$. The convention in Dirac notation in quantum mechanics is just to put the operator Q to the left of the state, as in $Q|\psi\rangle$ (as in common matrix-vector notation), rather than to write it with the more conventional notation of a function $Q(|\psi\rangle)$. Because of the importance of Hermitian operators in quantum mechanics, it's worth reviewing their notation. We defined the Hermitian conjugate of a linear transformation in Eq. (1.8), which translated into Dirac notation reads

$$\langle x|Qy\rangle = \langle x|Q|y\rangle = \langle Q^\dagger x|y\rangle. \tag{1.13}$$

Here, the notation $|Qy\rangle \equiv Q|y\rangle$ is the vector $|y\rangle$ after being transformed by Q; generally, though, only the notation $\langle x|Q|y\rangle$ in the middle expression above is used, except to emphasize a particular order of operations. It's also worth noting one common abuse of Dirac notation, which is to write

$$\big(|x\rangle\big)^\dagger = \langle x|. \tag{1.14}$$

Strictly speaking, this doesn't make any sense because $|x\rangle$ is a vector, not an operator, and only operators have Hermitian conjugates. The reason for this abuse is that conjugation of operators is something like complex conjugation of scalars. In particular, the conjugation of an inner product with a linear transformation reads

$$\big\langle x, L(y)\big\rangle^* = \big\langle L^\dagger(x), y\big\rangle^* = \big\langle y, L^\dagger(x)\big\rangle, \tag{1.15}$$

where we used Eq. (1.8) and then the second property of inner-product spaces; in Dirac notation we can equivalently write

$$\langle x|L|y\rangle^* = \langle y|L^\dagger|x\rangle, \tag{1.16}$$

in which complex conjugation of an inner product amounts to Hermitian conjugation of operators, the ''conjugation rule'' (1.14), and reversing the order of everything (see Problem 1.2 for reversing the order in products of operators). The same procedure works for Hermitian conjugates of operators of the form $|x\rangle\langle y|$, so, although not strictly correct, Eq. (1.14) still makes for a useful shortcut.

An important concept related to operators is their **eigenvalues**; the eigenvalues q of an operator Q are defined by the eigenvalue equation

$$Q|q\rangle = q|q\rangle, \tag{1.17}$$
(eigenvalue equation)

where $|q\rangle$ is an **eigenvector** corresponding to q. Of course, there may be many eigenvalues and eigenvectors; for the purposes of the discussion here we will assume a discrete set of eigenvalues, which can be labeled

[4] Technically, this should be self-adjoint operator instead of merely Hermitian, whenever it matters. See Section 21.1.

q_n, with eigenvectors $|q_n\rangle$ (i.e., there may be infinitely many, but only countably infinite). The case of a continuum of eigenvalues has some extra complications, to which we will return in Section 1.7.2.

An important result for observables follows from the result that all eigenvalues of Hermitian operators are real. To prove this, suppose that q is an eigenvalue of Q, as in the above eigenvalue equation. Then we can form the inner product

$$\langle q|\big(Q|q\rangle\big) = q\langle q|q\rangle = q. \tag{1.18}$$

But we can also regard $Q = Q^\dagger$ as operating on the left-hand vector, so that

$$\langle q|Q|q\rangle = \langle Q^\dagger q|q\rangle = \langle Qq|q\rangle = q^*\langle q|q\rangle = q^*, \tag{1.19}$$

where the complex conjugation follows from the eigenvalue equation and the scalar-multiple theorem $(ax, y) = a^*(x, y)$ intrinsic to inner-product spaces. Since these expressions are equivalent, $q = q^*$, and thus q is real.

A further useful result is that eigenvectors of a Hermitian operator Q corresponding to *distinct* eigenvales are orthogonal. To prove this, suppose $Q|q_1\rangle = q_1|q_1\rangle$ and $Q|q_2\rangle = q_2|q_2\rangle$, with $q_1 \neq q_2$. Then we can form the inner product

$$\langle q_2|Q|q_1\rangle = q_1\langle q_2|q_1\rangle\,, \tag{1.20}$$

with Q acting to the right. If it acts instead to the left,

$$\langle q_2|Q|q_1\rangle = q_2\langle q_2|q_1\rangle\,. \tag{1.21}$$

Since these expressions should be equivalent,

$$(q_2 - q_1)\langle q_2|q_1\rangle = 0. \tag{1.22}$$

Since $q_2 - q_1 \neq 0$ by assumption, it follows that $\langle q_2|q_1\rangle = 0$.

A more complicated situation arises when the eigenvalues of a Hermitian operator are degenerate, because the above argument for orthogonality of eigenvectors breaks down. However, the eigenvectors corresponding to a common eigenvalue define a subspace of $\mathscr{H}$, and it is still possible to choose an orthonormal basis of eigenvectors on this subspace (i.e., a minimal set of vectors such that any vector in the subspace may be written as a superposition of the basis vectors). The procedure for doing this is **Gram–Schmidt procedure** for constructing an orthonormal basis, which works as follows. Starting with a linearly independent set of vectors $|q_1\rangle, |q_2\rangle, \ldots, |q_n\rangle$ (here, linearly independent means that it is not possible to write any one of the vectors as a linear combination of the others), choose the first basis vector as

$$|q_1'\rangle := |q_1\rangle. \tag{1.23}$$

Then construct the second basis vector by taking $|q_2\rangle$, and subtracting away any part along $|q_1'\rangle$:

$$|q_2'\rangle := |q_2\rangle - \langle q_1'|q_2\rangle\,|q_1'\rangle. \tag{1.24}$$

Operating on this with $\langle q_1'|$ and using $\langle q_1'|q_1'\rangle = 1$ shows that $\langle q_1'|q_2'\rangle = 0$, so the vectors are orthogonal. As written, however, $|q_2'\rangle$ is not necessarily normalized, so it should be replaced by its normalized self: $|q_2'\rangle \longrightarrow |q_2'\rangle/\sqrt{\langle q_2'|q_2'\rangle}$. The next basis vector follows in the same way, subtracting any components along the already constructed basis vectors,

$$|q_3'\rangle := |q_3\rangle - \langle q_1'|q_3\rangle\,|q_1'\rangle - \langle q_2'|q_3\rangle\,|q_2'\rangle, \tag{1.25}$$

and the result should again be normalized, and so on until the nth basis vector is constructed. Linear independence ensures that the subtraction won't result in a null vector in any of the cases.

1.5 Third Axiom: Measurements of Observables

The third axiom details more about what it means for an operator to be an observable. Specifically, it says that a measurement of a physical observable, with corresponding operator Q, yields an eigenvalue q

of Q as the measurement result. Furthermore, the measurement leaves the system in an eigenstate $|q\rangle$ corresponding to q. In general many outcomes (eigenvalues) q_n of the measurement are possible, in which case the probability for outcome q_n is given by **Born's rule**,[5]

$$\text{Prob}(q_n) = \left|\langle q_n|\psi\rangle\right|^2, \tag{1.26}$$
(Born's rule)

given that the state of the system immediately before the measurement was $|\psi\rangle$. The statement of this axiom so far implicitly assumes nondegenerate eigenvalues, something we will correct shortly.

The measurement here, with a **collapse** of the state into one of the eigenstates of the observable, is often called a **von Neumann measurement**, although this term also refers to a model of the measurement process that includes a measuring apparatus. It is possible (and useful) to define more general notions of measurement, but the von Neumann measurement can serve as a theoretical basis for the more general types.

But first, the notion of a probability here has some handy consequences. First, the probabilities must sum to one, otherwise they aren't probabilities. That is,

$$\sum_n \left|\langle q_n|\psi\rangle\right|^2 = 1. \tag{1.27}$$

A further consequence is that the eigenstates of a Hermitian operator Q form a complete basis, so that an arbitrary state may be written as a linear combination of eigenstates $|q_n\rangle$,

$$|\psi\rangle = \sum_n c_n|q_n\rangle, \tag{1.28}$$
(completeness of eigenstates)

given of course the proper choice of the c_n.[6] To demonstrate that this completeness must work out, let $|\psi\rangle$ be an arbitrary state vector, and define the auxiliary vector

$$|\psi'\rangle = |\psi\rangle - \sum_n \langle q_n|\psi\rangle\,|q_n\rangle. \tag{1.29}$$

Now forming the self inner product

$$\begin{aligned}
\langle\psi'|\psi'\rangle &= \langle\psi|\psi\rangle - \sum_n \langle q_n|\psi\rangle\,\langle\psi|q_n\rangle - \sum_n \langle q_n|\psi\rangle^*\,\langle q_n|\psi\rangle + \sum_{nn'} \langle q_n|\psi\rangle^*\langle q_{n'}|\psi\rangle\,\langle q_n|q_{n'}\rangle \\
&= \langle\psi|\psi\rangle - 2\sum_n \left|\langle q_n|\psi\rangle\right|^2 + \sum_{nn'} \langle q_n|\psi\rangle^*\langle q_{n'}|\psi\rangle\,\delta_{nn'} \\
&= \langle\psi|\psi\rangle - \sum_n \left|\langle q_n|\psi\rangle\right|^2 \\
&= 0,
\end{aligned} \tag{1.30}$$

where $\langle\psi|\psi\rangle = 1$ due to the normalization assumption, and the sum is also unity, being the sum of probabilities according to the third axiom. The only way for the norm of $|\psi'\rangle$ to be zero is for $|\psi'\rangle$ itself to be zero, and thus Eq. (1.28) holds with

$$c_n = \langle q_n|\psi\rangle\,. \tag{1.31}$$
(probability amplitude)

[5] After Max Born, who introduced the probability interpretation of the wave function in "Zur Quantenmechanik der Stoßvorgänge [On the Quantum Mechanics of Collision Processes]," *Zeitschrift für Physik* **37**, 863 (1926) (doi: 10.1007/BF01397477); and Max Born, "Quantenmechanik der Stoßvorgänge [Quantum Mechanics of Collision Processes]," *Zeitschrift für Physik* **38**, 803–827 (1926) (doi: 10.1007/BF01397184). These papers also introduced the first treatment of particle collisions in quantum mechanics.

[6] Note that completeness *also* follows from the previous axiom, at least in the finite-dimensional case. If Q is a Hermitian operator on an N-dimensional Hilbert space, it will have N orthogonal eigenvectors, which must span the entire space. But it is handy (and general beyond finite Hilbert spaces) to think of completeness in terms of probability, so we will live with a bit of redundancy in our axioms. Remember our goal is to be clear about our assumptions, not to find a minimal set of axioms.

Because the *square* of this coefficient represents a probability for a measurement outcome, the coefficient $c_n = \langle q_n|\psi\rangle$ itself is called a **probability amplitude**. This argument obviously holds in the case of nondegenerate eigenstates, where we can assume orthonormal eigenstates. The completeness argument carries through in the degenerate case, provided we construct an orthonormal set of eigenstates, noting that the degenerate eigenstates are still complete on their subspaces.

A somewhat more elegant notation for the von Neumann measurement comes in the form of projection operators, and thus these measurements are also called **projective measurements**. The **projection operator** P_α for a state $|\alpha\rangle$ is simply given by[7]

$$P_\alpha := |\alpha\rangle\langle\alpha|. \tag{1.32}$$
(projection operator)

Operating on an arbitrary state, it selects only the component of the state along α, discarding the rest. Given an observable Q, the projectors associated with the eigenstates are

$$P_n := |q_n\rangle\langle q_n|. \tag{1.33}$$

The probability for outcome q_n in a measurement is then

$$\text{Prob}(q_n) = \left|\langle q_n|\psi\rangle\right|^2 = \langle\psi|q_n\rangle\langle q_n|\psi\rangle = \langle\psi|P_n|\psi\rangle \tag{1.34}$$

in terms of the projector. Note that the summation of probabilities to unity implies a completeness of eigenstate-projection operators,

$$\sum_n P_n = \sum_n |q_n\rangle\langle q_n| = 1, \tag{1.35}$$
(projection-operator completeness)

where the unity on the right-hand side stands for the identity operator on the relevant Hilbert space. Furthermore, the collapse of the state vector to an eigenstate can be represented by the projection

$$|\psi\rangle \longrightarrow \frac{P_n|\psi\rangle}{\|P_n|\psi\rangle\|} = \frac{P_n|\psi\rangle}{\sqrt{\langle\psi|P_n^2|\psi\rangle}} = \frac{P_n|\psi\rangle}{\sqrt{\langle\psi|P_n|\psi\rangle}}. \tag{1.36}$$

(Note that $P_n|\psi\rangle$ is not in general normalized, so it is necessary to normalize the result by dividing by the vector norm; also note the property $P_n^2 = P_n$.) The above transformation implicitly assumes nondegenerate eigenvalues. In the case of a degenerate eigenvalue, it is possible for the state to end up in some linear combination of the degenerate eigenvectors. However, the linear combination is not arbitrary: it should be the linear combination that represents the projection of the initial state onto the degenerate subspace. In the projector language, the above rules (1.34) and (1.36) carry through if the projector P_n is replaced by the sum of projectors for all the degenerate eigenstates (in which case, the probability for outcome q_n is the sum of probabilities to end up in the various degenerate states $|q_n\rangle_k$.

The projector language is also readily modified to more general measurements, such as weak measurements. In these cases, the measurement results are no longer represented by projectors, but by other families of operators (which are not necessarily orthogonal).

One technical detail of the discussion above comes from writing out the transformation (1.36) for a state of the form (1.28), which reads

$$|\psi\rangle \longrightarrow \frac{P_n|\psi\rangle}{\sqrt{\langle\psi|P_n|\psi\rangle}} = \frac{c_n|q_n\rangle}{|c_n|} = e^{i\arg c_n}|q_n\rangle \tag{1.37}$$

in the nondegenerate case. Earlier, when we stated the measurement left the state as $|q_n\rangle$, we ignored the phase factor inherited from c_n. This is acceptable, as this **global phase** or overall phase is of no consequence (for example in computing measurement probabilities $\langle\psi|P_n|\psi\rangle$, such a global phase drops out). Of course, a *local* phase, such as the one occurring in the (unnormalized) superposition $|0\rangle + e^{i\phi}|1\rangle$, is very important, leading to interference fringes when the state is detected in the appropriate basis.

[7] See Problem 1.11 for the general definition of projectors.

One final note is that the state-collapse process is a somewhat tricky one. If the measurement process is taken to occur at some well-defined time, then the state collapse is instantaneous, and thus should not be a physical process. On the other hand, for the collapse to be a physical process, the measurement should take place over some nonzero time, in which case there are presumably important details of the measurement that are left unmentioned by this axiom. While we will defer philosophical considerations until later, it is worth noting that it is possible to regard the collapse in terms of information change, not as a physical process.

1.5.1 Characterization of Measurements: Expectation Values

Given now that a measurement is a random event, and we have characterized the probability distribution of the result, it is useful to characterize the distribution with standard statistical measures. The **mean value** (mathematically, the **expected value** or in quantum mechanics, the **expectation value**) is defined as the weighted sum over measurement results:

$$\langle Q \rangle := \sum_n q_n \cdot \mathrm{Prob}(q_n). \tag{1.38}$$
(expectation value)

Using the Born rule (1.26) then gives

$$\langle Q \rangle = \sum_n q_n \big| \langle q_n | \psi \rangle \big|^2 = \sum_n q_n \langle \psi | q_n \rangle \langle q_n | \psi \rangle = \sum_n \langle \psi | Q | q_n \rangle \langle q_n | \psi \rangle = \langle \psi | Q \Big(\sum_n |q_n\rangle\langle q_n| \Big) | \psi \rangle. \tag{1.39}$$

Now using projector completeness (1.35), this becomes

$$\langle Q \rangle = \langle \psi | Q | \psi \rangle. \tag{1.40}$$
(quantum expectation value)

This statistic characterizes the ‘‘center’’ of the measurement range.

1.5.2 Characterization of Measurements: Uncertainty

We can also characterize the spread of measurement results by considering the **variance**

$$V_Q := \Big\langle \big(Q - \langle Q \rangle \big)^2 \Big\rangle = \langle Q^2 \rangle - \langle Q \rangle^2, \tag{1.41}$$
(variance)

and **uncertainty** or **standard deviation**

$$\sigma_Q := \sqrt{V_Q}. \tag{1.42}$$
(standard deviation.)

A central result in quantum mechanics is the **uncertainty principle**,[8] which we may write as

$$\sigma_P \sigma_Q \geq \frac{1}{2} \Big| \langle [P, Q] \rangle \Big| \tag{1.43}$$
(uncertainty principle)

for observables P and Q, where

$$[P, Q] := PQ - QP \tag{1.44}$$
(commutator bracket)

[8] The uncertainty principle is commonly called the **Heisenberg uncertainty principle**, after W. Heisenberg, ‘‘Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik,’’ *Zeitschrift für Physik* **43**, 172 (1927) (doi: 10.1007/BF01397280), who wrote down the *Genauigkeitsbeschränkung* (accuracy constraint) $p_1 q_1 = h/2\pi$ based on the commutator $pq - qp = h/2\pi i$ and a Gaussian state. The uncertainty principle in the form $p_i q_i \geqq h/2\pi$ (with p_i^2, q_i^2 being twice the respective variances) was proved by E. H. Kennard, ‘‘Zur Quantenmechanik einfacher Bewegungstypen,’’ *Zeitschrift für Physik* **44**, 326 (1927) (doi: 10.1007/BF01391200); see Eq. (27). The generalized form (1.43) is sometimes called the **Robertson inequality** after H. P. Robertson, ‘‘The Uncertainty Principle,’’ *Physical Review* **34**, 163 (1929) (doi: 10.1103/PhysRev.34.163), who gave the proof in terms of the Cauchy–Schwartz inequality.

is the **commutator bracket**.

To prove the uncertainty principle, first we can start with the Cauchy–Schwartz inequality (1.4)

$$\langle\alpha|\alpha\rangle\langle\beta|\beta\rangle \geq \big|\langle\alpha|\beta\rangle\big|^2. \tag{1.45}$$

Setting $|\alpha\rangle = P|\psi\rangle$ and $|\beta\rangle = Q|\psi\rangle$ then gives

$$\big\langle\psi|P^2|\psi\big\rangle\big\langle\psi|Q^2|\psi\big\rangle \geq \big|\langle\psi|PQ|\psi\rangle\big|^2. \tag{1.46}$$

The quantity $\langle\psi|PQ|\psi\rangle$ on the right-hand side is an ordinary complex scalar. For any complex number z, written in terms of real and imaginary parts as $z = x + iy$, the modulus satisfies

$$|z| = \sqrt{x^2+y^2} \geq \sqrt{y^2} = |y| = |\mathrm{Im}\, z| = \frac{1}{2}|z - z^*|. \tag{1.47}$$

Using this result on the right-hand side of Eq. (1.46), we find

$$\big\langle P^2\big\rangle\big\langle Q^2\big\rangle \geq \frac{1}{4}\Big|\big\langle[P,Q]\big\rangle\Big|^2. \tag{1.48}$$

Now since

$$\big[P - \langle P\rangle\,, Q - \langle Q\rangle\,\big] = [P,Q] - [\langle P\rangle, Q] - [P, \langle Q\rangle] + [\langle P\rangle, \langle Q\rangle] = [P,Q], \tag{1.49}$$

which follows from noting that scalars always commute with operators, we can make the replacements $P \longrightarrow P - \langle P\rangle$ and $Q \longrightarrow Q - \langle Q\rangle$ in Eq. (1.48) to obtain

$$V_P V_Q \geq \frac{1}{4}\Big|\big\langle[P,Q]\big\rangle\Big|^2. \tag{1.50}$$

Taking the square root of both sides leads to the desired result.

The form (1.45) of the uncertainty principle is the common one, but a stronger version may be written (Problem 1.9)[9]

$$V_P V_Q \geq \frac{1}{4}\Big|\big\langle[P,Q]\big\rangle\Big|^2 + \frac{1}{4}\Big|\big\langle[P,Q]_+\big\rangle - 2\langle P\rangle\langle Q\rangle\,\Big|^2, \tag{1.51}$$

(generalized uncertainty principle)

in terms of the anticommutator $[P,Q]_+ := PQ + QP$. This generalized uncertainty relation stronger in particular for Gaussian wave functions, which are always satisfied with the equality in Eq. (1.51), but only for some Gaussian wave functions in the standard form (1.43) (see Problem 2.4).

1.5.3 Compatible Observables

The appearance of the commutator on the right-hand side of the uncertainty principle (1.43) suggests that the commutator plays an important role in how exactly two observables "interact." In particular note that the uncertainty of an observable vanishes if and only if the state is an eigenstate of the observable (at least in the nondegenerate case). The uncertainty principle suggests that the uncertainties for two observables can only become very small (i.e., it is possible to occupy an eigenstate of both observables at the same time) only when the commutator vanishes (i.e., the observables **commute**).

The more precise statement is that commuting observables have simultaneous eigenstates, and thus they are called **compatible observables**. To see this directly, first consider two observables P and Q where $[P,Q] = 0$, and consider an eigenstate $|q_n\rangle$ of Q. Then because

$$QP|q_n\rangle = PQ|q_n\rangle = q_n P|q_n\rangle, \tag{1.52}$$

[9] This is sometimes called the **Schrödinger uncertainty principle**, after E. Schrödinger, "Zum Heisenbergschen Unschärfeprinzip," *Sitzungsberichte der Preussischen Akademie der Wissenschaften, Physikalisch-mathematische Klasse* **14**, 296 (1930).

it follows that $P|q_n\rangle$ is an eigenvector of Q. Now, there are two possibilities. If q_n is a nondegenerate eigenvalue, then by definition all corresponding eigenvectors are proportional. Thus, $P|q_n\rangle \propto |q_n\rangle$, and so $|q_n\rangle$ is also an eigenvector of P (with possibly a different eigenvalue). The more complicated possibility is that q_n is degenerate. In this case, we can at best say that $P|q_n\rangle$ lies in the subspace spanned by the degenerate eigenvectors $|q_n\rangle_k$ (with common eigenvalue q_n). That is, $P|q_n\rangle$ is a linear combination of the $|q_n\rangle_k$. However, even though $P|q_n\rangle$ is not one of the eigenvectors of $|q_n\rangle_k$, it turns out that it is always possible to find a common set of eigenvectors, such that they will act as a complete basis on the degenerate subspace.[10]

In general, to find a convenient basis with eigenvalues that completely parameterize the state of the system, it is necessary to find simultaneous eigenvalues of several commuting (but independent) observables. The number of required observables is equal to the number of degrees of freedom of the system (e.g., three degrees of freedom for a particle in three dimensions).

One more useful fact is worth mentioning. Suppose again we have commuting observables P and Q, and suppose $|q_1\rangle$ and $|q_2\rangle$ are eigenvectors of Q, with (nondegenerate) eigenvalues q_1 and q_2. We showed before that $\langle q_2|Q|q_1\rangle = 0$ (since $\langle q_2|q_1\rangle = 0$, but now we will show that

$$\langle q_2|P|q_1\rangle = 0. \tag{1.53}$$

To show this, let's first write out the inner product

$$\langle q_2|PQ|q_1\rangle = q_1\langle q_2|P|q_1\rangle, \tag{1.54}$$

while in the opposite order,

$$\langle q_2|QP|q_1\rangle = q_2\langle q_2|P|q_1\rangle. \tag{1.55}$$

However, the operators commute, so $\langle q_2|[P,Q]|q_1\rangle = 0$, so the two expressions above should be equal. Since by assumption $q_1 \neq q_2$, this is all only consistent if $\langle q_2|P|q_1\rangle = 0$. As we will discuss much later, an inner product such as this represents a tendency for an operator P, viewed as an interaction, to cause transitions between $|q_1\rangle$ and $|q_2\rangle$. The physical interpretation then of Eq. (1.53) is that, assuming Q does not cause transitions between $|q_1\rangle$ and $|q_2\rangle$, then neither does P—if two states are ''uncoupled'' according to an operator, they are also uncoupled according to any commuting operator.

1.6 Fourth Axiom: Time Evolution of States

The fourth axiom specifies the time evolution in quantum systems. It says that quantum states evolve in time according to the **Schrödinger equation**

$$i\hbar\partial_t|\psi\rangle = H|\psi\rangle, \tag{1.56}$$
(Schrödinger equation)

where $\hbar$ is the Planck constant (technically, the Planck constant divided by 2π, or the Dirac constant), and H is the Hamiltonian operator. The exact form of the Hamiltonian operator requires some discussion, however.

1.6.1 Canonical Quantization

In its purest form, the fourth axiom is exactly as we stated it—H is unspecified, and can be whatever it needs to be to get the job done. However, we can add a little extra guidance beyond the axiom, although any useful advice along these lines tends to run into trouble at some point. As a starting point, where possible, the quantum-mechanical Hamiltonian operator should come straight out of classical mechanics. Thus, it is

[10] We'll skip the argument here, as it's a bit tedious, but it can be found in Claude Cohen–Tannoudji, Bernard Diu, and Franck Laloë, *Quantum Mechanics*, vol. I, English ed. (Wiley, 1973), p. 140 (ISBN: 047116433X). The basic idea is that P may not have degenerate eigenvectors on the subspace, so we have to be careful to switch to a basis of the $|q_n\rangle_k$ subspace that is more ''compatible'' with P.

useful to review the classical Hamiltonian function and also the classical Lagrangian. This is a good time to go through the relevant material from classical mechanics, from Lagrangian mechanics (Section 0.3), through Hamiltonian mechanics (Section 0.4), and through the Poisson bracket (Section 0.4.3).

Returning to the fourth axiom, with classical tools in hand, we can discuss the form of the Hamiltonian operator. If the quantum system has a classical counterpart—that is, we aim to **quantize** the classical system—then the starting point is the classical Hamiltonian function, *written in canonical coordinates*. Then **canonical quantization** proceeds by promoting the canonical coordinates in the Hamiltonian function to operators, in order to obtain the Hamiltonian operator. Dirac postulated that the new coordinate operators should then satisfy the quantum-bracket relation[11]

$$[z_\alpha, z_\beta] = i\hbar [z^\alpha, z^\beta]_{\text{P}}. \tag{1.57}$$
(commutator for quantized coordinates)

Here, the z^α on the right-hand side stands for any of the (classical) generalized coordinates or conjugate momenta, and the quantum bracket on the left-hand side is just the commutator $[A, B] = AB - BA$. The commutator involves operator versions of the same z^α, but without bothering to raise the index. To be more specific, the Poisson brackets (0.39) imply the quantum commutators

$$[q_\alpha, q_\beta] = [p_\alpha, p_\beta]_{\text{P}} = 0, \qquad [q_\alpha, p_\beta] = i\hbar \delta_{\alpha\beta}. \tag{1.58}$$

(Note the lack of a raised index here; the raised and lowered indices reflect the symplectic structure—the action of the Poisson bracket in the dynamics—in the classical case, but this distinction is no longer useful in the quantum case, where the symplectic structure is lost.)

But why is the quantum commutator the counterpart to the classical Poisson bracket? At some level it is "just a postulate," but it is worth noting that the commutator satisfies some properties that are also satisfied by the Poisson bracket:

1. antisymmetry: $[A, B] = -[B, A]$
2. null bracket with scalars: $[c, A] = 0$ $(c \in \mathbb{C})$
3. associativity: $[A + B, C] = [A, C] + [B, C]; \qquad [A, B + C] = [A, B] + [A, C]$
4. product rules: $[AB, C] = A[B, C] + [A, C]B; \qquad [A, BC] = [A, B]C + B[A, C]$
5. Jacobi identity: $\big[A, [B, C]\big] + \big[B, [C, A]\big] + \big[C, [A, B]\big] = 0$

Actually, given that the classical bracket satisfies the above properties, and stipulating that the quantum bracket should also satisfy the above properties, it turns out that the commutator (up to a factor) is the *only* possible choice; see Problem 1.25. Then the factor of $i\hbar$ can be motivated as follows. The i is needed because the (classical) Poisson bracket is manifestly real, but the commutator of Hermitian operators, in view of its antisymmetry, is anti-Hermitian and thus imaginary. The $\hbar$ is a constant with dimensions of action, which is needed to make the dimensions come out right (the derivatives in the Poisson bracket contribute dimensions of inverse action that are absent in the commutator). As far as the axioms of quantum mechanics are concerned, the $\hbar$ here is a constant that must be empirically determined. However, note that it is the same constant that appears in the Schrödinger equation. We will see this later when we introduce the Heisenberg picture, where operators obey equations of motion as a consequence of the Schrödinger equation. The classical equation of motion (0.36) carries over via the same quantization rule (1.57) to the Heisenberg equations of motion provided these factors of $\hbar$ match.

Some additional comments are in order:

1. The above commutators (1.58) and underlying Poisson brackets are only valid in Cartesian coordinates; they could be more complicated in the case of more general coordinate systems.
2. It may be that there are quantum systems with no classical counterpart (e.g., a particle with spin), in which case it is not possible to promote a classical Hamiltonian by this procedure. Still, the Hamiltonian operator and corresponding commutators must be defined.

[11] P. A. M. Dirac, *The Principles of Quantum Mechanics*, 4th ed. (Oxford, 1958), p. 87, Eq. (7) (ISBN: 9780198520115).

3. If the (classical) Hamiltonian is of the typical form

$$H(q,p,t) = T_p(p) + V(q,t), \tag{1.59}$$

where the coordinates and momenta are separated in different terms, there are no special problems, and the above procedure will yield a sensible quantum Hamiltonian. On the other hand, if the Hamiltonian contains mixed terms, for example q^2p^2, then additional principles are needed to guide the choice of a quantum Hamiltonian, because multiple, inequivalent Hamiltonians [with different orderings of the mixed term, like p^2q^2, pq^2p, $(p^2q^2 + q^2p^2)/2$] correspond to the same classical Hamiltonian.

One well-known example is a charged particle coupled to the electromagnetic field. Where an uncoupled free particle has a Hamiltonian $H = p^2/2m$, the classical and quantum Hamiltonians for a particle of charge q coupled to a background vector potential $\mathbf{A}(\mathbf{r})$ may be written

$$H(\mathbf{q},\mathbf{p},t) = \frac{[\mathbf{p} - q\mathbf{A}(\mathbf{r})]^2}{2m}. \tag{1.60}$$

In the quantum case, this Hamiltonian implies a symmetric ordering of the form $\mathbf{p}\cdot\mathbf{A}(\mathbf{r}) + \mathbf{A}(\mathbf{r})\cdot\mathbf{p}$ when the kinetic energy is multiplied out. In this case the quantum coupled Hamiltonian is obtained from the free particle by the **minimal-coupling replacement** $\mathbf{p} \longrightarrow \mathbf{p} - q\mathbf{A}$, which acts as the extra assumption to fix the ordering (in this case, it amounts to assuming the simplest symmetrization that renders the Hamiltonian Hermitian). Note that in this case it turns out that the canonical momentum is $\mathbf{p} = m\dot{\mathbf{r}} + q\mathbf{A}(\mathbf{r})$, where $m\dot{\mathbf{r}}$ is the usual (kinematic) momentum.

A second example is for a space-dependent mass or a nontrivial coordinate system such that the classical Hamiltonian has the form

$$H(q,p) = \frac{p^2}{2mg(q)} + V(q). \tag{1.61}$$

Here the $g(q)$ function is not written with any ordering in mind, as it doesn't matter classically. In this case, it turns out that the corresponding quantum Hamiltonian has the nontrivially ordered kinetic energy (Problem 1.39)

$$H(q,p) = \frac{1}{2m} g^{-1/4} p\, g^{-1/2} p\, g^{-1/4} + V(q). \tag{1.62}$$

Here, the extra principle is to start with a ''flat space'' Hamiltonian $H = p^2/2m + V(x)$ where the quantization procedure is obvious, and perform a coordinate transformation in the classical and quantum cases to obtain the quantization rule.

4. Finally, the addition or presence of a constraint can cause this quantization procedure to break down, although there is a prescription for saving the procedure that works in many useful cases. This quantization of constrained system is discussed in Chapter 19.

In general, the **correspondence principle** states that quantum mechanics should reproduce classical mechanics in some appropriate regime (whatever that means—it turns out to be somewhat nontrivial even to define the appropriate regime without some more machinery). It is often stated that a quantization rule of the form (1.57) shows the correspondence principle in action, because by setting $\hbar = 0$ one obtains the classical commutation ''rule'' (i.e., that everything commutes with everything). However, this turns out to be a naïve point of view. For one thing, $\hbar \neq 0$ (and this turns out to be important for some systems that ''should'' behave classically), and in fact the limit $\hbar \longrightarrow 0$ is not even mathematically well-defined (witness states of the form $e^{-ipq/\hbar}$, which we will be coming to shortly), at least not without some more careful analysis.

1.7 Representations of States and Operators

So far, we have dealt with state vectors as relatively abstract elements of a Hilbert space, and with operators as abstract transformations on a space. In using these objects for calculations, they need to be translated

at some point into numbers, and **representations** allow us to do exactly this. A representation is simply the result of using an orthonormal basis to represent a state or an operator. For example, suppose we have a discrete (i.e., finite countably infinite) basis $|n\rangle$. Mathematically, the orthonormality is expressed in terms of the Kronecker delta:

$$\langle n|m\rangle = \delta_{nm}. \tag{1.63}$$

We already proved before [see Eq. (1.28)] the notion of completeness—that an arbitrary state may be written as a linear combination of the basis vectors,

$$|\psi\rangle = \sum_n c_n |n\rangle, \tag{1.64}$$

where

$$c_n = \langle n|\psi\rangle. \tag{1.65}$$

In this case, the (ordered) set of c_n serves as the representation of $|\psi\rangle$ in the basis $\{|n\rangle\}$. That is, the vector $(c_0, c_1, c_2, \ldots)$ is the representation of the abstract state vector $|\psi\rangle$ (in the case of a finite set, this would be the usual column vector from linear algebra, but for a countably infinite basis this is an infinite-dimensional generalization). Operators have similar representations; using that $\sum_n |n\rangle\langle n| = 1$, we can write

$$A = \left(\sum_m |m\rangle\langle m|\right) A \left(\sum_n |n\rangle\langle n|\right) = \sum_{m,n} \langle m|A|n\rangle\, |m\rangle\langle n| \tag{1.66}$$

for an arbitrary operator A. Then defining the **matrix element**

$$A_{mn} := \langle m|A|n\rangle, \tag{1.67}$$

the operator becomes

$$A = \sum_{m,n} A_{mn}\, |m\rangle\langle n|. \tag{1.68}$$

The matrix elements then form the representation of the abstract operator A in terms of the basis. Again, for a finite basis, this representation is just the usual notion of a (square) matrix in linear algebra, but for a countably infinite basis, it is an infinite-dimensional generalization of a matrix.

1.7.1 Linear Algebra in a Representation

Once expressed in some (finite) representation, states can of course be written as vectors in regular linear-algebra notation,

$$\big[|\psi\rangle\big] = \big[\langle n|\psi\rangle\big] = \big[c_n\big] = \begin{bmatrix} c_1 \\ c_2 \\ \vdots \end{bmatrix}, \tag{1.69}$$

and operators may be similarly written as regular matrices:

$$\big[A\big] = \big[\langle m|A|n\rangle\big] = \big[A_{mn}\big] = \begin{bmatrix} A_{11} & A_{12} & \cdots \\ A_{21} & A_{22} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix}. \tag{1.70}$$

Note that in writing these expressions, we are being careful to distinguish the representation-independent objects $|\psi\rangle$ and A from their expressions $[|\psi\rangle]$ and $[A]$ in some representation, in the latter case by using some kind of brackets or parentheses.

Once in a particular representation, we can recover ordinary linear-algebraic operations. For example, a linear operator transformation

$$|\phi\rangle = A|\psi\rangle \tag{1.71}$$

becomes, after inserting an identity and projecting with $\langle m|$,

$$\langle m|\phi\rangle = \sum_n \langle m|A|n\rangle\langle n|\psi\rangle. \tag{1.72}$$

In terms of the more explicit coefficient expansions

$$|\phi\rangle = \sum_n \phi_n|n\rangle, \qquad |\psi\rangle = \sum_n \psi_n|n\rangle, \tag{1.73}$$

the linear transformation becomes

$$\phi_m = \sum_n A_{mn}\psi_n, \tag{1.74}$$

which is of course just ordinary matrix-vector multiplication.

1.7.1.1 Diagonality

In the case where a linear operator A is an observable, the eigenstates $|n\rangle$ of A define a natural representation of the operator. That is, given the eigenvalue equation $A|n\rangle = a_n|n\rangle$, we have

$$A_{mn} = \langle m|A|n\rangle = a_n\langle m|n\rangle = a_n\delta_{mn}, \tag{1.75}$$

and the operator is said to be **diagonal** in this representation, because all off-diagonal elements vanish. The act of finding the eigenvectors of an operator is referred to as **diagonalizing** the operator precisely because it amounts to finding a diagonal representation. Recalling that commuting observables define simultaneous eigenstates, it is a primary first step in solving quantum-mechanical problems to find a set of independent, commuting observables whose eigenvalues (corresponding to said simultaneous eigenstates) parameterize the Hilbert space—these are the **quantum numbers**. Textbook problems conveniently have quantum numbers, but typical quantum problems (in the sense of pulling a Hamiltonian out of the hat of all possible Hamiltonians) don't have such ''good'' quantum numbers.

1.7.2 The Position Representation and the Delta Function

The position representation, of course, uses the eigenvalues and eigenvectors of the position operator. But as in classical physics, position is a *continuous* variable, and so the complication in quantum mechanics is to deal with the continuum of position eigenvalues. In particular, we will have to give up on the notion that $\langle x|x'\rangle = \delta_{xx'}$, and we will have to write down a more general notion

$$\langle x|x'\rangle = \delta(x - x'), \tag{1.76}$$
(''orthonormality'' in position)

where the object on the right-hand side is the **Dirac delta function**, which turns out to not be a function at all, at least in the strict sense. In particular, this object will have to diverge at $x = x'$ to make any sense. We'll come back to this in a moment, but first it is good to make contact with conventional notation. First, the state vector, expressed in the position representation, is

$$\psi(x) := \langle x|\psi\rangle\,, \tag{1.77}$$
(position-representation wave function)

and this function is called the **wave function**. In analogy to $|\langle n|\psi\rangle|^2$ representing the probability for a measurement of an observable with discrete eigenvalues to result in the nth eigenvalue as a result, the square of the wave function $|\psi(x)|^2 = |\langle x|\psi\rangle\,|^2$ represents a probability *density* function for the results of a position measurement (at least, in some idealized sense), because of the continuum of possible results. Operators can also work in the position representation, with matrix elements in the notation

$$\langle x|A|x'\rangle =: A(x, x'), \tag{1.78}$$

and the operation on a vector of the form

$$\langle x|A|\psi\rangle = \int dx' \, \langle x|A|x'\rangle\langle x'|\psi\rangle = \int dx' \, A(x,x') \, \psi(x'), \tag{1.79}$$

with analogous expressions for operator products.

Now returning to the delta function introduced in the ''orthonormality'' expression (1.76), let's work out the properties of the delta function.

1. $\langle x|x'\rangle = 0$ if $x \neq x'$ as a consequence of orthogonality of eigenstates. Recall that nondegenerate, distinct eigenvalues have orthogonal eigenvectors, and we certainly don't want to give that up.

2. The completeness of the position operator still holds in the form

$$\int_{-\infty}^{\infty} dx \, |x\rangle\langle x| = 1, \tag{1.80}$$

as the expectation value of this expression implies the proper normalization of a probability density. Combining this with an arbitrary vector $|f\rangle$ yields

$$f(x) = \langle x|f\rangle = \int dx' \, \delta(x-x') \, f(x'). \tag{1.81}$$

We may assume $f(x)$ to be real (although the expression still works for complex f), in which case the same expression results, but with $\delta(x-x')$ replaced by $\delta(x'-x)$, which shows that the delta function is even:

$$\delta(-x) = \delta(x). \tag{1.82}$$

3. Eq. (1.81) is then commonly written as

$$\int dx \, \delta(x-a) \, f(x) = f(a), \tag{1.83}$$

which is the **projection property** of the delta function—it selects only the function value at the point a.

4. Taking $f(x) = 1$ and $a = 0$ gives the normalization expression

$$\int dx \, \delta(x) = 1. \tag{1.84}$$

This shows why the delta function can't be a regular function: Since the delta function is zero everywhere except in an interval of width dx around $x = 0$, where it must take on the value $1/dx$, which is divergently large. To distinguish it from an ordinary function, delta functions are included in a more general notion of functions called **distributions**. We'll comment more on being careful with delta functions in a bit.

5. Using Eq. (1.84) to introduce an integral on the right-hand side of Eq.(1.83) gives

$$\int dx \, \delta(x-a) \, f(x) = \int dx \, \delta(x-a) \, f(a), \tag{1.85}$$

after shifting the integral and pulling $f(a)$ into the integrand. This statement is certainly true, but colloquially, this equation is often written without the integration as

$$\delta(x-a) \, f(x) = \delta(x-a) \, f(a). \tag{1.86}$$

This is really just a restatement of the projection rule (1.83), but strictly speaking, it is complete nonsense. It only makes sense in the context of integration as in Eq. (1.85), although with that in mind, it is a handy rule to keep around.

6. Finally, using the operator-completeness relation again gives

$$\delta(x-x') = \langle x|x'\rangle = \int dx''\, \langle x|x''\rangle\langle x''|x'\rangle = \int dx''\, \delta(x-x'')\,\delta(x''-x'). \tag{1.87}$$

   This is a convolution rule for delta functions, and shows that the *square* of a delta function (the case $x = x'$ here) is problematic, as even its integral diverges (unless it is handled in specific cases in a more careful way).

The delta function, in the sense of $\langle x|x'\rangle = \delta(x-x')$, is the position representation of a position eigenstate $|x'\rangle$. We already saw from the normalization condition that $\langle x|x\rangle$ diverges, and the convolution rule (1.87) confirms that this inner product is problematic in the position representation. These states are thus not normalizable, which violates the normalization condition (1.12) of the first axiom. So what gives? The answer is that position eigenstates are technically not physical states (the uncertainty relation says that they must have arbitrary extent in momentum, which implies a divergent kinetic energy), but so long as we are careful, they can be very useful in doing practical calculations.

Before we get back to what this means, let's first discuss broader approaches to being careful with delta functions. There are two basic approaches: the formal and the pragmatic. The basic idea behind the formal approach is to use the projection property (1.83) itself as an alternate way to define the delta function. Consider the inner-product expression

$$\langle \delta_a, f\rangle = f(a), \tag{1.88}$$

where the f in the inner product is an abstract representation of a function $f(x)$ in a Hilbert space $\mathscr{H}$, the δ_a is a similarly abstract representation of the delta function, and the $f(a)$ is the resulting scalar projection. The formal trick to make sure we avoid problematic (divergent) things like $\langle \delta_a, \delta_a\rangle$ is to insist that δ_a belongs to an *expanded* space Ω' of the Hilbert space, which go on the left-hand side of the inner product. The ones that go on the right-hand side of the inner product are taken from a *subset* Ω of the Hilbert space. Effectively this restricts delta functions to go ''only in the left-hand slot'' of an inner product, avoiding the mess of inner products of two delta functions. It's elegant in its own way, just defining away anything that might cause a problem.[12]

The pragmatic approach that often helps resolve issues (divergences) occurring in calculations is to define a sequence of functions (h_n) such that:

1. The functions all satisfy the normalization condition

$$\int_{-\infty}^{\infty} dx\, h_n(x) = 1. \tag{1.89}$$

2. The width of the functions converges to zero as $n \longrightarrow \infty$. This condition is (intentionally) vague, as there can be multiple useful ways to define this (and useful sequences may not satisfy every useful condition). But another way to enforce this is by noting that the sequence must satisfy $h_n(x') \longrightarrow 0$ for all $x' \neq x$.

3. The functions should be localized and centered at $x = 0$. Again, this is a vague condition, which could be satisfied by requiring that $\langle h_n|x|h_n\rangle = 0$, but it could be useful to impose weaker conditions.

A common sequence that satisfies these assumptions is the sequence of focusing Gaussians

$$h_n(x) = \frac{n}{\sqrt{\pi}}\, e^{-n^2x^2}, \tag{1.90}$$

[12] One interesting formal way to look at this approach is in terms of a **rigged Hilbert space**, in which inner products are formed from a subset and a superset of a Hilbert space (respectively, the nuclear and extended spaces). The extended space can be set up to include things like delta functions and otherwise unnormalizable functions like $e^{ipx/\hbar}$. We will revisit rigged Hilbert spaces in Chapter 21.

or that is, the sequence of centered, normalized Gaussian distributions with standard deviations $\sigma_n = 1/\sqrt{2}n$. Once the sequence of functions is set up, we can define the action of the delta function via limiting expressions like

$$\int dx\, \delta(x-a)\, f(x) = \lim_{n\to\infty} \int dx\, h_n(x-a)\, f(x). \tag{1.91}$$

The crucial point is: the limit $n \longrightarrow \infty$ and the integration are operations that **do not commute**. That is to say, one can commute the operations in colloquial math (e.g., by dropping the integral operations), but keeping in mind that fundamentally, the resulting expressions only make sense by taking a limit *after* integration with respect to an ordinary function (or sequence thereof). Thus, expressions like Eq. (1.86) act like shortcuts for this process. As long as everything works out, the shortcuts are okay; but if a nonphysical answer pops out of a calculation (e.g., a divergent answer), then you must backtrack and find out where the limit $n \longrightarrow \infty$ was taken too early.

This pragmatic approach to handling delta functions can also be translated into a physical interpretation. In a physical calculation, there may be some localized object (e.g., an atom), whose dimensions are small compared to every other length scale in the problem. It may be so small that we don't care about the dependence of the final result on the size of the atom. However, treating the atom as having **zero** size may cause some problems (such as may happen in the dipole approximation). Strictly speaking, the correct way to handle the calculation is to do the calculation with an atom of *finite* size (i.e., use an h_n), and then take the limit of zero size ($n \longrightarrow \infty$) at the *end* of the calculation. However, this ''correct'' procedure typically increases the complexity of the calculation, possibly crossing the boundary between tractable and intractable. The delta-function identities act as shortcuts for this correct procedure, and usually work well; if at any time they cause problems, then it is necessary to defer taking the limit for a bit longer, until after the problematic stage of the calculation. Any problem of an inner product of a delta function with itself should never occur in this pragmatic approach; if it does, it means that the small dimension of the localized object can't be regarded as ignorably small, because there is something else (like another atom) that is sensitive to this small dimension—a sign that the delta function isn't the appropriate tool for the problem at hand.

In the context of position eigenstates, the problem is that the eigenstates themselves, as we mentioned before, are not physical. Even in the measurement of position, an apparatus (''microscope'') that measures the position of a quantum particle will only be able to measure to within some resolution. Instead of delta-function states as the basis for this measurement, a countable set of states of finite width, with finite separation between outcomes, is a more physical choice that avoids the problems of normalizability. But taking the limit (in advance) of having arbitrarily good position resolution is a useful idealization for getting calculations done.

Note that it is also possible to temper the divergent normalization here by quantizing within a finite **quantization volume**; for details see Problem 1.42.

1.7.2.1 Operators in the Position Representation

In the position representation, there is a common, informal way of writing down the effect of operators that is worth discussing, because it borders on abuse of notation. Take, for example, the operation of translating a wave packet to the right by distance L. The informal way to write this is as an operator acting on the wave function:

$$T_L\, \psi(x) = \psi(x-L). \tag{1.92}$$

However, we have not defined operators in this way; strictly, we only deal with operators on abstract vectors in the sense of $T_L|\psi\rangle$. However, we can convert this into the position representation as

$$\begin{aligned} \langle x|T_L|\psi\rangle &= \int dx'\, \langle x|T_L|x'\rangle\langle x'|\psi\rangle \\ &= \int dx'\, T_L(x,x')\, \psi(x') \\ &= \psi(x-L), \end{aligned} \tag{1.93}$$

where T_L is expressed in the position representation as

$$T_L(x, x') := \langle x|T_L|x'\rangle, \tag{1.94}$$

and the integral in Eqs. (1.93) acts as the continuum generalization of matrix multiplication. From the action of this operation, we can conclude that the explicit representation of this operator is

$$T_L(x, x') = \delta(x - L - x'). \tag{1.95}$$

The informal statement (1.92) should then be viewed in an isomorphic way to the integral operation (1.93), where T_L is a function of the wave function:

$$T_L\,\psi(x) \equiv T_L[\psi(x)] := \psi(x - L). \tag{1.96}$$

However, this is again something of an informal notation if the abstract vectors are the objects that populate Hilbert space, and this T_L is *not* the same object that appears in Eqs. (1.93). Rather, the function (1.92) is a separate linear transformation, defined in terms of the operator T_L by the integral transformation (1.93).

1.7.3 Dirac Notation and Representations

As we have seen, in terms of vectors we have abstract vectors like $|\psi\rangle$, as well as representations of that vector such as $\langle n|\psi\rangle = \psi_n$ or $\langle x|\psi\rangle = \psi(x)$. In physics it is important and useful to distinguish whether a particular result is specific to a representation or if it is representation-independent. The latter kind of result is obviously more general than the former. For example, the Schrödinger equation can be written in a representation as $i\hbar\dot{\psi}_n = H_{nm}\psi_m$, but since it is valid in *any* representation, we can more powerfully express this in terms of an abstract vector/operator pair as $i\hbar|\dot{\psi}\rangle = H|\psi\rangle$. Dirac notation also efficiently expresses how to put an abstract object into a particular representation, or to switch representation (embodied by ''inserting an identity''). In fact, Dirac's motivation in introducing this notation[13] was to have a single notation that could deal equally well with abstract linear-algebraic objects and their representation-dependent counterparts. He noted that previously, calculations could use either abstract vectors and operators, or their expressions in particular bases (or coordinates). He said, ''For the two styles of calculation two distinct notations are used, which do not fit together very naturally and which give rise to an awkward jump in the flow of one's thoughts when one changes from one to the other.'' The notation also expresses the inner product as a simple product of vectors like $\langle\phi|\psi\rangle$, whereas in traditional notation an extra notation like $\langle\,,\,\rangle$ is typically introduced. Visually, one can also quickly scan efficiently through an equation an recognize bracketed objects as scalars and open brackets as vectors (or even operators, as in $|n\rangle\langle n|$). Dirac notation has proven to be such an efficient tool for working with quantum mechanics that it is overwhelmingly popular in modern practice.

1.7.4 The Momentum Operator

The momentum operator, and its relation to the position operator, is defined via the commutation relations (1.58)

$$[q_\alpha, q_\beta] = [p_\alpha, p_\beta]_{\text{P}} = 0, \qquad [q_\alpha, p_\beta] = i\hbar\delta_{\alpha\beta}. \tag{1.97}$$

Now the question is, what is $\mathbf{p}$ when expressed in the position representation?[14]

1.7.4.1 The Derivative Operator

To start, first let's stick to one dimension and study the derivative operator ∂_q. As an operator, its action is defined by the regular differentiation operation when it is expressed in the position representation. That is, $\partial_q|\psi\rangle$ is *defined* by setting

$$\langle q|\partial_q|\psi\rangle := \partial_q\langle q|\psi\rangle \equiv \psi'(q). \tag{1.98}$$

[13] P. A. M. Dirac, ''A new notation for quantum mechanics,'' *Mathematical Proceedings of the Cambridge Philosophical Society* **35**, 416 (1939) (doi: 10.1017/S0305004100021162).

[14] This section parallels P. A. M. Dirac, *op. cit.*, Section 22, p. 89.

An alternate (but equivalent) definition of ∂_q as an operator comes from examining its matrix elements in the position representation:

$$\langle q|\partial_q|q'\rangle = \delta'(q-q'). \tag{1.99}$$

This statement, first of all, states that, although $\delta'(x)$ is a peculiar object, it should certainly be the case that $\delta'(x) = 0$ away from $x = 0$. However, ∂_q is not *quite* a diagonal operator in the position representation, because of "the funny stuff that happens at $x = 0$." Nonetheless, we can see the equivalence of Eqs. (1.98) and (1.99), because by inserting an identity operator, we can write

$$\langle q|\partial_q|\psi\rangle = \int dq'\,\langle q|\partial_q|q'\rangle\langle q'|\psi\rangle = \int dq'\,\delta'(q-q')\,\psi(q'). \tag{1.100}$$

We will leave it as a short exercise in integration by parts to show that the last expression reduces to $\psi'(q)$ (see Problem 1.26). The commutator $[q, \partial_q]$, being an operator, is defined by its action on a vector—in this case, a test function, say $\psi(q)$.

Incidentally, the derivative operator is a purely imaginary operator, in the sense that $\partial_q^\dagger = -\partial_q$. To see this, recall that the Hermitian conjugate is defined by having an equivalent action "to the left" in the inner product:

$$\langle \partial_q^\dagger \psi_1|\psi_2\rangle = \langle \psi_1|\partial_q\psi_2\rangle. \tag{1.101}$$

Introducing a position identity,

$$\int dq\,\langle \partial_q^\dagger\psi_1|q\rangle\langle q|\psi_2\rangle = \int dq\,\langle\psi_1|q\rangle\langle q|\partial_q\psi_2\rangle, \tag{1.102}$$

which in conventional function notation reads

$$\int dq\,\left[\partial_q^\dagger\psi_1(q)\right]^*\psi_2(q) = \int dq\,\psi_1^*(q)\,\partial_q\psi_2(q). \tag{1.103}$$

Integration by parts on the right hand side,

$$\begin{aligned}\int dq\,\left[\partial_q^\dagger\psi_1(q)\right]^*\psi_2(q) &= -\int dq\,\left[\partial_q\psi_1^*(q)\right]\psi_2(q)\\ &= \int dq\,\left[-\partial_q\psi_1(q)\right]^*\psi_2(q),\end{aligned} \tag{1.104}$$

where we assume that boundary terms may be discarded (because, for example, $\psi(x) \longrightarrow 0$ as $|x| \longrightarrow \infty$ for normalizable wave functions). For this equation to hold for an arbitrary inner product, it must be that $\partial_q^\dagger = -\partial_q$. In this sense, integration by parts always defines Hermitian conjugation for derivative-type operators in the position representation.

Now to explore commutation with the derivative operator, for example the product rule for differentiation gives

$$\partial_q q\psi(q) = \psi(q) + q\partial_q\psi(q), \tag{1.105}$$

and thus

$$[q, \partial_q]\psi(q) = -\psi(q). \tag{1.106}$$

This in turn implies the commutator

$$[q, \partial_q] = -1, \tag{1.107}$$

independent of the test function $\psi(q)$.

1.7.4.2 The Momentum Operator from The Canonical Commutator

The commutator (1.107) is basically the same as the $[q, p] = i\hbar$ commutation relation from Eqs. (1.97), and we could thus *guess*

$$p = -i\hbar\partial_q, \tag{1.108}$$

where the i is needed because ∂_q is anti-Hermitian (this follows from integration by parts in the position representation), but p should be Hermitian. While this guess is certainly a possibility, at this stage it is not the *only* possibility, because by adding an arbitrary function of position

$$p = -i\hbar\partial_q + f(q), \tag{1.109}$$

we *still* satisfy $[q, p] = i\hbar$. Note that we will assume $f(q)$ to be real, because we want a Hermitian operator p, and the derivative term $-i\hbar\partial_q$ already has the proper phase to be Hermitian. While this constrains $f(q)$ a bit, it will be handier to argue it away.

1.7.4.3 Transforming Away the Arbitrary Function

First, let's extend the analysis to multiple dimensions, where the above reasoning applies dimensionwise, so that

$$p_\alpha = -i\hbar\partial_\alpha + f_\alpha(\mathbf{q}), \tag{1.110}$$

(where $\partial_\alpha \equiv \partial/\partial q_\alpha$) so that there is a different undetermined function in each direction. Consider the commutator

$$[f_\alpha(\mathbf{q}) - p_\alpha, f_\beta(\mathbf{q}) - p_\beta] = \left(\frac{\hbar}{i}\right)^2 [\partial_\alpha, \partial_\beta] = 0, \tag{1.111}$$

which follows from using Eq. (1.110) to eliminate the momentum operators. On the other hand, we can use the associative property of the commutator to write the same expression as

$$[f_\alpha(\mathbf{q}) - p_\alpha, f_\beta(\mathbf{q}) - p_\beta] = [f_\alpha(\mathbf{q}), f_\beta(\mathbf{q})] - [p_\alpha, f_\beta(\mathbf{q})] - [f_\alpha(\mathbf{q}), p_\beta] + [p_\alpha, p_\beta]. \tag{1.112}$$

The first and last terms vanish on the right-hand side; removing these and requiring the result to vanish leads to

$$\partial_\beta f_\alpha = \partial_\alpha f_\beta, \tag{1.113}$$

after using the commutator

$$[f_\alpha(\mathbf{q}), p_\beta] = i\hbar\partial_\beta f_\alpha. \tag{1.114}$$

Eq. (1.113) says that the f_α can be written as a gradient of a *scalar* function

$$f_\alpha(\mathbf{q}) = \partial_\alpha F, \tag{1.115}$$

in the same way that a static electric field may be written as the gradient of a scalar potential. Thus, we may replace the momentum-operator expression (1.110) with

$$p_\alpha = -i\hbar\partial_\alpha + \partial_\alpha F(\mathbf{q}), \tag{1.116}$$

so that the same (undetermined) function now appears in all degrees of freedom.

Now consider an *alternate* position representation, defined by

$$|\mathbf{x}\rangle = e^{i\varphi(\mathbf{q})}|\mathbf{q}\rangle, \tag{1.117}$$

where the position eigenvalues $\mathbf{x} = \mathbf{q}$ are equivalent between representations. The idea is to compare the derivative operators $\partial/\partial q_\alpha$ and $\partial/\partial x_\alpha$ in the two representations. Now the action of the derivative operator in the $\mathbf{x}$ representation is given by the matrix element corresponding to $\partial\psi(\mathbf{x})/\partial x_\alpha$. Writing this out gives (noting that no summation is implied here by the repeated index α)

$$\begin{aligned}\langle x'_\alpha|\frac{\partial}{\partial x_\alpha}|x_\alpha\rangle &= \langle q'_\alpha|e^{-i\varphi(q'_\alpha)}\frac{\partial}{\partial x_\alpha}e^{i\varphi(q_\alpha)}|q_\alpha\rangle \\ &= \langle q'_\alpha|e^{-i\varphi(q_\alpha)}\frac{\partial}{\partial x_\alpha}e^{i\varphi(q_\alpha)}|q_\alpha\rangle.\end{aligned} \tag{1.118}$$

The last step follows because the result always vanishes if $q'_\alpha \neq q_\alpha$. The two position representations should behave equivalently, in the sense that the same matrix element has the same value in either representation,

$$\langle x'_\alpha | \frac{\partial}{\partial q_\alpha} | x_\alpha \rangle = \langle q'_\alpha | \frac{\partial}{\partial q_\alpha} | q_\alpha \rangle, \tag{1.119}$$

and so we can conclude that the derivative operators are connected by

$$\frac{\partial}{\partial q_\alpha} = e^{-i\varphi} \frac{\partial}{\partial x_\alpha} e^{i\varphi} = \frac{\partial}{\partial x_\alpha} + i \frac{\partial \varphi}{\partial x_\alpha}. \tag{1.120}$$

The last expression here follows from applying the commutator (1.114) in the form $[f(\mathbf{q}), \partial_q] = -f'(q)$. In the $\mathbf{x}$ representation, the $\mathbf{q}$-form (1.116) of the momentum operator becomes

$$p_\alpha = -i\hbar \frac{\partial}{\partial x_\alpha} + \frac{\partial F(\mathbf{q})}{\partial x_\alpha} + \hbar \frac{\partial \varphi}{\partial x_\alpha}. \tag{1.121}$$

If we choose $\hbar\varphi(\mathbf{x}) = -F(\mathbf{x}) + \text{const}$ (where the constant corresponds to an irrelevant global phase), then the momentum operator becomes

$$p_\alpha = -i\hbar \frac{\partial}{\partial x_\alpha}. \tag{1.122}$$
(momentum operator)

Thus, while this is not a *unique* form for the momentum operator, it is always possible to choose a representation (by making a phase choice) in which this is the proper expression. This is the long way of saying that the original guess (1.108) was not a bad one!

1.7.5 Unitary Transformations

The above transformation between different position representations is a good example of a more general type of transformation, the **unitary transformation**. An operator U is **unitary** if $U^\dagger = U^{-1}$; that is, if

$$UU^\dagger = U^\dagger U = 1. \tag{1.123}$$

Such an operator corresponds to a change in representation, because given an orthonormal basis $|q_n\rangle$, satisfying $\langle q_m | q_n \rangle = \delta_{mn}$, U defines a transformation to a new basis via

$$|\tilde{q}_n\rangle = U|q_n\rangle, \tag{1.124}$$

where the new basis is still orthonormal:

$$\langle \tilde{q}_m | \tilde{q}_n \rangle = \langle q_m | U^\dagger U | q_n \rangle = \langle q_m | q_n \rangle = \delta_{mn}. \tag{1.125}$$

Besides preserving orthonormality, unitary operators also preserve *all* angles between vectors—in real space they correspond to rotations and reflections.

As it turns out, unitary operators are diagonalizable, and their eigenvectors form orthonormal bases. Their eigenvalues have unit modulus. For these reasons, given a unitary operator U, it is possible in general to find a Hermitian operator A such that $U = e^{iA}$.

A change in representation should not affect the more general notion of a matrix element, just like it should not affect an inner product:

$$\langle q_n | A | q_n \rangle = \langle \tilde{q}_n | \tilde{A} | \tilde{q}_n \rangle. \tag{1.126}$$

Here $\tilde{A}$ is the operator A in the representation of the $|\tilde{q}_n\rangle$, and the above relation *defines* what we mean by $\tilde{A}$. Using Eq. (1.124) gives

$$\langle \tilde{q}_n | \tilde{A} | \tilde{q}_n \rangle = \langle q_n | U A U^\dagger | q_n \rangle, \tag{1.127}$$

and thus we have

$$\tilde{A} = UAU^\dagger \tag{1.128}$$
(unitary transformation for operators)

for the transformation rule for operators under the unitary transformation U, as in Eq. (1.124).

Although the operator transformation rule (1.128) is quite general, the Hamiltonian is a bit special, and transforms somewhat differently. Both the original and transformed states must satisfy the Schrödinger equation,

$$i\hbar|\dot{\psi}\rangle = H|\psi\rangle, \qquad i\hbar|\dot{\tilde{\psi}}\rangle = \tilde{H}|\tilde{\psi}\rangle, \tag{1.129}$$

where $\tilde{H}$ is the transformed Hamiltonian. We can write the first equation here as

$$i\hbar\partial_t(U^\dagger|\tilde{\psi}\rangle) = HU^\dagger|\tilde{\psi}\rangle. \tag{1.130}$$

Then we can expand the time derivative and operate on the left by U:

$$i\hbar|\dot{\tilde{\psi}}\rangle + i\hbar U\partial_t U^\dagger|\tilde{\psi}\rangle = UHU^\dagger|\tilde{\psi}\rangle. \tag{1.131}$$

Noting that $\partial_t(UU^\dagger) = \dot{U}U^\dagger + U\dot{U}^\dagger = 0$, we can rewrite this as

$$i\hbar|\dot{\tilde{\psi}}\rangle = \left[UHU^\dagger + i\hbar\dot{U}U^\dagger\right]|\tilde{\psi}\rangle. \tag{1.132}$$

Comparing this to the Schrödinger equation in the transformed variables, we can identify the transformation law

$$\begin{aligned}\tilde{H} &= UHU^\dagger + i\hbar\dot{U}U^\dagger \\ &= UHU^\dagger - i\hbar U\dot{U}^\dagger\end{aligned} \tag{1.133}$$

(time-dependent transformation)

for the Hamiltonian under a general time-dependent, unitary transformation. Of course, for a time-independent transformation, this reduces to the more basic rule (1.128).

1.7.6 Canonical Transformations vs. Unitary Transformations

From the discussion in Section 1.6.1, we saw how quantum mechanics sprang from the loins of classical mechanics. At this point it is interesting to revisit the parallel structure of the theories—in particular the classical analogue of the unitary transformation. This is the **canonical transformation**, which we introduced before in Section 0.4.4.

Although the canonical transformation appears to have a structure that is quite different from the unitary transformation (reflecting different structures underlying the theories), they can produce the same results. As a nice example, consider the Hamiltonian

$$H(q,p,t) = \frac{p^2}{2m} + V[q + f(t)], \tag{1.134}$$

representing a potential displaced arbitrarily in time. Consider a transformation into the rest frame of the potential,

$$\tilde{q} = q + f(t), \qquad \tilde{p} = m\dot{\tilde{q}} = p + m\dot{f}. \tag{1.135}$$

The generating function for this transformation,

$$F_2(q,\tilde{p},t) = \tilde{p}q - mq\dot{f}(t) + \tilde{p}f(t) + g(t), \tag{1.136}$$

where

$$\dot{g} = -\left[mf(t)\ddot{f}(t) + \frac{m}{2}[\dot{f}(t)]^2\right], \tag{1.137}$$

produces the transformed Hamiltonian

$$\tilde{H}(\tilde{q},\tilde{p},t) = \frac{\tilde{p}^2}{2m} + V_0\cos\left(k\tilde{q}\right) - m\tilde{q}\ddot{f}, \tag{1.138}$$

which is something like a comoving-frame version of the lab-frame Hamiltonian (1.134). It is possible to find a unitary transformation to accomplish the same transformation for the quantum Hamiltonian (see Problem 1.37), although the transformation itself of course looks quite different.

1.7.6.1 Infinitesimal Unitary Transformations

To make the identification between unitary and canonical transformations more formal, consider the *infinitesimal* unitary transformation

$$U = 1 + \frac{i\epsilon}{\hbar} G, \tag{1.139}$$

in terms of the vanishingly small parameter ϵ and the Hermitian operator G—the **generator** of the unitary transformation. An operator Q then changes under this transform according to

$$\tilde{Q} = UQU^\dagger = \left(1 + \frac{i\epsilon}{\hbar} G\right) Q \left(1 - \frac{i\epsilon}{\hbar} G\right) = Q + \frac{i\epsilon}{\hbar}[G, Q] + O(\epsilon^2). \tag{1.140}$$

Considering the small change $\delta Q := \tilde{Q} - Q$ in the operator, we have

$$\delta Q = \frac{\epsilon}{i\hbar}[Q, G]. \tag{1.141}$$
(infinitesimal unitary transformation)

Now if we compare this to the infinitesimal *canonical* transformation [Eq. (0.63)]

$$\delta f = \epsilon [f, G]_{\text{P}} \tag{1.142}$$

for a general phase-space function f, we can see that these are equivalent under Dirac's identification (1.57)

$$\frac{1}{i\hbar}[\,\cdot\,,\,\cdot\,] = [\,\cdot\,,\,\cdot\,]_{\text{P}} \tag{1.143}$$

between the commutator and Poisson bracket.[15]

1.7.7 The Momentum Representation

Returning to the momentum operator, let's now consider the momentum representation, and in particular the expression for the momentum eigenstate in the position representation $\langle x|p\rangle$, which acts to transform between the position and momentum representations.

First, we'll start writing out the inner product in two ways:

$$\langle x|p|p\rangle = p\langle x|p\rangle = \frac{\hbar}{i}\partial_x \langle x|p\rangle\,. \tag{1.144}$$

Some care in notation is important here. The first expression involves the *operator* p, while the second expression involves its *eigenvalue*. It is usually clear from the context which one is meant, so we won't bother with notations that make this difference explicit (like the common notations $\hat{p}$ vs. p or P vs. p). This equation then determines a differential equation for the inner product, which we may write as

$$\partial_x \langle x|p\rangle = \frac{ip}{\hbar}\langle x|p\rangle\,. \tag{1.145}$$

This is a simple first-order differential equation, with exponential solution

$$\langle x|p\rangle = ce^{ipx/\hbar}, \tag{1.146}$$

[15] It turns out that the identification between canonical and unitary transformations is true as we have written for finite-dimensional systems, but for infinitely many degrees of freedom (as in quantized fields), canonical transformations make up a much more general class. This is also relevant to our axiomatic approach to quantization, where we assume that the commutators that carried over from classical mechanics are sufficient to fix the quantum theory. Any classical set of canonical variables works, because once quantized they are related to other choices by unitary transformations. This is not necessarily true in the infinite-degree-of-freedome case, however. See R. Haag, ''Canonical Commutation Relations in Field Theory and Functional Integration,'' in *Lectures in Theoretical Physics, Volume III: Lectures Delivered at the Summer Institute for Theoretical Physics, University of Colorado at Boulder, 1960*, Wesley E. Britten, B. W. Downs, and Joanne Downs, Eds. (Interscience, 1961), p. 353 (see comments on p. 361 in particular).

where c is an undetermined constant (which could depend on p, but not x). Note that the sign of the exponential is already determined by the form of the momentum operator, which was in turn determined by the form of the commutator $[x, p]$.

To fix the normalization constant, let's consider the orthonormality relation, which we can start off with by writing

$$\langle p|p'\rangle = \int dx\, \langle p|x\rangle\langle x|p'\rangle = cc' \int dx\, e^{i(p'-p)x/\hbar}. \tag{1.147}$$

The lesson from treating the continuous position basis is that there are problems, and we are seeing them here, because this integral is not well-defined—it oscillates asymptotically, so it diverges. A big part of the art of physics, however, is giving meaning to such ill-defined expressions. We have already done some of this in dealing with the position-representation pathologies that we have already seen. In particular, to make sense of the integral

$$g(k) = \int dx\, e^{ikx}, \tag{1.148}$$

suppose we let $k \longrightarrow k + i\,\mathrm{sgn}(x)\,\epsilon$ (with $\epsilon > 0$) to obtain the manifestly convergent integral

$$g_\epsilon(k) := \int dx\, e^{ikx}\, e^{-\epsilon|x|}. \tag{1.149}$$

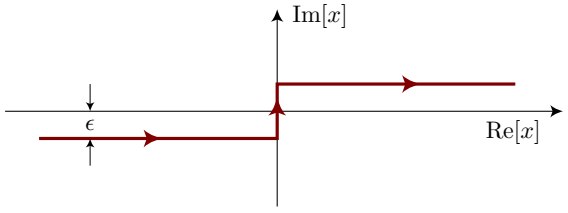
Now as $\epsilon \longrightarrow 0$, the integrand here approaches the pathological integrand. Since we can get "arbitrarily close" to the original integral using a well-defined integral, we can *define* the **regularized** result for the pathological integral as

$$g(k) := \lim_{\epsilon\to 0^+} g_\epsilon(k). \tag{1.150}$$

Now to find out, what exactly is this limit? First, the integral in Eq. (1.149) is not hard to carry out:

$$g_\epsilon(k) = \int dx\, e^{ikx}\, e^{-\epsilon|x|} = \frac{1}{\epsilon - ik} + \frac{1}{\epsilon + ik} = \frac{2\epsilon}{k^2 + \epsilon^2}. \tag{1.151}$$

Physically, we can interpret the modified integral (1.149) as one where contributions from arbitrarily large distances are discarded—this should be okay, because contributions from arbitrarily large distances shouldn't matter much anyway. In a mathematical sense, we are deforming the contour away from the real axis in the complex plane as shown below (ignoring the segment along the imaginary axis, which won't contribute anything as $\epsilon \longrightarrow 0$).



Then observe that $g_\epsilon(k)$ is a Lorentzian, with an ϵ-independent normalization, as we can explicitly calculate:

$$\int dk\, g_\epsilon(k) = 2\pi. \tag{1.152}$$

Now $g_\epsilon(k)/2\pi$ is a normalized Lorentzian distribution with a full width at half max of 2ϵ. Since this distribution becomes arbitrarily narrow as $\epsilon \longrightarrow 0$, the "limit" of $g_{\epsilon\to 0}(k)$ is $2\pi\delta(k)$. Again using this limit to define the meaning of the pathological integral (1.148), we can write

$$\delta(k) = \frac{1}{2\pi} \int dx\, e^{ikx}, \tag{1.153}$$

and repeating the argument in terms of $p = \hbar k$, we can write

$$\delta(p) = \frac{1}{2\pi\hbar}\int dx\, e^{ipx/\hbar}, \tag{1.154}$$
(integral representation of δ function)

which acts as a representation of the delta function in terms of an oscillatory integral.

Using this result, we can go back to the inner product (1.147) to write

$$\langle p|p'\rangle = 2\pi\hbar cc'\int dx\,\delta(p'-p) = 2\pi\hbar cc'\int dx\,\delta(p-p'). \tag{1.155}$$

In analogy to $\langle x|x'\rangle = \delta(x-x')$, it is conventional to choose $c = c' = 1/\sqrt{2\pi\hbar}$, so that

$$\langle p|p'\rangle = \delta(p-p'), \tag{1.156}$$
(momentum orthonormality)

and the inner product (1.146) becomes

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ipx/\hbar}, \tag{1.157}$$
(momentum eigenstate)

which was the result we originally sought.

Position and momentum have a symmetry—they're a lot alike. The main asymmetry is in the commutation relation $[x,p] = i\hbar$, but we can still think of obtaining the dual of any result we have gotten so far by replacing x by p, simultaneously replacing p by $-x$. Thus, for example,

$$x = i\hbar\partial_p \tag{1.158}$$
(momentum eigenstate)

is the position operator in the momentum representation, and the position eigenstate in the momentum representation is

$$\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{-ipx/\hbar}, \tag{1.159}$$
(position eigenstate)

which is of course just the complex conjugate of Eq. (1.157), and the delta-function representation (1.154)

$$\delta(x) = \frac{1}{2\pi\hbar}\int dp\, e^{-ipx/\hbar}, \tag{1.160}$$
(integral representation of δ function)

where note that either sign in the exponential is acceptable because the delta function itself is real.

In the momentum representation, it is conventional to write a state as the momentum-space wave function

$$\phi(p) := \langle p|\phi\rangle\,, \tag{1.161}$$
(momentum-representation wave function)

to better visually distinguish this representation from the position-space form $\psi(x) := \langle x|\psi\rangle$. It is straightforward to transform between the position and momentum representations. For example, inserting an identity operator gives

$$\langle p|\psi\rangle = \int dx \langle p|x\rangle\langle x|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}}\int dx\,\langle x|\psi\rangle\, e^{-ipx/\hbar}, \tag{1.162}$$

after using Eq. (1.159). In terms of wave functions, this gives the transformation

$$\phi(p) = \frac{1}{\sqrt{2\pi\hbar}}\int dx\,\psi(x)\, e^{-ipx/\hbar}, \tag{1.163}$$
(Fourier transform)

which is otherwise known as a **Fourier transform**, which is a representation of a function in terms of harmonic functions (here, the momentum eigenstates, or rather conjugates thereof). The inverse relation follows from the analogous procedure starting with $\langle x|\psi\rangle$ and inserting a momentum-based identity, or by using the above-mentioned symmetry of x and p, to obtain

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\, \phi(p)\, e^{ipx/\hbar}, \tag{1.164}$$
(inverse Fourier transform)

which is otherwise known as an **inverse Fourier transform**. Note that we didn't assume explicitly that $\psi(x)$ and $\phi(p)$ form a Fourier-transform pair—this result popped out of the fundamental axioms of quantum mechanics.

1.8 Unitary Time Evolution

Now we turn back to the issue of time evolution in quantum mechanics. So far, we have only briefly mentioned the time evolution of quantum states in the context of the Schrödinger equation (1.56) as the fourth axiom in Section 1.6.

Fundamentally, we are dealing with time evolution as a mapping of a state at some (''initial'') time t_0 to some (''final'') time t:

$$|\psi(t_0)\rangle \longrightarrow |\psi(t)\rangle. \tag{1.165}$$

Suppose that we have a basis $|q_n\rangle$, which serves to define a representation for vectors and operators. These vectors can also evolve in time, thus defining a new basis and a new representation via time evolution:

$$|q_n(t_0)\rangle \longrightarrow |q_n(t)\rangle. \tag{1.166}$$

Because the final basis is still a basis, we can think of the evolution as defining a transformation between representations. Time evolution is therefore representable in terms of a unitary operator. Writing this statement out formally, time evolution is the transformation

$$|\psi(t_0)\rangle \longrightarrow |\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle,$$
(time-evolution operator, definition) (1.167)

where, $U(t,t_0)$ is the **unitary time-evolution operator** that evolves the state from time t_0 to t. To see explicitly that the time-evolution operator is unitary, note that unitarity is necessary to preserve the norm of the state vector. Since

$$\langle\psi(t)|\psi(t)\rangle = \langle\psi(t_0)|U^\dagger(t,t_0)U(t,t_0)|\psi(t_0)\rangle, \tag{1.168}$$

if we require this to be equal to $\langle\psi(t_0)|\psi(t_0)\rangle$ for any initial state $|\psi(t_0)\rangle$, then it follows that

$$U^\dagger(t,t_0)\, U(t,t_0) = 1, \tag{1.169}$$
(unitary condition)

and thus $U(t,t_0)$ is unitary. In other words, unitarity of the evolution is required to conserve probability.

The time-evolution operator also must have the composition property

$$U(t_2,t_0) = U(t_2,t_1)\, U(t_1,t_0), \tag{1.170}$$
(composition property)

which is sensible for the representation of time evolution. In this relation, note that with the time ordering $t_0 < t_1 < t_2$, the earliest time appears to the right, since it is that one that operates first on the state vector. Finally, we must have the inversion property

$$U(t,t') = U^{-1}(t',t) = U^\dagger(t',t), \tag{1.171}$$
(inversion property)

so that the inverse of an evolution operator corresponds to backwards-time evolution.

1.8.1 Infinitesimal Form

The Schrödinger equation

$$\partial_t|\psi\rangle = -\frac{i}{\hbar}H|\psi\rangle, \tag{1.172}$$

as a differential equation, can be rewritten in differential form as

$$|\psi(t+dt)\rangle - |\psi(t)\rangle = -\frac{i}{\hbar}H|\psi(t)\rangle\,dt, \tag{1.173}$$

using the derivative definition

$$\frac{df(t)}{dt} := \frac{f(t+dt)-f(t)}{dt} \equiv \lim_{\Delta t\to 0}\frac{f(t+\Delta t)-f(t)}{\Delta t}. \tag{1.174}$$

Thus, the Schrödinger equation defines the evolution over an infinitesimal time interval dt according to

$$|\psi(t)\rangle \longrightarrow |\psi(t+dt)\rangle = \left(1-\frac{i}{\hbar}H\,dt\right)|\psi(t)\rangle. \tag{1.175}$$

Therefore the infinitesimal time-evolution operator is given by

$$U(t+dt,t) = 1-\frac{i}{\hbar}H\,dt. \tag{1.176}$$
(infinitesimal time-evolution operator)

We can verify the above properties for this form of the evolution operator. For example,

$$U^\dagger(t+dt,t)\,U(t+dt,t) = \left(1+\frac{i}{\hbar}H\,dt\right)\left(1-\frac{i}{\hbar}H\,dt\right) = 1+O(dt^2) = 1. \tag{1.177}$$

(Note that as a standard rule of the calculus of continuous functions, we can always take $dt^2 = 0$.) A similar argument works for the composition property, which gives the form of $U(t+2\,dt,t)$.

1.8.2 Differential Equation for the Evolution Operator

Now using the composition property of the evolution operator,

$$U(t+dt,t_0) = U(t+dt,t)\,U(t,t_0) = \left(1-\frac{i}{\hbar}H\,dt\right)U(t,t_0). \tag{1.178}$$

Thus, $U(t,t_0)$, regarded as a function of t, undergoes time translation in the same way as the state vector $|\psi(t)\rangle$. In particular, then, we can write

$$\frac{d}{dt}U(t,t_0) = -\frac{i}{\hbar}H\,U(t,t_0), \tag{1.179}$$
(Schrödinger equation for evolution operator)

and thus we see that the evolution operator satisfies the Schrödinger equation in the same way as the state vector $|\psi(t)\rangle$.

1.8.3 General Form

Noting again that $dt^2 = 0$ for infinitesimal time increments, we can write

$$U(t+dt,t) = 1-\frac{i}{\hbar}H\,dt = e^{-iH\,dt/\hbar}. \tag{1.180}$$

Then the composition property extends to give the general form of the evolution operator over finite time intervals,

$$U(t,t_0) = \prod_{t_0}^{t} e^{-iH(t_\alpha)\,dt_\alpha/\hbar}, \tag{1.181}$$

where the product is over all infinitesimal time intervals dt_α between t_0 and t. More precisely, this form follows from dividing the time interval $[t_0, t]$ into N small intervals of duration $\delta t = (t - t_0)/N$; in the limit $N \longrightarrow \infty$, the time-evolution operator for each subinterval is given in the form (1.180). Note that the product (1.181) is ordered such that earlier times are to the right of later times. In the case where $H(t)$ commutes with $H(t')$ for all $t \neq t'$, the elements of the product combine into a single exponential, using the relation (Problem 1.22)

$$e^A e^B = e^{A+B}, \tag{1.182}$$

which holds when $[A, B] = 0$. Then

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}\sum_{t_0}^{t} H(t_\alpha)\, dt_\alpha\right], \tag{1.183}$$

or rewriting the sum as an integral,

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} H(t')\, dt'\right]. \tag{1.184}$$
(general form, $[H(t), H(t')] = 0$)

If the Hamiltonian does *not* commute with itself at different times, then we can't use this form, and we must stick with the more general form (1.181). A common shorthand for this form of the operator is[16]

$$U(t, t_0) = \mathscr{T} \exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} H(t')\, dt'\right], \tag{1.185}$$
(general form)

where $\mathscr{T}$ is the **chronological operator**. This operator indicates that the exponential is really a time-ordered product of infinitesimal time-evolution operators, as in Eq. (1.181). On the other hand, if the Hamiltonian is time-independent, so that $H(t) = H$,

$$U(t, t_0) = \exp\left[-\frac{i}{\hbar}H(t - t_0)\right], \tag{1.186}$$
(general form, time-independent H)

and we see that the time-evolution operator simplifies considerably—it is essentially just the exponentiated Hamiltonian operator.

1.8.4 Pictures of Evolution

The way time evolution works in quantum mechanics, as we have discussed it so far, is called the **Schrödinger picture**. In the Schrödinger picture, the state vector $|\psi(t)\rangle$ evolves according to the Schrödinger equation. The operators, on the other hand, are time-independent, so that time-dependent expectation values are computed according to

$$\langle A(t)\rangle = \langle\psi(t)|A|\psi(t)\rangle. \tag{1.187}$$
(Schrödinger picture)

An alternate scheme, the **Heisenberg picture**, is formulated differently. In the Heisenberg picture, the time dependence is carried by the *operators*, not the state vector. The state vectors are time-*independent* here. Thus, the same expectation value in the Heisenberg picture is given as

$$\langle A(t)\rangle = \langle\psi|A(t)|\psi\rangle. \tag{1.188}$$
(Heisenberg picture)

How do we transform between the two pictures? We will use the subscripts "S" and "H" for the Schrödinger and Heisenberg pictures, respectively, so that $A_{\rm S}$ is the Schrödinger-picture operator, and $A_{\rm H}(t)$ is the

[16] V. B. Berestetskii, E. M. Lifshitz, and L. P. Pitaevskii, *Relativistic Quantum Theory*, (Pergamon Press, 1971).

Heisenberg-picture operator. Then we can use the time-evolution operator to write

$$\begin{aligned}\langle\psi(t)|A_{\text{S}}|\psi(t)\rangle &= \langle\psi(0)|U^\dagger(t,0)A_{\text{S}}U(t,0)|\psi(0)\rangle \\ &= \langle\psi(0)|A_{\text{H}}(t)|\psi(0)\rangle,\end{aligned} \tag{1.189}$$

where we have identified the transformation between pictures as

$$A_{\text{H}}(t) = U^\dagger(t,0)A_{\text{S}}U(t,0). \tag{1.190}$$
(operator transformation)

We also identify the Heisenberg-picture state vector as

$$|\psi\rangle_{\text{H}} = |\psi(0)\rangle_{\text{S}} = U^\dagger(t,0)|\psi(t)\rangle_{\text{S}}, \tag{1.191}$$
(state transformation)

which is just the initial state vector in the Schrödinger picture.

1.8.5 Heisenberg-Picture Evolution

In the Heisenberg picture, since the operators evolve in time, the equation of motion for Heisenberg-picture operators is essential. Differentiating a Heisenberg operator A with respect to t, while also using U as shorthand for $U(t,0)$,

$$\begin{aligned}\dot{A}_{\text{H}} &= \frac{d}{dt}\left[U^\dagger A_{\text{S}}U\right] \\ &= \dot{U}^\dagger A_{\text{S}}U + U^\dagger A_{\text{S}}\dot{U} + U^\dagger \dot{A}_{\text{S}}U \\ &= \frac{i}{\hbar}U^\dagger H_{\text{S}}A_{\text{S}}U - \frac{i}{\hbar}U^\dagger A_{\text{S}}H_{\text{S}}U + U^\dagger \dot{A}_{\text{S}}U \\ &= \frac{i}{\hbar}U^\dagger H_{\text{S}}(t)UU^\dagger A_{\text{S}}U - \frac{i}{\hbar}U^\dagger A_{\text{S}}UU^\dagger H_{\text{S}}(t)U + U^\dagger \dot{A}_{\text{S}}U,\end{aligned} \tag{1.192}$$

after using Eq. (1.179). Collecting the first two terms together, the equation of motion becomes

$$\dot{A}_{\text{H}} = -\frac{i}{\hbar}\left[A_{\text{H}}, U^\dagger H_{\text{S}}(t)U\right] + U^\dagger \dot{A}_{\text{S}}U. \tag{1.193}$$
(Heisenberg-picture evolution)

Note that the $\dot{A}_{\text{S}}$ term accounts for any *explicit* time dependence of the operator (by definition, $\dot{A}_{\text{S}} = \partial A_{\text{S}}/\partial t$ in the Schrödinger picture). Recall that the Hamiltonian *generates* time evolution, and so any time dependence of the Hamiltonian is *externally* imposed; this is emphasized here by writing the Hamiltonian $H_{\text{S}}(t)$ as possibly time-dependent. The "S" subscript to denote that we *introduced* the Hamiltonian the Schrödinger picture. Correspondingly, it is common to write Eq. (1.193) in the more compact form

$$\dot{A}_{\text{H}} = -\frac{i}{\hbar}\left[A_{\text{H}}, H_{\text{H}}(t)\right] + \left(\dot{A}_{\text{S}}\right)_{\text{H}}, \tag{1.194}$$

where $(\dot{A}_{\text{S}})_{\text{H}} := U^\dagger \dot{A}_{\text{S}}U$ and $H_{\text{H}}(t) := U^\dagger H_{\text{S}}(t)U$. However, this definition of the "Heisenberg Hamiltonian" is at least a little misleading because it does not match the proper transformation relation (1.133) for a time-dependent unitary transformation. *That* unitary transformation maps H_{S} to $\tilde{H}_{\text{S}} = 0$, which is sensible because in the Heisenberg picture, the Hamiltonian should generate no time-dependence via the Schrödinger equation.

Note that for a time-*independent* Hamiltonian, where $U(t,0) = \exp(-iHt/\hbar)$, the equation of motion simplifies because $U(t,0)$ commutes with the Hamiltonian. Thus there is no modification required to H_{S} for the Heisenberg equation of motion, which becomes

$$\dot{A}_{\text{H}} = -\frac{i}{\hbar}\left[A_{\text{H}}, H\right] + \left(\dot{A}_{\text{S}}\right)_{\text{H}},$$
(Heisenberg evolution, time-independent H) (1.195)

with no need for an explicit notation for H to be in the Schrödinger picture. Of course, this simplification also holds when the evolution operator takes the form (1.184), where the Hamiltonian commutes with itself at different times. Recalling the classical equation of motion (0.36) for a general phase-space function, we can rewrite this as

$$\frac{dA}{dt} = [A, H]_{\text{P}} + \frac{\partial A}{\partial t} \tag{1.196}$$

for a phase-space function $A(x, p, t)$. Then recalling the correspondence rule (1.57), the classical Poisson bracket goes over to the quantum commutator if we introduce a factor of $(i\hbar)^{-1}$—and thus we see that the Heisenberg-picture equation of motion is the analogue of the classical (bracket) equation of motion.

1.8.6 The Energy Representation

We have so far discussed the position and momentum representations in Sections 1.7.2 and 1.7.7, respectively. Another very useful representation arises in the case of a time-independent Hamiltonian operator ($\partial H/\partial t = 0$), if we use the eigenstates of the Hamiltonian

$$H|E_n\rangle = E_n|E_n\rangle \tag{1.197}$$

as the basis of the **energy representation**. The main advantage of this representation is that the time evolution of the eigenstates, according to the Schrödinger equation

$$\partial_t|E_n\rangle = -\frac{i}{\hbar}H|E_n\rangle = -\frac{i}{\hbar}E_n|E_n\rangle, \tag{1.198}$$

is given simply by phase precession at the rate $E_n/\hbar$:

$$|E_n(t)\rangle = |E_n(0)\rangle\, e^{-iE_nt/\hbar}. \tag{1.199}$$
(energy-eigenstate evolution)

Since the probability of being found in one of these states is time-independent, they are often called **stationary states**. Given the simple evolution of a single stationary state, expressing a general state as a superposition of stationary states also gives the time evolution as a combination of phase precessions:

$$|\psi(t)\rangle = \sum_n c_n\, e^{-iE_nt/\hbar}|E_n(0)\rangle. \tag{1.200}$$
(energy-eigenstate evolution)

This expression is quite general—the trick in solving quantum problems, then, is in finding the eigenenergies and corresponding eigenstates, and in expressing this evolution in useful forms. Note that the above solution can also be written by making the phase precession implicit, as, for example,

$$|\psi(t)\rangle = \sum_n c_n(t)|E_n\rangle = \sum_n c_n|E_n(t)\rangle. \tag{1.201}$$

In the middle expression, we are associating the time dependence $e^{-iE_nt/\hbar}$ with the superposition coefficient c_n, while the state is the fixed initial state $|E_n(0)\rangle$. In the last expression, the coefficients are time-dependent, but the superposition is expressed in terms of the time-dependent basis states (1.199). It is critical to keep track of the source of the time dependence in any given expression, as well as its meaning, because (as we see here and we'll see below), there are all manner of conventions for the time dependence and where it is tucked away.

The other implication of the simple time dependence (1.199) is that the time-evolution operator is diagonal in the energy basis. Again, this makes sense for a time-independent Hamiltonian, in which case

$$\langle E_m|U(t, t_0)|E_n\rangle = \langle E_m|e^{-iH(t-t_0)/\hbar}|E_n\rangle = \langle E_m|E_n\rangle\, e^{-iE_n(t-t_0)/\hbar} = \delta_{mn}\, e^{-iE_n(t-t_0)/\hbar}. \tag{1.202}$$

(Make sure you're clear on the reasoning here—the exponential of the Hamiltonian is defined in terms of the exponential power series, and the terms each act in the form $H^p|E_n\rangle = E_n^p|E_n\rangle$ before resumming the series.)

1.8.7 The Propagator

We just finished up talking about the matrix elements of the evolution operator in the energy representation. A generalization of this notion is the **propagator**, which is essentially just the matrix representation of the evolution operator in some representation:

$$K(\beta, t; \alpha, t_0) := \langle \beta | U(t, t_0) | \alpha \rangle. \tag{1.203}$$
(propagator)

The propagator here has the interpretation of a *transition amplitude* from $|\alpha\rangle$ at time t_0 to $|\beta\rangle$ at time t—that is, given an initial state $|\alpha\rangle$, time evolution changes the state to $U(t, t_0)|\alpha\rangle$, and then the propagator is the probability amplitude for the result to be found in state $|\beta\rangle$ for a measurement of the corresponding observable. So although this interpretation applies where $|\alpha\rangle$ and $|\beta\rangle$ are elements of a common basis, this interpretation as a transition amplitude is more general.

As a more concrete example, consider the position-representation propagator

$$K(x, t; x_0, t_0) := \langle x | U(t, t_0) | x_0 \rangle = \langle x, t | x_0, t_0 \rangle.$$
(propagator, position representation) (1.204)

In the last expression here, the evolution operator has been hidden inside the states according to the notation

$$|x, t\rangle = e^{iHt/\hbar} |x\rangle. \tag{1.205}$$

The "wrong" time dependence comes not from regarding $|x, t\rangle$ as time-evolving states in the sense of $|x(t)\rangle$, but as eigenstates of the Heisenberg-picture operator $x(t)$. Then using the general evolution expression

$$|\psi(t)\rangle = U(t, t_0)|\psi(t_0)\rangle, \tag{1.206}$$

we can project into the position basis by applying $\langle x|$ and then insert a position-representation identity to yield

$$\langle x|\psi(t)\rangle = \langle x|U(t, t_0)|\psi(t_0)\rangle = \int dx_0 \langle x|U(t, t_0)|x_0\rangle\langle x_0|\psi(t_0)\rangle, \tag{1.207}$$

or in terms of the wave function,

$$\psi(x, t) = \int dx_0 \, K(x, t; x_0, t_0) \, \psi(x_0, t_0), \tag{1.208}$$
(evolution via propagator)

so that $K(x, t; x_0, t_0)$ acts as an integration kernel to the effect time evolution.

The analogue of the composition property (1.170) of the time-evolution operator arises directly in terms of the propagator. We simply insert the identity operator, expanded in the position basis at some intermediate time t', into the inner product of the propagator,

$$\begin{aligned} K(x, t; x_0, t_0) &= \langle x, t | x_0, t_0 \rangle \\ &= \int dx' \langle x, t | x', t' \rangle \langle x', t' | x_0, t_0 \rangle, \end{aligned} \tag{1.209}$$

with the result

$$K(x, t; x_0, t_0) = \int dx' K(x, t; x', t') \, K(x', t'; x_0, t_0).$$
(composition property of propagator) (1.210)

Recalling the interpretation of the propagator as a probability amplitude, we can see that this is the analogue of the **Chapman–Kolmogorov equation** for classical conditional probability densities in diffusion problems. This relation basically says that we can regard the transition from x_0 to x at the corresponding times to be as if the particle passed through the intermediate x' point at time t', so long as we sum the amplitude over all possible intermediate points x'.

1.9 Exercises

Problem 1.1

Consider the m-dimensional vector space $\mathbb{C}^m$ (i.e., the set of all complex m-tuples), and let $\phi : \mathbb{C}^m \longrightarrow \mathbb{C}^m$ be a linear transformation (operator). Show that ϕ can be represented by an $m \times m$ matrix; that is, show that there exists a matrix $\mathbf{A}$ such that $\mathbf{A} \cdot \mathbf{x} = \phi(\mathbf{x})$ for every vector $\mathbf{x} \in \mathbb{C}^m$.

Problem 1.2

Let L and M be linear transformations on an inner-product space V. The **composition** of L with M is a function defined by

$$(L \circ M)(\mathbf{x}) := L[M(\mathbf{x})], \tag{1.211}$$

where $\mathbf{x} \in V$. Using the axioms satisfied by linear transformations and inner-product spaces:

(a) Show that $L \circ M$ is also a linear transformation. (In quantum mechanics, this means that the product AB of linear operators A and B is still a linear operator.)

(b) Show that $(L \circ M)^\dagger = M^\dagger \circ L^\dagger$. [In quantum mechanics, this is the product-adjoint rule $(AB)^\dagger = B^\dagger A^\dagger$.]

Problem 1.3

Let Q be a linear operator (not necessarily Hermitian) with eigenvalue q and eigenvector $|q\rangle$:

$$Q|q\rangle = q|q\rangle. \tag{1.212}$$

Remembering that linear operators transform states on the right,

$$\langle\psi'|Q|\psi\rangle := \langle\psi'|Q\psi\rangle, \tag{1.213}$$

show *explicitly* that Q effectively "acts to the left" as

$$\langle q|Q|\psi\rangle = q\langle q|\psi\rangle, \tag{1.214}$$

using *only* the assumptions spelled out in this problem, along with the conjugation rule $\langle a|b\rangle = \langle b|a\rangle^*$ and the definition of the adjoint (Hermitian conjugate) of an operator.

Problem 1.4

The space of all square-integrable functions is a Hilbert space $\mathscr{H}$, and thus all Cauchy sequences in the space must converge to a function in $\mathscr{H}$.

(a) Let $G_n(x)$ denote a unit-normalized Gaussian distribution of standard deviation $1/n$. The "limit" of $G_n(x)$ as $n \longrightarrow \infty$ is $\delta(x)$, but $\delta(x) \notin \mathscr{H}$. Give a *precise* explanation of why this is not a contradiction.

(b) Is the set of all *unit-normalized*, square-integrable functions a Hilbert space?

Problem 1.5

(a) Given an observable Q, use the Schrödinger equation to derive an equation of motion for $\langle Q\rangle$. (Assume that Q has no explicit time dependence.)

(b) Show that, for a time-independent Hamiltonian, the energy uncertainty ΔE (uncertainty associated with the Hamiltonian) is time-independent.

Problem 1.6

Show that for any observable Q that $\langle Q^2\rangle \geq 0$, and that all of Q^2's eigenvalues are nonnegative.

Problem 1.7

Let P and Q be *anti*commuting Hermitian operators,

$$[P, Q]_+ = PQ + QP = 0. \tag{1.215}$$

Assuming that both P and Q have nondegenerate spectra, is it possible for P and Q to have a simultaneous eigenstate? Justify your answer either way.

Also give a specific example of two anticommuting operators that illustrates your answer.

Problem 1.8

(a) Suppose that a Hermitian operator Q has eigenvalues q_n and eigenvectors $|q_n\rangle$,

$$Q|q_n\rangle = q_n|q_n\rangle, \tag{1.216}$$

for $n \in \mathbb{Z}^+$. If the eigenvectors $|q_n\rangle$ form a complete set, prove that Q may always be written in the form

$$Q = \sum_{n=1}^{\infty} q_n |q_n\rangle\langle q_n|. \tag{1.217}$$

Note: to prove this equivalence you must consider the action of *both* expressions here on an *arbitrary* vector, not just an eigenvector.

(b) Show that Q has the same form if it is not necessarily Hermitian, but is **normal**, which means that $QQ^\dagger = Q^\dagger Q$.

Problem 1.9

Consider two observables Q and R, such that $[Q, R] = 0$. In this case the uncertainty principle says that $\sigma_Q \sigma_R \geq 0$. Is it *always* the case that $\sigma_Q \sigma_R = 0$? If yes, prove it; if not, give a counterexample.

Problem 1.10

Prove the generalized uncertainty relation [Eq. (1.51)]

$$V_P V_Q \geq \frac{1}{4}\Big|\langle [P, Q]\rangle\Big|^2 + \frac{1}{4}\Big|\langle [P, Q]_+\rangle - 2\langle P\rangle\langle Q\rangle\Big|^2, \tag{1.218}$$

where $[A, B]_+ := AB + BA$ is the **anticommutator**.

Problem 1.11

Any Hermitian operator P that satisfies $P^2 = P$ is called a **projection operator** or **projector**.

Suppose that P_1 and P_2 are projectors. Then show that the product $P_1 P_2$ is a projector if and only if $[P_1, P_2] = 0$.

Problem 1.12

(a) For a projection operator P, show that $e^P = 1 + (e - 1)P$.

(b) Suppose that $P_1, \ldots P_n$ are (nonidentical) projectors. Give a necessary and sufficient condition for $P_1 + \cdots + P_n$ to be a projection operator (and prove necessity and sufficiency).

(c) An **elementary projector** is one that can be written $P = |a\rangle\langle a|$ in terms of some state vector $|a\rangle$. Suppose that $P_1, \ldots P_n$ are (nonidentical, elementary) projectors, and let Q be a linear combination of these. Give a sufficient condition for Q to be an elementary projector (and prove sufficiency).

Problem 1.13

Suppose that Q is a Hermitian operator satisfying $Q^3 = Q$. Then Q could be a projector, but is it necessarily? If yes, prove it; if no, give a counterexample.

Problem 1.14

(a) Suppose that Q is a Hermitian operator that satisfies $Q^4 = 1$. What are Q's eigenvalues?

(b) What if you relax the requirement that Q be Hermitian?

Problem 1.15

Suppose u is an eigenvalue of a unitary operator U. Use the definition of unitarity to show that $|u|^2 = 1$.

Problem 1.16

Show that if a unitary operator $U = 1 + \delta U$ represents an infinitesimal transformation, then the infinitesimal part δU is anti-Hermitian ($\delta U^\dagger = -\delta U$).

Problem 1.17

Consider an observable Q with eigenvalues q and corresponding eigenvectors $|q\rangle$. A displacement operator D_a acts to "displace" the state by an amount a:

$$D_a|q\rangle := |q + a\rangle. \tag{1.219}$$

(a) Show that $[Q, D_a] = aD_a$.

(b) Show that D_a is unitary.

(c) Show that $D_a^\dagger Q D_a = Q + a$.

(d) A displacement by an *infinitesimal* amount δa must have the form

$$D_{\delta a} = 1 + \frac{i\,\delta a}{\hbar}\,G_a, \tag{1.220}$$

where G_a is the generator of the transformation. Derive an expression for the commutator $[G_a, Q]$.

(e) Derive an expression for the *finite*-displacement operator D_a in terms of G_a.

Problem 1.18

Recall that the commutator satisfies the Jacobi identity

$$\big[A, [B, C]\big] + \big[B, [C, A]\big] + \big[C, [A, B]\big] = 0 = 0 \tag{1.221}$$

for any operators A, B, and C. This is true of the classical Poisson bracket as well. What does this mean intuitively? Well, this problem may not do *that*, but it *is* useful to see one consequence of the Jacobi identity for infinitesimal transformations.

Consider two infinitesimal unitary transformations,

$$U_a = 1 + \frac{i\epsilon}{\hbar}\,G_a, \qquad U_b = 1 + \frac{i\epsilon}{\hbar}\,G_b, \tag{1.222}$$

here written in terms of their infinitesimal generators G_a and G_b. Let $Q_a = U_a Q U_a^\dagger$ denote the transformed version of Q according to U_a, with the same idea applying to $Q_b = U_b Q U_b^\dagger$. Then use the Jacobi identity and the antisymmetry property of the commutator to show that

$$Q_{ab} - Q_{ba} = \frac{\epsilon^2}{\hbar^2}[[G_a, G_b], Q], \tag{1.223}$$

where $Q_{ab} := U_b Q_a U_b^\dagger$ and $Q_{ba} := U_a Q_b U_a^\dagger$. That is, this expression gives the difference between applying the a transformation and then the b transformation, vs. applying the transformations in the opposite order. This relation says that $(\epsilon/i\hbar)[G_a, G_b]$ acts as an effective generator for the transformation going from Q_{ba} to Q_{ab}, and that $Q_{ba} = Q_{ab}$ if and only if the generators commute.

Note that since the Poisson bracket satisfies these same properties, an analogous result holds in classical mechanics (and in general for the effects of two flows on a manifold); see Eq. (0.81)

For a more explicit example of this property in action, see Problem 7.12.

Problem 1.19

Let U be a unitary operator. Then show that

$$A = i\frac{1+U}{1-U} \tag{1.224}$$

is Hermitian, provided that 1 is not an eigenvalue of U.

Problem 1.20

An operator A is **antilinear** if for any vectors $|\psi\rangle$ and $|\varphi\rangle$ and complex number c,

$$A\big(|\psi\rangle + |\varphi\rangle\big) = A|\psi\rangle + A|\varphi\rangle \tag{1.225}$$

and

$$Ac|\psi\rangle = c^* A|\psi\rangle. \tag{1.226}$$

Furthermore, A is also **antiunitary** if it has an inverse A^{-1} (i.e., $AA^{-1} = A^{-1}A = 1$) and $\langle\psi|A^\dagger A|\psi\rangle = \langle\psi|\psi\rangle$ for any vector $|\psi\rangle$ (i.e., A does not change $|\psi\rangle$'s norm).

(a) If A is antiunitary antilinear, show that A^{-1} is also antiunitary antilinear. (Throughout this problem, don't waste time proving obvious things, for example the distributive property for A^{-1}.)

(b) Show that

$$\langle\varphi|A^\dagger A|\psi\rangle = \langle\varphi|\psi\rangle^* = \langle\psi|\varphi\rangle \tag{1.227}$$

for any vectors $|\psi\rangle$ and $|\varphi\rangle$.

Hint: the trick is to work out and compare the norms of $|\chi\rangle := |\psi\rangle + |\varphi\rangle$ and $A|\chi\rangle$. Then repeat with $|\chi'\rangle := |\psi\rangle - i|\varphi\rangle$.

(c) If A and B are antiunitary antilinear, show that AB is unitary.

(d) Show that the complex-conjugation operator C, defined by

$$\langle x|C|\psi\rangle = \langle x|\psi\rangle^*, \tag{1.228}$$

is antiunitary antilinear.

(e) The time-reversal operator T is an antiunitary antilinear operator satisfying $TpT^{-1} = -p$ and $TxT^{-1} = x$. Show that the conjugation operator C also satisfies these two defining relations.

(f) Complete the proof and show that T is uniquely determined (up to a phase factor) by its defining properties. In doing this you have shown that $T = C$ (up to a phase factor).

Hint: start with two time-reversal operators T and T', and work with the combination $T'T^{-1}$.

Problem 1.21

An operator $A(\lambda)$ that depends on a parameter λ has a derivative given by

$$\frac{dA}{d\lambda} := \lim_{\epsilon \to 0} \frac{A(\lambda + \epsilon) - A(\lambda)}{\epsilon}. \tag{1.229}$$

Let $A(\lambda)$ and $B(\lambda)$ be two such operators, and use this definition to[17]

(a) prove that

$$\frac{d}{d\lambda}(AB) = \frac{dA}{d\lambda}B + A\frac{dB}{d\lambda}. \tag{1.230}$$

(b) prove that

$$\frac{d}{d\lambda}A^{-1} = -A^{-1}\frac{dA}{d\lambda}A^{-1}. \tag{1.231}$$

Problem 1.22

Prove that

$$e^{A+B} = e^A e^B \tag{1.232}$$

for two operators A and B such that $[A, B] = 0$.

Hint: working with the full series expansions will be messy. Try working with $e^{A+\lambda B}$, and consider taking derivatives with respect to λ.

Problem 1.23

For the operator

$$A = \epsilon\Big(|1\rangle\langle 1| - |0\rangle\langle 0|\Big) + \gamma|0\rangle\langle 1| + \gamma^*|1\rangle\langle 0| \tag{1.233}$$

on the Hilbert space $\{|0\rangle, |1\rangle\}$, where $\epsilon \in \mathbb{R}$ and $\gamma \in \mathbb{C}$, show that the eigenvectors may be written as

$$\begin{aligned} |+\rangle &= \sin\theta|0\rangle + e^{i\phi}\cos\theta|1\rangle \\ |-\rangle &= \cos\theta|0\rangle - e^{i\phi}\sin\theta|1\rangle, \end{aligned} \tag{1.234}$$

where

$$\tan 2\theta = \frac{|\gamma|}{\epsilon} \qquad \left(0 \le \theta < \frac{\pi}{2}\right). \tag{1.235}$$

Also find the corresponding eigenvalues.

Problem 1.24

For operators A and B, show that

$$\left[A, \frac{1}{B}\right] = \frac{1}{B}[B, A]\frac{1}{B}. \tag{1.236}$$

Problem 1.25

Recall that both the Poisson bracket and the quantum commutator satisfy the following properties.

1. antisymmetry: $[A, B] = -[B, A]$
2. null bracket with scalars: $[c, A] = 0$ $(c \in \mathbb{C})$
3. associativity: $[A + B, C] = [A, C] + [B, C]$; $\qquad [A, B + C] = [A, B] + [A, C]$

[17] Albert Messiah, *Quantum Mechanics* (Wiley, 1958) p. 339, Problem 3 (ISBN: 0486409244).

4. product rules: $[AB, C] = A[B, C] + [A, C]B; \qquad [A, BC] = [A, B]C + B[A, C]$
5. Jacobi identity: $[A, [B, C]] + [B, [C, A]] + [C, [A, B]] = 0$

Suppose that we haven't yet settled on a quantum bracket $[A, B]$, but we wish to choose one that satisfies the above properties. Show that the *only* possible choice is the quantum commutator $[A, B] = AB - BA$ (up to an overall real factor).

Hint: starting with $[AA', BB']$ for arbitrary operators A, A', B, and B', apply the two product rules to write this expression as the sum of four brackets. Applying the product rules in either order gives two expressions; you should require that they be equivalent.

Problem 1.26

Show that

$$\int_{-\infty}^{\infty} dx\, \delta'(x - y)\, f(x) = -f'(y), \tag{1.237}$$

giving whatever suitable conditions on $f(x)$ that you require for this relation to hold. Also show that

$$\int_{-\infty}^{\infty} dx\, \delta'(y - x)\, f(x) = f'(y), \tag{1.238}$$

thereby showing that $\delta'(x)$ is odd, $\delta'(-x) = -\delta'(x)$. Generalize these results to the kth derivative $\delta^{(k)}(x)$.

Problem 1.27

Suppose that we *define* the derivative operator ∂_x in the position representation by $\langle x|\partial_x|x'\rangle = \delta'(x - x')$. Show that this definition implies that $\langle x|\partial_x|\psi\rangle = \partial_x\langle x|\psi\rangle$.

Problem 1.28

Consider the oddball expression

$$\delta(x - y) = \delta(x) - \delta'(x)\, y + \frac{1}{2}\delta''(x)\, y^2 - \frac{1}{3!}\delta'''(x)\, y^3 + \cdots . \tag{1.239}$$

Demonstrate why this is a problematic expression if taken as a literal expression (where the delta function "acts like a function"). Also explain how this expression can be given a sensible (and useful) interpretation in the context of an integral.

Problem 1.29

Using *only* the projection property

$$\delta(x - a)\, f(x) = \delta(x - a)\, f(a) \tag{1.240}$$

of the delta function, derive the scaling property of the delta function:

$$\delta(\alpha x) = \frac{1}{|\alpha|}\delta(x) \qquad (\alpha \in \mathbb{R},\ \alpha \neq 0). \tag{1.241}$$

That is, derive whatever other properties you need from

Problem 1.30

(a) In analogy with

$$\delta(\alpha x) = \frac{\delta(x)}{|\alpha|} \qquad (\alpha \neq 0), \tag{1.242}$$

derive an expression for $\delta'(\alpha x) \quad (\alpha \neq 0)$.

(b) Same for $\delta''(\alpha x)$.

Problem 1.31

Show that

$$\frac{\delta(x)}{x} = -\delta'(x), \tag{1.243}$$

in the sense that

$$\int_{-\infty}^{\infty} dx\, \frac{\delta(x)}{x} f(x) = -\int_{-\infty}^{\infty} dx\, \delta'(x) f(x), \tag{1.244}$$

where

$$\int_{-\infty}^{\infty} \frac{dx}{x} = \lim_{\epsilon \to 0} \left[\int_{\epsilon}^{\infty} \frac{dx}{x} + \int_{-\infty}^{-\epsilon} \frac{dx}{x} \right] = 0 \tag{1.245}$$

explicitly handles the singularity. State any conditions on the test functions or integration that you need for your result to work.

Problem 1.32

Prove that

$$\delta[(x_1 - x)(x_2 - x)] = \frac{\delta(x_1 - x) + \delta(x_2 - x)}{|x_1 - x_2|} \tag{1.246}$$

for $x, x_1, x_2 \in \mathbb{R}$.

Problem 1.33

Carry out the limit in the expression

$$L(x) := \lim_{a \to 0^+} \Big[(a-1)\delta(a^2 x + a^3) + 2\delta(a^2 x) - (a+1)\delta(a^2 x - a^3) \Big]. \tag{1.247}$$

Problem 1.34

Problems with delta functions can arise in expressions like

$$\int_{-\infty}^{\infty} dx\, \Theta(x)\, \delta(x) = ?, \tag{1.248}$$

where $\Theta(x)$ is the Heaviside function

$$\Theta(x) = \begin{cases} 1 & (x > 0) \\ 0 & (x < 0). \end{cases} \tag{1.249}$$

Note that the point at $x = 0$ is (intentionally) left undefined.

One can then think of the integration in a couple of ways. For example, suppose we take the "sensible" definition that $\Theta(x = 0) = 1/2$, which is the average of the limits at this point from each direction. Then using $\Theta(x)\,\delta(x) = \Theta(0)\,\delta(x) = \delta(x)/2$, and so

$$\int_{-\infty}^{\infty} dx\, \Theta(x)\, \delta(x) = \frac{1}{2}. \tag{1.250}$$

Another method corroborates this result: suppose we take the sequence $h_n(x) = (n/\sqrt{\pi})\, e^{-n^2 x^2}$. Because the functions are normalized and even,

$$\int_{-\infty}^{\infty} dx\, \Theta(x)\, h_n(x) = \frac{1}{2}, \tag{1.251}$$

and so the limit $n \longrightarrow \infty$ gives the same result for the integral.

But now let's see how things start to fall apart if we consider

$$\int_{-\infty}^{\infty} dx\, \Theta^m(x)\, \delta(x) = ?. \tag{1.252}$$

The first method would then give an answer of 2^{-m}, while the second method gives $1/2$ for any m. Not good. In fact neither of these answers is particularly appealing; the goal of this problem is to give yet another (arguably, better) meaning to this integral. The point of this problem is for you to see that, in some cases where delta functions arise, some extra information (which was lost by taking a limit too soon) is necessary to know how to properly interpret the expression.

(a) Let's assume that the delta and Heaviside functions are related, and we will build this into a "regularization" of the integral. For $n > 0$, define the sequence of functions

$$h_n(x) := \begin{cases} n & (0 < x < 1/n) \\ 0 & \text{otherwise} \end{cases} \tag{1.253}$$

as a regularization of the delta function, and

$$u_n(x) := \begin{cases} 0 & (x < 0) \\ nx & (0 < x < 1/n) \\ 1 & (x > 1/n) \end{cases} \tag{1.254}$$

as a regularization of the Heaviside function. (Note that these functions aren't each "centered," but are centered in an asymptotic sense.) Then compute the integral

$$I_n := \int_{-\infty}^{\infty} dx\, [u_n(x)]^m\, h_n(x), \tag{1.255}$$

and compute the limit as $n \longrightarrow \infty$, to obtain a value for the integral (1.252).

(b) Note that in part (a), the regularization functions satisfy $u_n'(x) = h_n(x)$. Show that by regarding $\delta(x) = \Theta'(x)$ that the same result follows for the integral (1.252) without invoking any explicit regularization functions.

Problem 1.35

If a wave function $\psi(x)$ is a localized function that becomes arbitrarily narrow, then $|\psi(x)|^2$ becomes a delta function. So what happens to $\psi(x)$? It becomes something more like $\sqrt{\delta(x)}$. The point of this problem is to see if an object like this has a useful meaning on its own.

Give a suitable definition of $\delta^\beta(x)$ for an exponent $0 < \beta < 1$, and work out its effect when multiplying a test function $f(x)$ in the sense of the integral

$$\int dx\, \delta^\beta(x)\, f(x). \tag{1.256}$$

State explicitly whatever conditions on $f(x)$ that you need to assume for your solution to be valid.

Problem 1.36

Let Q be a Heisenberg-picture operator corresponding to an observable, with no explicit time dependence ($\partial Q/\partial t = 0$).

(a) Show that the expectation value of $\dot{Q}$ vanishes for an energy eigenstate (stationary state), assuming a discrete, nondegenerate energy spectrum.

(b) Suppose we relax the assumption of a discrete, nondegenerate energy spectrum. Consider a free particle, $H = p^2/2m$, and let Q be the position operator x. First, show that

$$\langle \dot{x} \rangle = \frac{1}{m} \langle p \rangle. \tag{1.257}$$

For momentum eigenstates (which are also energy eigenstates), this is clearly nonvanishing for any $p \neq 0$. On the other hand, you should be able to apply your argument from (a) to this case, and conclude that the expectation value should always vanish (so go ahead and do this). What gives?

Problem 1.37

The idea behind this problem is to compare the structure of canonical (classical) vs. unitary (quantum) transformations between different coordinate systems.

(a) Consider the (classical) Hamiltonian

$$H(q, p, t) = \frac{p^2}{2m} + V[q - f(t)], \tag{1.258}$$

representing a potential displaced arbitrarily in time. Consider a transformation into the rest frame of the potential,

$$\tilde{q} = q - f(t), \qquad \tilde{p} = m\frac{d\tilde{q}}{dt} = p - m\dot{f}. \tag{1.259}$$

Derive the generating function for this transformation,

$$F_2(q, \tilde{p}; t) = \tilde{p}q + mq\dot{f}(t) - \tilde{p}f(t) + g(t), \tag{1.260}$$

where

$$\dot{g} = -mf(t)\ddot{f}(t) - \frac{m}{2}[\dot{f}(t)]^2, \tag{1.261}$$

and show that the new Hamiltonian under this canonical transformation is given by

$$\tilde{H}(\tilde{q}, \tilde{p}, t) = \frac{\tilde{p}^2}{2m} + V(\tilde{q}) + m\tilde{q}\ddot{f}. \tag{1.262}$$

Interpret this form physically.

(b) Consider the quantum Hamiltonian with the same form as in Eq. (1.258), and consider a general unitary transformation

$$U = e^{ip\alpha(t)/\hbar} e^{-iq\beta(t)/\hbar} e^{-i\gamma(t)/\hbar}, \tag{1.263}$$

where the three factors correspond respectively to shifts of position, momentum, and energy. Show that this unitary transformation results in a quantum Hamiltonian of the form of Eq. (1.262) provided the shift functions satisfy

$$\alpha = f, \qquad \beta = m\dot{\alpha}, \qquad \dot{\gamma} = -\frac{\beta^2}{2m} - \dot{\beta}\alpha. \tag{1.264}$$

Note, however, that the new Hamiltonian should be written in terms of the *old* coordinates in order to have the right form.

(c) Show that by taking $\beta = 0$ that the Hamiltonian may alternately be transformed to

$$\tilde{H}(p, q; t) = \frac{[p + m\dot{f}(t)]^2}{2m} + V(q). \tag{1.265}$$

Give the forms of $\alpha(t)$ and $\gamma(t)$ needed to effect this transformation. Again, give a physical interpretation for this form.

Problem 1.38

Consider the classical Lagrangian

$$L = \dot{q}^3 - q^3. \tag{1.266}$$

Work out the quantum Hamiltonian.

Problem 1.39

Consider the classical Lagrangian

$$L(x, \dot{x}) = \frac{m}{2} g(x)\, \dot{x}^2 - V(x). \tag{1.267}$$

The goal of this problem is to develop the corresponding quantum theory via canonical quantization.

(a) Show that the classical Hamiltonian is

$$H(x, p) = \frac{p^2}{2mg(x)} + V(x). \tag{1.268}$$

(b) Argue that, in quantizing this system, that the commutator should still be

$$[x, p] = i\hbar \tag{1.269}$$

as usual.

(c) The problem of course with simply promoting x and p to operators in the Hamiltonian is the ordering ambiguity in the kinetic-energy term. To resolve the ambiguity, consider the transformation to a new generalized coordinate q, defined by

$$\frac{dq}{dx} = \sqrt{g(x)}. \tag{1.270}$$

Rewrite the Lagrangian (1.267) in terms of q, write down the momentum p_q conjugate to q, and write down the Hamiltonian. You should find that the resulting Hamiltonian is readily carried over to quantum mechanics via canonical quantization.

(d) The coordinate transformation also induces some other changes in the structure of the Hilbert space. In terms of the q coordinate, the inner product has the usual form

$$\langle \psi_1 | \psi_2 \rangle = \int dq\, \psi_1^*(q)\, \psi_2(q). \tag{1.271}$$

Write down the analogous expression in terms of the original coordinate x. Show also that the identity in the position representation must now be

$$\int dx\, \sqrt{g(x)}\, |x\rangle\langle x| = 1. \tag{1.272}$$

(e) Derive a modified "orthonormality" expression for the position representation; that is, derive an expression for $\langle x|x'\rangle$. [Consider an arbitrary state $\psi(x) = \langle x|\psi\rangle$, and try inserting an identity.]

(f) Turning now to the momentum operator, recall that it is defined (in part) by the standard commutator rule (1.269). Show that a modified form of the momentum operator, obtained by inserting factors of g,

$$p = \frac{\hbar}{i} g^{-\alpha}(x) \partial_x g^{\alpha}(x), \tag{1.273}$$

still satisfies this commutation rule.

(g) Furthermore, the momentum operator must be Hermitian with respect to the modified inner product that you derived in part (d). Show that this constraint implies that $\alpha = 1/4$.

(h) Starting with this form of the momentum operator, derive an expression for the momentum eigenstates, expressed in the position representation.

(i) Use your result from (h) to show that the identity expressed in the momentum representation is

$$\int dp\, |p\rangle\langle p| = 1. \tag{1.274}$$

Note that this implies the momentum orthonormality relation $\langle p|p'\rangle = \delta(p - p')$.

(j) Finally, show that the properly quantized and ordered Hamiltonian corresponding to the Lagrangian (1.267) is

$$H(x,p) = \frac{1}{2m}\left(\frac{1}{g^{1/4}} p \frac{1}{\sqrt{g}} p \frac{1}{g^{1/4}}\right) + V(x). \tag{1.275}$$

To do this, start with the operator ∂_q^2 and rewrite it in terms of the x coordinate. Use this result to infer how the p^2 term from the q-form Hamiltonian should carry over to the x-form Hamiltonian.

Problem 1.40

Consider the observable q, which in the position (x) representation is defined to have the diagonal form $\langle x|q|x'\rangle = q(x)\,\delta(x - x')$. Further, suppose that $dq/dx \equiv q'(x) > 0$ everywhere.

(a) Show that the state $|q(x)\rangle$, which in the position representation is defined by

$$\langle x|q(x')\rangle := \big[q'(x')\big]^{-1/2}\delta(x - x'), \tag{1.276}$$

is an eigenvector of q, and find the eigenvalue.

(b) Since these are eigenstates of a Hermitian operator, they ought to form an orthonormal basis. Demonstrate the orthonormality explicitly by computing $\langle q(x)|q(x')\rangle \equiv \langle q|q'\rangle$, and explain how your result makes sense.

For this part it may be useful to remember the composition property of the delta function

$$\delta[f(x)] = \sum_{x_0 \in f^{-1}(0)} \frac{\delta(x - x_0)}{|f'(x_0)|}, \tag{1.277}$$

where the sum is over all (simple) roots x_0 of f.

(c) Work out the probability density for q, and demonstrate that your result makes sense.

Problem 1.41

An operator in the position representation has the form $\langle x|V|x'\rangle = \delta(x - x')\,V(x)$. What is this property expressed in the momentum representation?[18]

Problem 1.42

For eigenstates of operators with continuous eigenvalues, we discussed in Section 1.7.2 some normalization-related problems, and argued that it is acceptable to write down "normalization" conditions of the form $\langle x|x'\rangle = \delta(x - x')$. However, this is not the *only* possible approach. The purpose of this problem is to explore an alternate (and useful) approach to normalizing these states.

Suppose we restrict the "universe" to a box of dimensions $L \times L \times L$ (for concreteness, spanning $[-L/2, L/2]$ in each dimension). The box imposes boundary conditions on the eigenstates; these could

[18] Leslie E. Ballentine, *Quantum Mechanics: A Modern Development* (World Scientific, 1998) Problem 5.3 (ISBN: 9810241054).

easily be Dirichlet conditions (as in a three-dimensional infinite square well), but choosing periodic boundary conditions like

$$\psi(x+L,y,z)=\psi(x,y+L,z)=\psi(x,y,z+L)=\psi(x,y,z) \tag{1.278}$$

will yield eigenstates that more closely resemble the conventional form.

A generalization of the argument from Section 1.7.7 of the form of the momentum eigenstates leads to

$$\langle\mathbf{r}|\mathbf{p}\rangle = c_{\mathbf{p}}\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{1.279}$$

for an undetermined coefficient $c_{\mathbf{p}}$. Normalization with respect to the finite box is straightforward, however, and leads to $c_{\mathbf{p}} = L^{-3/2}$, and so

$$\psi_{\mathbf{p}}(\mathbf{r}) := \langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{\sqrt{V}}\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{1.280}$$

where $V = L^3$ is the box volume.

Like the infinite square well, the boundary conditions lead to discrete allowed values for the momentum,

$$\mathbf{p}(\mathbf{n}) = \frac{2\pi\hbar n_x}{L}\hat{x} + \frac{2\pi\hbar n_y}{L}\hat{y} + \frac{2\pi\hbar n_z}{L}\hat{z}, \tag{1.281}$$

where $n_x, n_y, n_z \in \mathbb{Z}$ (i.e., positive, negative, and zero integer values are all allowed). Expressed explicitly in the position representation, the orthonormality condition for momentum eigenstates is

$$\int_V d^3r\, \psi^*_{\mathbf{p}'}(\mathbf{r})\, \psi_{\mathbf{p}}(\mathbf{r}) = \frac{1}{V}\int_V d^3r\, e^{i(\mathbf{p}-\mathbf{p}')\cdot\mathbf{r}/\hbar} = \delta^3_{\mathbf{p}',\mathbf{p}}, \tag{1.282}$$

as it should be according to the axioms of quantum mechanics.

Now, how does this finite-box approach relate to the standard way of handling momentum eigenstates? Consider the now-discrete completeness relation for the momentum operator:

$$\sum_{\mathbf{p}} |\mathbf{p}\rangle\langle\mathbf{p}| = 1. \tag{1.283}$$

Operating with $\langle\mathbf{r}|$ on the left and $|\mathbf{r}'\rangle$ on the right gives the completeness relation

$$\sum_{\mathbf{p}} \psi^*_{\mathbf{p}}(\mathbf{r})\psi_{\mathbf{p}}(\mathbf{r}') = \delta^3(\mathbf{r}-\mathbf{r}'). \tag{1.284}$$

With the explicit form (1.280) for the eigenfunctions, this becomes

$$\frac{1}{V}\sum_{\mathbf{p}} e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} = \delta^3(\mathbf{r}-\mathbf{r}'). \tag{1.285}$$

Of course, the box itself and its boundary conditions are not physical, and so they should not have any ultimate effect on the calculation—at some point V must cancel out of the calculation (at least in the limit of large V). With this in mind, there isn't much reason to go carrying around factors of V that are going to disappear anyway, particularly when the cancellation is not so obvious, as in Eq. (1.285).

So let's go ahead and see how the cancellation works, and then we can see how to short-circuit the procedure. We can start by requiring V to be (arbitrarily) large. In this regime, the discrete set of momenta can be approximated by a continuum. The recipe for converting a discrete sum into an integral is by the replacement

$$\sum_{\mathbf{p}} (\Delta p)^3 \longrightarrow \int d^3p, \tag{1.286}$$

where $\Delta p = 2\pi\hbar/L$ is the distance in momentum between adjacent momentum states along one momentum axis. Rewriting this, the recipe is to replace the summation sign by a scaled integral as

$$\sum_{\mathbf{p}} \longrightarrow \frac{V}{(2\pi\hbar)^3} \int d^3p. \tag{1.287}$$

However, with this replacement Eq. (1.285) becomes

$$\frac{1}{(2\pi\hbar)^3} \int d^3p\, e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')/\hbar} = \delta^3(\mathbf{r}-\mathbf{r}'), \tag{1.288}$$

which is a bit more familiar as the standard integral representation of the delta function. Since something like this must *always* happen, the convention is to simplify life by associating the (square root of the) factor $V/(2\pi\hbar)^3$ with the momentum eigenstates, giving the more familiar normalization

$$\psi_{\mathbf{p}}(\mathbf{r}) := \langle \mathbf{r}|\mathbf{p}\rangle \longrightarrow \frac{1}{(2\pi\hbar)^{3/2}}\, e^{i\mathbf{p}\cdot\mathbf{r}/\hbar} \tag{1.289}$$

as an alternative to Eq. (1.280). This is a shortcut for the more careful procedure of keeping the quantization volume around and then taking the limit $V \longrightarrow \infty$ at the end of the calculation.

Now we finally get to the problem! Besides being a regularization principle, a representation in terms of a discrete momentum basis can be a useful thing in its own right, as for example in handling quantum-mechanical calculations on a computer. Suppose that we stick to the discrete momentum representation, where we quantize in a finite box of volume V. Let's also do the same thing in momentum where we impose periodic boundary conditions over a momentum "distance" $\tilde{L}$ along each axis, effectively imposing a maximum on each momentum component of $\tilde{L}/2$. This implies a discrete set of position eigenstates, which can be written in the momentum representation as

$$\phi_{\mathbf{r}}(\mathbf{p}) := \langle \mathbf{p}|\mathbf{r}\rangle = \frac{1}{\sqrt{\tilde{V}}}\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}, \tag{1.290}$$

where $\tilde{V} = \tilde{L}^3$. In fact the eigenstates in either representation must be *finite*, because the range of eigenvalues in either representation is discrete and bounded.

(a) Show directly that the number of states N_x in each direction in the position representation must be the same as the number of states N_p in each direction in the momentum representation, $N = N_x = N_p$. (This should be clear because either representation must span an equivalent Hilbert space, but you should do this by direct calculation of N_x and N_p.)

(b) Write down the analogous expressions to Eqs. (1.283)–(1.285) for the present case of a finite basis. Demonstrate from your expressions that it is again possible to change to using eigenstates with the same normalization as in the continuum case (thus cancelling any quantization volumes at the outset), provided every sum is accompanied by the appropriate volume element; that is, the new normalization should be accompanied by the replacements

$$\sum_{\mathbf{p}} \longrightarrow \sum_{\mathbf{p}} (\Delta p)^3, \qquad \sum_{\mathbf{r}} \longrightarrow \sum_{\mathbf{r}} (\Delta x)^3. \tag{1.291}$$

Again, this is a common and handy way to handle discretely sampled wave functions in a numerical calculation on a computer.

Problem 1.43

Consider the wave function

$$\psi(x) = \frac{1}{\sqrt{\pi\hbar(e-1)}} \sum_{n=1}^{\infty} \frac{1}{\sqrt{n!}} \cos\Big(\frac{n\pi x}{L}\Big). \tag{1.292}$$

where $L > 0$.

(a) Show that this state is sensibly normalized. (*Hint*: think in terms of free-particle momentum eigenstates.)

(b) For this state, write down expressions for $\langle p^{683} \rangle$ and $\langle p^{684} \rangle$. (Your answer can be in the form of a series.)

Problem 1.44

Working in the position representation, derive an explicit expression for the operator that effects the transformations

$$x \longrightarrow p, \qquad p \longrightarrow -x, \tag{1.293}$$

where x and p are the usual (canonical) operators.

Problem 1.45

(a) Compute $[x^2, p^2]$ (obtain a form with only second-order terms), and compare it to the (classical) Poisson bracket $[x^2, p^2]_{\text{P}}$.

(b) Compute $[x^3, p^3]$ (obtain a form with only fourth-order terms), and again compare it to the (classical) Poisson bracket $[x^3, p^3]_{\text{P}}$.

Chapter 2

Particles in Potentials: Fundamental Examples

Now it's time to start applying the axioms of quantum mechanics to solving actual problems. First, we'll keep things simple by considering a single particle moving in a potential, (mostly) in one dimension, and then move on to other simple (piecewise constant) potentials.

2.1 Free Particle

The simplest particle-in-a-potential problem is the free particle, which has no potential at all: $V(x) = 0$. At least, this is the simplest problem in a certain sense.

Because the Hamiltonian is just the kinetic-energy operator,

$$H = \frac{p^2}{2m}, \tag{2.1}$$

then clearly the momentum operator commutes with the Hamiltonian:

$$[p, H] = \frac{1}{2m}[p, p^2] = 0. \tag{2.2}$$

This means that the momentum operator has simultaneous eigenstates with the Hamiltonian. We can write the energy eigenvalues E_p in terms of the momentum eigenvalues simply as $E_p = p^2/2m$. This also means that the evolution operator is diagonal in the momentum representation:

$$\langle p'|U(t, t_0)|p\rangle = e^{-ip^2(t-t_0)/2m\hbar}\delta(p' - p). \tag{2.3}$$

This last expression follows directly from letting $U(t, t_0) = \exp(-iHt/\hbar)$ operate directly on $|p\rangle$.

2.1.1 Momentum-Representation Solution

In the momentum representation, the solution to the free-particle problem is quite simple, as we have essentially already written it down. Starting off with the evolving state

$$|\psi(t)\rangle = U(t, 0)|\psi(0)\rangle, \tag{2.4}$$

we can project into the momentum representation and introduce a momentum-basis identity to write

$$\langle p|\psi(t)\rangle = \int dp' \, \langle p|U(t, 0)|p'\rangle\langle p'|\psi(0)\rangle. \tag{2.5}$$

The momentum-representation propagator (2.3) appears here, so we can use it to write

$$\langle p|\psi(t)\rangle = \langle p|\psi(0)\rangle\, e^{-ip^2t/2m\hbar}, \tag{2.6}$$

where the delta function from the propagator has done away with the p' integral. Thus, the propagation in the momentum representation amounts to phase evolution, of course with different momenta precessing at different rates.

2.1.2 Position-Representation Solution

In the position representation, the solution to the free-particle problem is only a bit more complicated. Starting off in the same way as in the momentum representation, we have the evolved state

$$\langle x|\psi(t)\rangle = \int dx'\, \langle x|U(t,0)|x'\rangle\langle x'|\psi(0)\rangle. \tag{2.7}$$

This involves the position-representation form of the propagator, which we don't know. However, it's easy enough to transform to a propagator that we *do* know, by introducing momentum identities:

$$\langle x|\psi(t)\rangle = \int dx' \int dp \int dp'\, \langle x|p\rangle\langle p|U(t,0)|p'\rangle\langle p'|x'\rangle\langle x'|\psi(0)\rangle. \tag{2.8}$$

Using the momentum eigenstate in the position representation (1.157), the conjugate (1.159), and the momentum propagator (2.3), this becomes

$$\langle x|\psi(t)\rangle = \int dx'\, \frac{1}{2\pi\hbar} \int dp\, e^{-ip^2t/2m\hbar}\, e^{ip(x-x')/\hbar} \langle x'|\psi(0)\rangle \tag{2.9}$$

after using the delta function to remove the p' integration. Comparing to the propagator relation (1.208), we can identify

$$K(x,t;x_0,t_0) = \frac{1}{2\pi\hbar} \int dp\, e^{-ip^2(t-t_0)/2m\hbar}\, e^{ip(x-x_0)/\hbar}, \tag{2.10}$$

after changing $x' \longrightarrow x_0$ and shifting $t \longrightarrow t - t_0$ to restore the initial time. This integral is divergent, but Gaussian, and therefore it is possible to carry it out, with the result (Problem 2.2)

$$K(x,t;x_0,t_0) = \sqrt{\frac{m}{i2\pi\hbar(t-t_0)}}\, \exp\left[\frac{im(x-x_0)^2}{2\hbar(t-t_0)}\right]. \tag{2.11}$$
(free-particle propagator)

Note that the propagator depends on the position coordinates only through the combination $(x - x_0)$, a consequence of the translation symmetry of the Hamiltonian. In this sense, when considering the evolution via this propagator in the propagation integral (1.208),

$$\psi(x,t) = \int dx_0\, K(x,t;x_0,t_0)\, \psi(x_0,t_0) = \int dx_0\, K(x-x_0,t-t_0)\, \psi(x_0,t_0), \tag{2.12}$$

this integration is just a convolution integral, with convolution kernel (2.11). If we represent the Fourier integral (1.163) in terms of a Fourier-transform operator $\mathscr{F}$ as

$$\phi(p,t) = \mathscr{F}\big[\psi(x,t)\big], \tag{2.13}$$

then the free-particle solution (2.6) is

$$\phi(p,t) = \mathscr{F}\big[\psi(x,t)\big] = \sqrt{2\pi\hbar}\, \mathscr{F}\big[K(x,t)\big]\mathscr{F}\big[\psi(x,0)\big] \tag{2.14}$$

where $K(x,t) = K(x,t;0,0)$. This is a form of the **convolution theorem**, which says that a convolution integral, if transformed to the Fourier-transform space, is just a simple multiplication of the Fourier transforms.

2.2 Continuity of the Energy-Basis Eigenfunctions

Before moving on to particles in potentials that *don't* vanish, let's consider some general results about energy eigenfunctions. For an energy eigenstate, we have

$$E|\psi_E\rangle = H|\psi_E\rangle. \tag{2.15}$$

For a one-dimensional particle in a potential, the Hamiltonian has the form $H = p^2/2m + V(x)$. Putting this in the position representation, we have the time-independent Schrödinger equation

$$E\psi_E(x) = \left(-\frac{\hbar^2}{2m}\partial_x^2 + V(x)\right)\psi_E(x). \tag{2.16}$$

Let's pick an arbitrary position and call it $x = 0$. Then we can integrate the above equation from $-\epsilon$ to ϵ, where $\epsilon > 0$ is a small number:

$$E\int_{-\epsilon}^{\epsilon} dx\,\psi_E(x) = -\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon} dx\,\psi_E''(x) + \int_{-\epsilon}^{\epsilon} dx\,V(x)\psi_E(x). \tag{2.17}$$

We can solve the integral of the second derivative, and then rearrange the equation to solve for this result:

$$\psi_E'(\epsilon) - \psi_E'(-\epsilon) = \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon} dx\,\big[V(x) - E\big]\psi_E(x). \tag{2.18}$$

Now to make some assumptions:

1. E is finite
2. $V(x)$ is bounded
3. $\psi_E(x)$ is bounded (which is a reasonable assumption because of the normalization requirement—we are basically assuming the energy eigenfunction won't be something like a delta function)

Under these conditions, the integrand on the right-hand side of Eq. (2.18) is bounded, which means there is a $B > 0$ such that

$$|V(x) - E| < B \qquad \forall x \in (-\epsilon, \epsilon). \tag{2.19}$$

Then the magnitude of the right-hand side of Eq. (2.18) is bounded by $4mB\epsilon/\hbar^2$. Taking the limit $\epsilon \longrightarrow 0^+$ in Eq. (2.18), the right-hand side vanishes, and we are left with

$$\psi_E'(0^+) = \psi_E'(0^-), \tag{2.20}$$

which means $\psi_E'(x)$ is continuous wherever the above assumptions hold. In particular, $\psi_E'(x)$ is continuous *even* if $V(x)$ is discontinuous, provided $V(x)$ is bounded (i.e., V has only finite, isolated discontinuities).

A similar argument applies to $\psi_E(x)$ itself. Writing out the integral of the derivative,

$$\psi_E(0^+) - \psi_E(0^-) = \lim_{\epsilon\to 0^+}\int_{-\epsilon}^{\epsilon} dx\,\psi_E'(x). \tag{2.21}$$

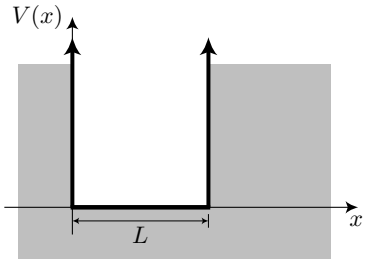
The right-hand side vanishes provided $\psi_E'(x)$ is bounded. This is a fairly reasonable assumption, as boundedness of $\psi_E'(x)$ is typically also leads to boundedness of $\psi_E''(x)$. The latter is required for the Schrödinger equation (2.16) to make any sense.

2.3 Particle in an Infinite Square Well

The simplest example of a particle in a nonvanishing potential is the infinite square well, where

$$V(x) = \begin{cases} 0, & x \in (0, L) \\ \infty, & x \notin (0, L), \end{cases} \tag{2.22}$$

as illustrated below.



This potential of course does *not* satisfy the assumptions listed in Section 2.2, so we do not expect a continuous derivative of the eigenstates at the boundaries. Continuity of the function itself is a reasonable requirement, however. Also in order for the Schrödinger equation to make sense (i.e., have no divergent terms), the eigenfunctions $\psi_E(x)$ must vanish outside $(0, L)$—hence the particle is completely excluded from the exterior region (thus this problem sometimes goes by the name of a particle in a ''box with rigid walls''). Another common way of expressing these boundary conditions is to say that $\psi_E(x)$ satisfies **Dirichlet boundary conditions** at $x = 0$ and $x = L$, which simply means $\psi_E(0) = \psi_E(L) = 0$.

The solution of the energy eigenfunctions is simple for this problem, but this is a good prototype problem to work through as a warm up to more difficult potentials. We still have the Schrödinger equation for the free particle,

$$\psi_E'' = -\frac{2mE}{\hbar^2}\psi_E, \tag{2.23}$$

or better yet,

$$\psi_E'' = -k^2\psi_E, \tag{2.24}$$

where

$$k := \sqrt{\frac{2mE}{\hbar^2}} \tag{2.25}$$

has the dimension of inverse length, and end up having an interpretation as the **wave number** of the solutions.

The Schrödinger equation (2.24) is a second-order ODE, and is solved in terms of exponentials involving the square root of the coefficient:

$$\psi_E(x) = \alpha_E e^{ikx} + \beta_E e^{-ikx}. \tag{2.26}$$

Actually a more convenient solution arises if we take odd and even linear combinations of the two independent solutions, writing

$$\psi_E(x) = a_E \sin kx + b_E \cos kx, \tag{2.27}$$

where a_E and b_E remain to be determined. This is a better choice because we're going to be forcing the solution to have particular zeros, and that's easier with functions that already have zeros.

The boundary condition (continuity plus exclusion conditions) $\psi_E(0) = 0$ then implies $b_E = 0$. For the other boundary, $\psi_E(L) = 0$ gives

$$\sin kL = 0, \tag{2.28}$$

which implies that the argument of the sine function is an integer multiple of π. Thus,

$$k_n L = \sqrt{\frac{2mE_n}{\hbar^2}}\, L = n\pi, \qquad n \in \mathbb{Z}^+, \tag{2.29}$$

where we restrict the choice to positive integers to exclude trivial and redundant solutions. Solving for the energies,

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \qquad n \in \mathbb{Z}^+. \tag{2.30}$$

(eigenenergies, infinite square well)

Now we see, as noted before, that k_n represents the wave number of the solutions, since the wavelengths are

$$\lambda_n = \frac{2\pi}{k_n} = \frac{2L}{n}. \tag{2.31}$$

The remaining quantity to be determined, the coefficient a_n, is fixed by normalization; that is,

$$\int_0^L dx\,|\psi_n(x)|^2 = |a_n|^2 \int_0^L dx\,\sin^2\frac{n\pi x}{L} = |a_n|^2\frac{L}{2} = 1 \tag{2.32}$$

gives

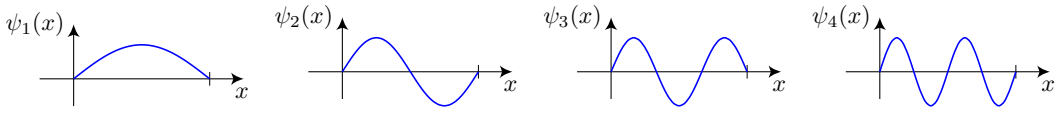
$$a_n = \sqrt{\frac{2}{L}}, \tag{2.33}$$

discarding a possible global phase. Thus, we are left with the eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\frac{n\pi x}{L} \tag{2.34}$$

(eigenfunctions, infinite square well)

as a discrete but complete basis for an arbitrary solution to this problem. The first few eigenfunctions are sketched below to illustrate the pattern.



These are the same modes as, for example, the transverse vibrational modes of a string under tension, clamped at both ends. Also, note that the nth eigenfunction has exactly $n-1$ zeros, a pattern that holds generally for bound states of one-dimensional potentials.[1]

2.4 Parity and Symmetric Potentials

An important feature of the infinite-square-well eigenfunctions (2.34) is that they are all either symmetric or antisymmetric about the midpoint $x = L/2$. This is a general feature of symmetric potentials, as we will now discuss.

2.4.1 Properties of the Parity Operator

The **parity operator** Π is defined by its action on position eigenstates,

$$\Pi|x\rangle = |-x\rangle, \tag{2.35}$$

(parity operator definition)

so that the parity operator produces a reflection of space via $x \longrightarrow -x$. (More generally, in multiple dimensions, the parity operator maps $\mathbf{r} \longrightarrow -\mathbf{r}$). As a consequence, this operator also produces the mirror of the wave function, in the sense that if $\langle x|\psi\rangle = \psi(x)$, then

$$\langle x|\Pi|\psi\rangle = \psi(-x). \tag{2.36}$$

Try working through this before proceeding; the solution follows.

First, let's expand an arbitrary state in the position representation:

$$|\psi\rangle = \int dx\,|x\rangle\langle x|\psi\rangle = \int dx\,\psi(x)|x\rangle. \tag{2.37}$$

Then applying the parity operator,

$$\Pi|\psi\rangle = \int dx\,\psi(x)\,|-x\rangle = \int dx\,\psi(-x)\,|x\rangle, \tag{2.38}$$

[1] See M. Moriconi, "Nodes of wavefunctions," *American Journal of Physics* **7**5, 284 (2007) (doi: 10.1119/1.2404960) (arXiv: quant-ph/0702260). The approach to proving this is to continuously change a potential from an infinite square well to some particular arbitrary potential. A related theorem proved in this paper is that for an interval bounded between zeros of an eigenfunction of a one-dimensional potential, a higher energy eigenfunction will have a zero in this interval.

where we have changed integration variables by $x \longrightarrow -x$. Then projecting into the position representation,

$$\langle x|\Pi|\psi\rangle = \int dx'\, \psi(-x')\, \langle x|x'\rangle = \psi(-x), \tag{2.39}$$

where we used $\langle x|x'\rangle = \delta(x - x')$ and then carried out the x' integration.

However, note that the expression (2.39) is a little odd because we are considering the action of an operator on a vector $|\psi\rangle$, and giving the result in a particular representation, $\psi(-x)$. By inserting an identity, we can then write

$$\langle x|\Pi|\psi\rangle = \int dx'\, \langle x|\Pi|x'\rangle\langle x'|\psi\rangle = \psi(-x), \tag{2.40}$$

which gives the action of the parity operator *in the position representation*, $\Pi(x, x') \equiv \langle x|\Pi|x'\rangle$, on a vector $\psi(x') \equiv \langle x'|\psi\rangle$ expressed in the same representation. In fact, the expression

$$\Pi(x, x') = \delta(x + x') \tag{2.41}$$

defines the parity operator in the position representation (Problem 2.14). You will commonly see people write colloquial expressions like $\Pi\psi(x) = \psi(-x)$, but strictly speaking this is nonsense because of the inconsistency in representation; the corresponding, correctly written statements are Eqs. (2.35) and (2.46).

This whole exercise leading to expression (2.39) can be carried out easily by recognizing that the parity operator is Hermitian, and thus can act on the left:

$$\langle x|\Pi|\psi\rangle = \langle -x|\psi\rangle = \psi(-x). \tag{2.42}$$

This causes the projection to yield the $-x$ component of ψ. However, we should show that the parity operator is indeed Hermitian. Consider an inner product involving two arbitrary states:

$$\begin{aligned}
\langle f|\Pi|g\rangle &= \int dx \int dx'\, \langle f|x\rangle\langle x|\Pi|x'\rangle\langle x'|g\rangle \\
&= \int dx \int dx'\, f^*(x)\, \Pi(x, x')\, g(x') \\
&= \int dx \int dx'\, f^*(x)\, \delta(x + x')\, g(x') \\
&= \int dx\, f^*(x)\, g(-x).
\end{aligned} \tag{2.43}$$

This last equation demonstrates the action of the parity operator "to the right" on $|g\rangle$. Changing the integration variable via $x \longrightarrow -x$ gives instead

$$\langle f|\Pi|g\rangle = \int dx\, f^*(-x)\, g(x), \tag{2.44}$$

which is what should happen when Π acts "to the left" on $\langle f|$. Since it doesn't matter which way Π acts, Π is Hermitian.

From the defining relation (2.35), we can see that

$$\Pi^2|x\rangle = \Pi|-x\rangle = |x\rangle. \tag{2.45}$$

Since this result holds for an arbitrary element of a complete basis, in general

$$\Pi^2|\psi\rangle = |\psi\rangle. \tag{2.46}$$

That is, Π^2 is the identity operator, and thus Π is its own inverse. Such an operator is called an **involution**. Combining this result with the Hermitian property, the parity operator is therefore also a *unitary* operator ($\Pi^\dagger\Pi = \Pi^2 = 1$).

Part of the point of this analysis is to consider the action of Π on $V(x)$. However, we have not yet defined how the parity operator transforms an *operator*, in particular the position operator x. The defining

transformation (2.35) is a unitary transformation of a state. The corresponding unitary transformation of an operator has the form [Eq. (1.128)]

$$\Pi^\dagger x \Pi = \Pi x \Pi = -x, \tag{2.47}$$

in order to be consistent with the state transformation (2.35). Multiplying on the right by Π gives

$$\Pi x = -x\Pi, \tag{2.48}$$

which leads to the important anticommutation relation

$$[\Pi, x]_+ = 0. \tag{2.49}$$
(parity anticommutator)

Furthermore, it is useful to consider the commutator of Π with x^2. By applying Eq. (2.48) twice, we can see that

$$\Pi x^2 = -x\Pi x = x^2 \Pi, \tag{2.50}$$

and thus

$$[\Pi, x^2] = 0. \tag{2.51}$$

Analogous results follow for the momentum operator: Considering the action on a momentum eigenstate,

$$\Pi|p\rangle = \int dx\, \Pi|x\rangle\langle x|p\rangle = \int dx\, |-x\rangle\langle x|p\rangle = \int dx\, |x\rangle\langle -x|p\rangle. \tag{2.52}$$

But $\langle -x|p\rangle = e^{-ipx/\hbar}/\sqrt{2\pi\hbar} = \langle x|-p\rangle$, and thus

$$\Pi|p\rangle = -|p\rangle. \tag{2.53}$$
(parity transformation of $|p\rangle$)

It also then follows that

$$[\Pi, p]_+ = 0, \tag{2.54}$$
(parity anticommutator with p)

and thus that

$$[\Pi, p^2] = 0. \tag{2.55}$$

The commutators involving x^2 and p^2 are particularly useful for our purposes.

2.4.2 Parity and the Hamiltonian

Now consider a particle in a symmetric potential, defined by

$$H = \frac{p^2}{2m} + V(x), \qquad V(-x) = V(x). \tag{2.56}$$

Note that $V(x)$ is a function of the position *operator* x, not a coordinate. Because it is an *even* function, its Taylor expansion involves only even powers of x; effectively, it is a function of x^2. Because of the commutator (2.51), Π commutes with any function of x^2, and thus

$$[\Pi, V(x)] = 0. \tag{2.57}$$

Furthermore, we have already shown in Eq. (2.55) that $[\Pi, p^2] = 0$. Since both $p^2/2m$ and $V(x)$ commute with Π, then

$$[\Pi, H] = 0. \tag{2.58}$$

The parity operator is also Hermitian, and thus Π and H have simultaneous eigenstates.

2.4.3 Energy Eigenstates of Definite Parity

So what are the eigenvalues of Π? Since Π is unitary, the eigenvalues must have unit modulus. More specifically, we have from Eq. (2.46) that

$$\Pi^2 = 1. \tag{2.59}$$

The eigenvalues of Π then are the square roots of unity: ± 1. In terms of the simultaneous energy eigenstates, we can write the effect of the eigenvalues as

$$\psi_E(-x) = \pm\psi_E(x). \tag{2.60}$$

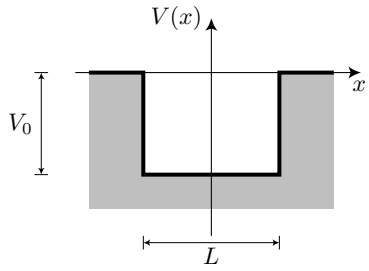
That is, we may take energy eigenfunctions $\psi_E(x)$ to be either even (parity eigenvalue $+1$) or odd (parity eigenvalue -1). These are states of **even parity** or **odd parity**, respectively. As we will see in a number of examples, the ground (lowest-energy) state tends to have even parity, and the subsequent energy eigenfunctions tend to alternate in parity as energy increases. (Can you think of a simple potential in which the previous sentence does *not* apply? How about an example of a simple, symmetric potential that has energy eigenstates that do *not* satisfy Eq. (2.60)? Is that a contradiction?)

2.5 Finite Square-Well Potential

Now let's consider the finite-depth version of the square-well potential, defined by

$$V(x) = \begin{cases} -V_0, & x \in (-L/2, L/2) \\ 0, & x \notin (-L/2, L/2), \end{cases} \tag{2.61}$$

and shown schematically below.



This potential is constructed to explicitly take advantage of the parity argument of the previous section, and is constructed to have zero asymptotic potential as $x \longrightarrow \pm\infty$.

For the moment, we will only consider bound states with $-V_0 < E < 0$, and return to the free states with $E > 0$ later. The time-independent Schrödinger equation (2.16) is

$$\psi_E''(x) = -\frac{2m}{\hbar^2}\big[E - V(x)\big]\psi_E(x) \tag{2.62}$$

in general, and in terms of the three regions,

$$\psi_E''(x) = \begin{cases} -\dfrac{2mE}{\hbar^2}\psi_E(x) & = \dfrac{2m|E|}{\hbar^2}\psi_E(x) \quad \text{(regions I, III)} \\ -\dfrac{2m}{\hbar^2}(E+V_0)\psi_E(x) & = -\dfrac{2m}{\hbar^2}\big(V_0 - |E|\big)\psi_E(x) \quad \text{(region II)}, \end{cases} \tag{2.63}$$

where in the last expressions we are being careful with the sign of $E < 0$. Defining region-specific wave numbers by

$$k_{\text{I}}^2 := \frac{2m|E|}{\hbar^2} = k_{\text{III}}^2, \qquad k_{\text{II}}^2 := \frac{2m(V_0 - |E|)}{\hbar^2}, \tag{2.64}$$

Eq. (2.63) is simply

$$\psi_E''(x) = \begin{cases} k_{\text{I}}^2 \psi_E(x) & \text{(regions I, III)} \\ -k_{\text{II}}^2 \psi_E(x) & \text{(region II).} \end{cases} \tag{2.65}$$

This equation has the solution

$$\psi_E(x) = \begin{cases} a_{\text{I}} e^{k_{\text{I}} x} & \text{(region I)} \\ a_{\text{II}} \cos k_{\text{II}} x + b_{\text{II}} \sin k_{\text{II}} x & \text{(region II)} \\ a_{\text{III}} e^{-k_{\text{I}} x} & \text{(region III),} \end{cases} \tag{2.66}$$

where we have already discarded the $e^{-k_{\text{I}}x}$ solution in region I and the $e^{k_{\text{I}}x}$ solution in region III to ensure normalizability of the wave function. Note that the exponentially decaying solutions in regions I and III, called **evanescent waves**, correspond to a nonzero probability for the particle to occupy the classically forbidden regions where $E < V(x)$. Note also that there are four unknowns here (the four undetermined coefficients in the solution), while there are four continuity conditions (continuity of $\psi_E(x)$ and $\psi_E'(x)$ at $\pm L/2$), as well as the normalization condition. This is thus an *overdetermined* system of equations, and we thus expect that there will be constraints on the allowable energies.

2.5.1 Definite-Parity Solutions

Because the potential here is symmetric, we can take all of the eigenfunctions to be symmetric or antisymmetric. Furthermore, we can seek these solutions separately, as we'll now do.

Even parity. In this case, $a_{\text{III}} = a_{\text{I}}$, and $b_{\text{II}} = 0$. Continuity of $\psi_E(x)$ at $x = \pm L/2$ gives the condition

$$a_{\text{I}} e^{\mp k_{\text{I}} x}\big|_{x=\pm L/2} = a_{\text{II}} \cos(k_{\text{II}} x)\big|_{x=\pm L/2}\,, \tag{2.67}$$

or

$$a_{\text{I}} e^{-k_{\text{I}} L/2} = a_{\text{II}} \cos(k_{\text{II}} L/2). \tag{2.68}$$

Similarly, continuity of $\psi_E'(x)$ at $x = \pm L/2$ gives the condition

$$\mp k_{\text{I}} a_{\text{I}} e^{\mp k_{\text{I}} x}\big|_{x=\pm L/2} = -k_{\text{II}}\ a_{\text{II}} \sin(k_{\text{II}} x)\big|_{x=\pm L/2}\,, \tag{2.69}$$

or

$$\mp k_{\text{I}} a_{\text{I}} e^{-k_{\text{I}} L/2} = \mp k_{\text{II}} a_{\text{II}} \sin(k_{\text{II}} L/2). \tag{2.70}$$

Dividing Eq. (2.68) by Eq. (2.70) gives

$$\cot(k_{\text{II}} L/2) = \frac{k_{\text{II}}}{k_{\text{I}}}. \tag{2.71}$$

This is a transcendental equation for k_{II}, given k_{I}, which will in turn yield the allowed energies. However, it must be solved numerically.

Odd parity. In this case, $a_{\text{III}} = -a_{\text{I}}$, and $a_{\text{II}} = 0$. Continuity of $\psi_E(x)$ at $x = \pm L/2$ gives the condition

$$\mp\ a_{\text{I}} e^{\mp k_{\text{I}} x}\big|_{x=\pm L/2} = b_{\text{II}} \sin(k_{\text{II}} x)\big|_{x=\pm L/2}\,, \tag{2.72}$$

or

$$\mp a_{\text{I}} e^{-k_{\text{I}} L/2} = \pm b_{\text{II}} \sin(k_{\text{II}} L/2). \tag{2.73}$$

Similarly, continuity of $\psi_E'(x)$ at $x = \pm L/2$ gives the condition

$$k_{\text{I}} a_{\text{I}} e^{\mp k_{\text{I}} x}\big|_{x=\pm L/2} = k_{\text{II}}\ b_{\text{II}} \cos(k_{\text{II}} x)\big|_{x=\pm L/2}\,, \tag{2.74}$$

or

$$k_{\text{I}} a_{\text{I}} e^{-k_{\text{I}} L/2} = k_{\text{II}} b_{\text{II}} \cos(k_{\text{II}} L/2). \tag{2.75}$$

Dividing Eq. (2.73) by Eq. (2.75) gives

$$\tan(k_{\text{II}} L/2) = -\frac{k_{\text{II}}}{k_{\text{I}}}. \tag{2.76}$$

This is a similar transcendental equation for k_{II} and thus the allowed energies.

2.5.2 Solutions of the Transcendental Equations

To summarize what we have so far, we can rewrite the conditions (2.71) and (2.76),

$$\cot\frac{kL}{2} = \frac{kL/2}{\sqrt{mL^2V_0/2\hbar^2 - (kL/2)^2}} \qquad \text{(even parity)}$$
$$\tan\frac{kL}{2} = -\frac{kL/2}{\sqrt{mL^2V_0/2\hbar^2 - (kL/2)^2}} \qquad \text{(odd parity),}$$

(allowed-energy conditions) (2.77)

where we have used

$$k \equiv k_{\text{II}} = \sqrt{\frac{2m(V_0 - |E|)}{\hbar^2}}, \qquad k_{\text{I}} = \sqrt{\frac{2m|E|}{\hbar^2}} = \sqrt{\frac{2mV_0}{\hbar^2} - k^2}. \tag{2.78}$$

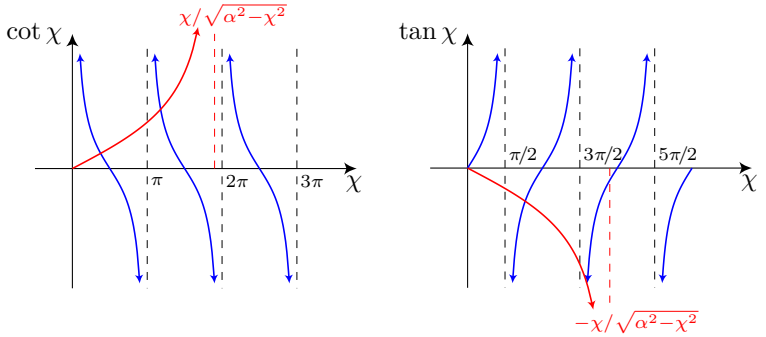
Schematically, the conditions (2.77) have the form

$$\cot\chi = \frac{\chi}{\sqrt{\alpha^2 - \chi^2}}, \qquad \tan\chi = -\frac{\chi}{\sqrt{\alpha^2 - \chi^2}}, \tag{2.79}$$

where $\chi = kL/2$ and $\alpha^2 = mL^2V_0/2\hbar^2$.

Now hang on for just a second, because what we just did is a **big deal** (cue record-player-scratch sound effect[2]). We started off solving a problem with four parameters (V_0, L, m, $\hbar$), but in moving to Eqs. (2.79), we have reduced the problem to *one* parameter, which is a vast improvement. This is something that a pro problem-solver will *always* do: look for the simplest possible expression of the problem. The exact way to do this is a bit of an art, but in general you can always try maneuvers that glom parameters together, and especially, try to form *dimensionless* combinations of variables. Here, the dimensionless parameter is α, which will determine the dimensionless wave number x; as a bonus, the condition we will derive will involve all the parameters at once, in this dimensionless form. (It's also very handy when making plots, as dimensionless parameters can potentially cover many different parameters in a single, two-dimensional plot.)

The solutions of Eqs. (2.79) are illustrated below.



First, note that $\cot\chi$ diverges at multiples of π; noting that $\chi/\sqrt{\alpha^2 - \chi^2}$ is also superimposed on the graph (for the example value $\alpha = 1.9\pi$), it is the intersection of the curves that determines the allowed solutions (of which there are two here). The solution of the second condition proceeds in the same way, with $\tan\chi$ diverging at odd multiples of $\pi/2$. The intersections with the inverted curve $-\chi/\sqrt{\alpha^2 - \chi^2}$ determine the energies of the odd eigenfunctions (of which there are again two here).

Considering the $\cot\chi$ condition again for the even-eigenfunction energies, note that there can be at most one solution in each interval of width π, and there can be no solutions beyond $\chi = \alpha$. From this graph we can then see that the condition has N allowed solutions provided

$$(N-1)\pi < \alpha \leq N\pi. \tag{2.80}$$

[2]Like this: `https://www.youtube.com/watch?v=Z_rBo-M9MgY`.

Similarly, for the $\tan\chi$ condition for the odd-eigenfunction energies, there are N allowed solutions provided

$$(N - 1/2)\pi < \alpha \leq (N + 1/2)\pi. \tag{2.81}$$

Aggregating these conditions together, there are N *total* solutions (corresponding to even *or* odd eigenfunctions) provided

$$(N-1)\frac{\pi}{2} < \alpha \leq \frac{N\pi}{2}. \tag{2.82}$$

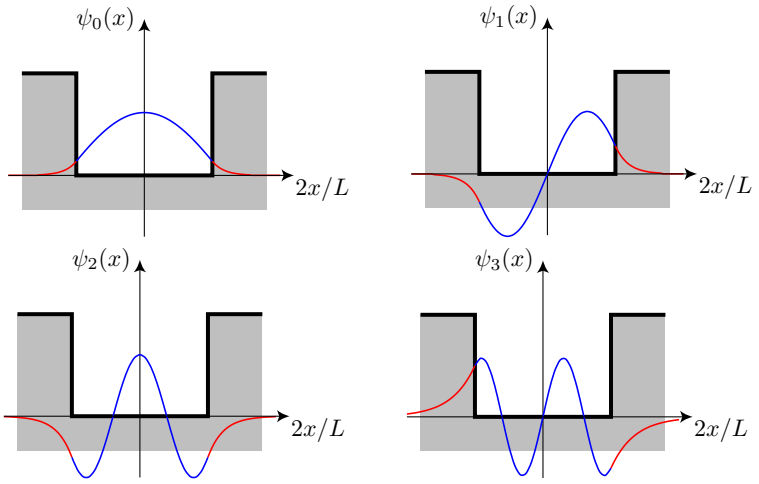
Recalling that $\alpha^2 = mL^2V_0/2\hbar^2$, we can rewrite this last condition as

$$\frac{(N-1)^2\pi^2\hbar^2}{2mL^2} < V_0 \leq \frac{N^2\pi^2\hbar^2}{2mL^2}, \tag{2.83}$$

(condition for N bound states)

as the condition on V_0 (or L) for having exactly N total bound states of either parity. Note that the bounds on V_0 here have the same form as the infinite-square-well energies (2.30). From the above graphical construction, we can also see that the lowest-energy bound state is even, and subsequent bound states alternate between odd and even parity as the eigenenergy increases.

Given the eigenenergy and the normalization condition, all of the coefficients in Eq. (2.66) are now determined, at least in principle. As examples, the lowest four eigenfunctions are plotted below, corresponding to the case $\alpha = 1.9\pi$.



Notice how the wave function increasingly occupies the forbidden regions as the energy increases. This is especially the case for the fourth eigenstate, which is close to the binding limit. It wants to be free!

2.5.2.1 Infinite-Well Limit

At this point it's useful to touch base with the infinite square well, which is the limit $V_0 \longrightarrow \infty$ here. Equation (2.83), says for example that we should expect arbitrarily many bound states, which is comforting. The eigenstate conditions (2.77) reduce to the simple equations

$$\begin{aligned} \cot\frac{kL}{2} &= 0 \qquad \text{(even parity)} \\ \tan\frac{kL}{2} &= 0 \qquad \text{(odd parity)} \end{aligned} \tag{2.84}$$

in this limit, which amounts to saying that

$$\begin{aligned} \frac{kL}{2} &= (n - 1/2)\pi \qquad \text{(even parity)} \\ \frac{kL}{2} &= n\pi \qquad \text{(odd parity).} \end{aligned} \tag{2.85}$$

In all, $kL/2$ should be a half-integer multiple of π. Comparing this condition to Eq. (2.29), which effectively said that kL should be an integer multiple of π, we can see that the conditions are compatible. Note that there isn't a problem with the bottom of the well dropping to arbitrarily low energies, because the wave vector (2.78) was defined in terms of the energy *difference* with respect to V_0.

2.5.3 Delta-Function Limit

As another useful limiting case of the finite square well, consider the delta-function potential well

$$V(x) = -\beta\,\delta(x), \tag{2.86}$$

where β is a "strength" constant with dimensions of (energy) × (length). We can adapt the above solution to the finite square well by setting

$$\beta = V_0 L, \tag{2.87}$$

and then letting $L \longrightarrow 0$. In the eigenenergy conditions (2.79), we have the constant

$$\alpha^2 = \frac{mL^2V_0}{2\hbar^2} = \frac{mL\beta}{2\hbar^2}, \tag{2.88}$$

which becomes arbitrarily small as $L \longrightarrow 0$ (at fixed β). According to the above discussion, there is thus only one bound state in the delta-function limit. The solution occurs for very small x, such that if we rewrite the first condition in Eqs. (2.79) as

$$\tan\chi = \frac{\sqrt{\alpha^2 - \chi^2}}{\chi}, \tag{2.89}$$

we may then use the approximation $\tan(\chi) \approx \chi$, solving the result for χ in terms of α (for both χ and α small). Mapping this back into the original problem, the result is that the bound-state energy is

$$E = -\frac{m\beta^2}{2\hbar^2}, \tag{2.90}$$

(bound-state energy, δ-function potential)

and the normalized wave function is

$$\psi(x) = \sqrt{\frac{m\beta}{\hbar^2}}\, e^{-m\beta|x|/\hbar^2}. \tag{2.91}$$

(bound-state wave function, δ-function potential)

We'll leave the derivation of these two results as an exercise (Problem 2.21).

2.5.3.1 Direct Solution

It is also possible to obtain the results (2.90) and (2.91) directly, without going through the finite square well. In the case of the delta-function potential (2.86), the time-independent Schrödinger equation (2.62) becomes

$$\psi_E''(x) = -\frac{2m}{\hbar^2}\big[E + \beta\delta(x)\big]\psi_E(x). \tag{2.92}$$

The continuity argument of Section 2.2 doesn't apply here because the potential is not bounded. To generalize the continuity condition, we can integrate from 0^- to 0^+ in x to find

$$\psi_E'(0^+) - \psi_E'(0^-) = -\frac{2m}{\hbar^2}\beta\psi_E(0). \tag{2.93}$$

Note that only the delta-function term gave a contribution on the right-hand side. This condition says that the function has a "kink," because the first derivative decreases discontinuously by $-(2m/\hbar^2)\beta\psi_E(0)$ at $x = 0$. This condition, in addition to the solutions from regions I and III in Eqs. (2.66) are sufficient to reproduce the above solution to the delta-potential problem (Problem 2.21).

2.5.4 Energy Conservation

One odd and manifestly nonclassical feature of the square-well eigenfunctions (as shown on p. 129) is the nonzero population in the forbidden regions where $E < V(x)$. Let's put it this way. What if we perform a position measurement, and find the particle in the forbidden region? Clearly, a negative energy makes no sense, so it must be that $E > 0$ after the measurement, even though we started with $E < 0$. So what gives? Did we just violate energy conservation?

To sort out this issue, it's first a good idea to review what exactly energy conservation *means*. The idea is that, if we have a time-independent Hamiltonian ($\partial H/\partial t = 0$), then in the energy representation, the magnitudes of the coefficients for the various eigenstates (i.e., the probabilities for being in the various energy eigenstates) are time-independent. That is, at least, according to *Schrödinger-equation evolution*. Part of what we can infer from this is that the measurement process is *not* described by Schrödinger-equation evolution, at least not directly. So, to some extent, a little slip in energy during certain types of measurements is an acceptable side effect.

It is, however, possible to model the measurement process to some extent by including a second system, the **measurement apparatus** in with the quantum system, and then describe the whole schmear by the Schrödinger equation. In this case, it's much more reasonable to insist on energy conservation for the combined system and apparatus. Energy may flow between the system and the measuring apparatus, though.

The position measurement is itself a good illustration of the above comments. Consider a minimum-uncertainty Gaussian initial state, for which $\sigma_x \sigma_p = \hbar/2$. Any measurement of position effectively reduces σ_x. Correspondingly, σ_p must *increase* to maintain the uncertainty principle. This increase in σ_p is a "heating" of the wave function, or an increase in the kinetic energy of the system. In fact, a measurement-apparatus model of the position-measurement process should act like a stochastic force from the apparatus acting on the system, or equivalently it is like putting the quantum system in thermal contact with a "bath" (system with many degrees of freedom) at infinite temperature. This effect of the measurement apparatus, which disturbs the quantum system, is called **measurement back-action** or **quantum back-action**.

Let's do a back-of-the-envelope calculation to see if this works out in some consistent way for our particle in the forbidden region. Recall that the wave function in the forbidden region has the form $\psi \sim e^{-k_{\text{I}} x}$, where from Eq. (2.64),

$$k_{\text{I}} = \sqrt{\frac{2m|E|}{\hbar^2}}, \tag{2.94}$$

and here $|E|$ is the energy "deficit" associated with finding the particle in the forbidden region. Thus, for this issue to be of any concern, the position measurement must localize the particle to a width of order

$$\Delta x \sim \frac{1}{k_{\text{I}}} = \frac{\hbar}{\sqrt{2m|E|}}. \tag{2.95}$$

To maintain the uncertainty principle, the back-action heating must increase the momentum width of the state by an amount of order

$$\Delta p \sim \frac{\hbar}{\Delta x} = \sqrt{2m|E|}. \tag{2.96}$$

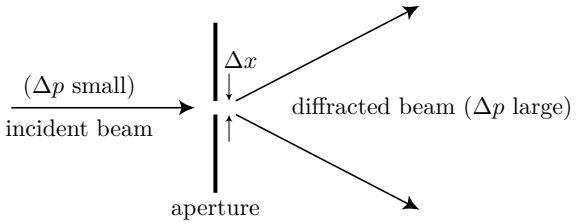
The associated increase in kinetic energy is thus of order

$$\frac{\Delta p^2}{2m} \sim |E|. \tag{2.97}$$

That is, the measurement back-action has involves just the kind of energy that is needed to kick the particle up to a positive energy, as required for it to exist in the (formerly) forbidden region.

2.5.4.1 Another Measurement Example

It's easy to dismiss the energy gained as some abstract "energy that came from the apparatus," but it's sometimes tricky to pinpoint what exactly this means. So before moving on, let's consider another concrete (and classic) example of a position measurement: the single-slit diffraction problem.



Consider a beam of quantum particles (electrons, neutrons, photons, etc.) incident on an aperture, and we'll focus on the position transverse to the beam. The aperture acts as a position measurement, because any particles making it through the slit of width Δx have been effectively measured to be within this position interval (assume that the initial beam width is large compared to Δx, and the transverse momentum Δp is close to zero). This implies that the transverse momentum $\Delta p \sim \hbar/\Delta x$ is much larger than before the aperture, leading to diffraction. But this also implies a large kinetic energy associated with the transverse momentum, $(\Delta p)^2/2m$. Where did this energy come from? (Not the aperture, which we can assume has no effect other than to absorb particles that hit it.)

2.5.5 Parity and Searching for Eigenfunctions

To recap the derivation of the square-well eigenfunctions, remember that we explicitly and separately treated the cases of even and odd parity, deriving separate eigenvalue equations for each, as in Eqs. (2.77). Now let's revisit this and ask the question, was this assumption of parity really necessary? What if we weren't very clever and didn't know that we should fix the parity? Or what if the potential lacked the symmetry necessary for the eigenstates to have definite parity? (That is, a slight perturbation to one side of the square-well potential shouldn't have much effect on the eigenstates, but it would completely upset the parity assumption.)

Recall the time-independent Schrödinger equation, which in one dimension is a simple ordinary differential equation (ODE) for the wave function:

$$\psi_E''(x) = -\frac{2m}{\hbar^2}\big[E - V(x)\big]\psi_E(x). \tag{2.98}$$

It will be a bit more convenient to think of this as a *pair* of coupled, first-order equations, rather than a single, second-order ODE:

$$\partial_x \begin{bmatrix} \psi_E' \\ \psi_E \end{bmatrix} = \begin{bmatrix} -(2m/\hbar^2)[E - V(x)]\psi_E \\ \psi_E' \end{bmatrix}. \tag{2.99}$$

Schematically, we can write this as

$$\partial_x \boldsymbol{\psi}(x) = \mathbf{F}(\boldsymbol{\psi}), \tag{2.100}$$

where $\boldsymbol{\psi} := (\psi_E', \psi_E)$. The point of this is, if $\psi_E(x)$ and $\psi_E'(x)$ are fixed at some point x, then the wave function at other positions is already determined. This is essentially the content of the ODE system (2.100), as we can see by writing it in differential form as

$$\boldsymbol{\psi}(x + dx) = \boldsymbol{\psi}(x) + \mathbf{F}[\boldsymbol{\psi}(x)]\, dx. \tag{2.101}$$

Of course, this means that we compute $\boldsymbol{\psi}$ at a *finite* distance Δx away from x, and continue to other positions by iterating the process; the solution according to this process becomes exact in the limit $\Delta x \longrightarrow 0$.

Now when we apply continuity boundary conditions like

$$\psi_E(x + 0^+) = \psi_E(x + 0^-), \qquad \psi_E'(x + 0^+) = \psi_E'(x + 0^-) \tag{2.102}$$

at the boundary between two regions, these say that once ψ_E and ψ_E' are fixed at some point within one region, the solution is *also* determined in the adjacent regions. However, the boundary conditions themselves do *not* uniquely fix the wave function—we still need to fix ψ_E and ψ_E' at some point (or, perhaps, not even at the same point, but *somewhere*).

In the case of a symmetric potential and the eigenstates have definite parity, then we can *guess* that either $\psi_E(0) = 0$ or $\psi'_E(0) = 0$. Of course, this is a *good* guess, but guessing is the principal method behind the analytic solution of ODE's. The magnitude of the nonzero variable isn't so critical, as it will be fixed at some point by the normalization condition.

But if we don't have this symmetry, then some *linear combination* of $\psi_E(0)$ and $\psi'_E(0)$ will vanish for any particular eigenstate. If there is some other physical principle that determines this, it would allow us to proceed based on the appropriate guess, or at least to set up some equation to determine it. But fundamentally, it will be a more difficult guess.

2.5.5.1 Shooting Method

The above considerations are the basis of a numerical method, called the **shooting method**, for finding the eigenvalues and eigenfunctions of one-dimensional potentials. Given a symmetric potential, the idea behind this method is to set $\psi_E(0) = 1$ and $\psi'_E(0) = 0$ to find an even-parity state, or $\psi_E(0) = 0$ and $\psi'_E(0) = 1$ to find an odd-parity state. Then guess some value of E, and numerically integrate the ODE (the time-independent Schrödinger equation, that is) to a large value of $+x$. Generally speaking, the solution for $\psi_E(x)$ will diverge to $\pm\infty$ if E is not an energy eigenvalue. The idea is to then tune E to find a value where ψ_E is small at large x (i.e., this is a root-finding problem, to find E such that ψ_E satisfies the proper boundary condition $\psi_E \longrightarrow 0$ as $x \longrightarrow \infty$). After a proper value of E is found, the eigenfunction can then be normalized.

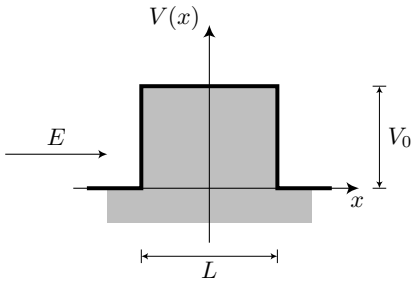
In the case of an asymmetric potential, though, the initial assumption breaks down. We could more generally set $\psi_E(0)\cos\theta + \psi'_E(0)\sin\theta = 0$, and tune *both* θ and E to make $\psi_E \longrightarrow 0$ at $x \longrightarrow \pm\infty$. Alternately, one could tune the position x to find locations where either ψ_E or its derivative vanishes. In any case, this is a root-finding problem in *two* variables, a more complicated problem than in the symmetric-potential case.

2.6 Square-Barrier Potential

A problem closely analogous to the finite square-well potential is the square-barrier potential, defined by

$$V(x) = \begin{cases} V_0, & x \in (-L/2, L/2) \\ 0, & x \notin (-L/2, L/2), \end{cases} \tag{2.103}$$

where $V_0 > 0$, as illustrated below.



In fact, in the case $V_0 < 0$, this problem is just the finite square well, a connection we'll exploit later on when we return to the unbound states of the well potential.

To solve this, we will set this up as a kind of scattering problem, with one incident wave from the left, and outgoing waves on either side. Mathematically, assuming the case $E < V_0$, we have

$$\psi_E(x) = \begin{cases} e^{ikx} + re^{-ikx} & \text{(region I)} \\ ae^{-\kappa x} + be^{\kappa x} & \text{(region II)} \\ \tau e^{ikx} & \text{(region III).} \end{cases} \tag{2.104}$$

In region I, we have the incoming (right-going) wave e^{ikx} and the reflected (left-going) wave, weighted by the **amplitude reflection coefficient** r. We aren't going to end up with a normalizable state anyway, so we're just setting the amplitude of the incoming wave to unity. The transmitted wave in region III is another right-going wave, weighted by the **amplitude transmission coefficient** τ. The intermediate region II has a superposition of damped waves, because $E < V_0$.

From the time-independent Schrödinger equation,

$$\psi_E''(x) = -\frac{2m}{\hbar^2}\big[E - V(x)\big]\psi_E(x) = \begin{cases} -\dfrac{2mE}{\hbar^2}\psi_E(x) & \text{(regions I, III)} \\ \dfrac{2m}{\hbar^2}(V_0 - E)\psi_E(x) & \text{(region II),} \end{cases} \tag{2.105}$$

we can identify the corresponding wave vectors

$$k = \frac{\sqrt{2mE}}{\hbar}, \qquad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{2.106}$$

Both of these parameters are real, provided $E < V_0$.

To take stock of the situation, note that we have four undetermined parameters (r, τ, a, b) and four constraint equations (continuity of ψ_E and ψ_E' at $x = \pm L/2$). The normalization condition is no longer relevant because we have already fixed it by choosing the amplitude of the incoming wave. Thus, unlike the $E < 0$ situation in the finite square well, the system here is properly constrained such that any incident energy E should correspond to a solution (before, we had 4 parameters and 5 constraints, leading to a discrete spectrum).

Note that we aren't missing anything by assuming an incoming wave only from the left. By symmetry, we can easily generate the set of corresponding solutions with waves incident from the right. The choice of a particular incident wave is essentially a choice of boundary conditions at $x = \pm\infty$, so that an extra undetermined parameter associated with another incoming wave would be balanced by an extra boundary condition "at infinity."

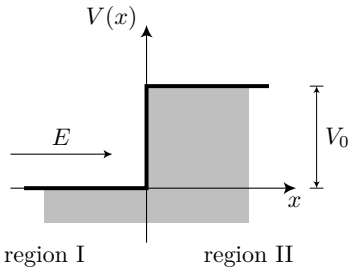
Imposing the boundary conditions, we can proceed to solve for all the parameters. However, before doing so, let's step back for a minute and solve a *simpler* problem—a problem whose solution will make for a tidier solution in this more complicated case.

2.6.1 Digression: Reflection at a Potential Step

The simpler problem to solve is a single potential step, defined by

$$V(x) = \begin{cases} V_0, & x > 0 \\ 0, & x < 0, \end{cases} \tag{2.107}$$

as illustrated below.



We can set up the solution in the same way, with an incident wave from the left,

$$\psi_E(x) = \begin{cases} e^{ikx} + re^{-ikx} & \text{(region I)} \\ \tau e^{-\kappa x} & \text{(region II),} \end{cases} \tag{2.108}$$

where k and κ are still given in Eqs. (2.106) for $E < V_0$.

The condition that ψ_E be continuous at $x = 0$ is

$$1 + r = \tau, \tag{2.109}$$

while the condition that ψ'_E be continuous at $x = 0$ is

$$ik - ikr = -\kappa\tau. \tag{2.110}$$

We can write the solution of these two equations as

$$r = -\frac{\kappa + ik}{\kappa - ik}, \qquad \tau = -\frac{2ik}{\kappa - ik},$$

(reflection and transmission coefficients, potential step, $E < V_0$) (2.111)

One thing to notice immediately is that $|r| = 1$ for this case (with the complex phase indicating some phase shift of the reflected wave). This makes physical sense: the incident particle doesn't have enough energy to be on the right-hand side, so it must reflect with unit probability. Note that the **evanescent wave** (decaying exponential) solution on the right-hand side means that there is some probability of finding the particle in the forbidden zone $x > 0$, but this probability is vanishingly small when compared to the probabilities associated with the unnormalizable incident and reflected plane waves.

2.6.1.1 Higher-Energy Solution

With the $E < V_0$ solutions for the potential step in hand, it's not hard to adapt them to the case of higher incident energies where $E > V_0$. In this case, the evanescent $e^{-\kappa x}$ should be replaced by the propagating solution $e^{i\kappa x}$. Thus, we can obtain the $E > V_0$ solutions by replacing $\kappa \longrightarrow -i|\kappa|$. Note that this is consistent with the definition of κ in Eqs. (2.106), where the $-i$ comes from the change of sign of $(V_0 - E)$ under the square root, so that κ is now

$$\kappa = -i\frac{\sqrt{2m|E - V_0|}}{\hbar}. \tag{2.112}$$

(Either sign is in principle possible by this second argument, but only the minus sign leads to the physically sensible right-propagating transmitted wave.) Making the replacement $\kappa \longrightarrow -i|\kappa|$ in the coefficients (2.111) gives

$$r = \frac{k - |\kappa|}{k + |\kappa|}, \qquad \tau = \frac{2k}{k + |\kappa|},$$

(reflection and transmission coefficients, potential step, $E > V_0$) (2.113)

so that now the coefficients are real, thus involving no phase shift (except for a possible π phase shift in the reflected wave.

Now let's do some checking to make sure everything makes sense. As $V_0 \longrightarrow 0$, then $|\kappa| \longrightarrow k$, and Eqs. (2.113) reduce to $r = 0$ and $\tau = 1$, as we expect for no step at all. So long as $V_0 > 0$ and $E > V_0$, then $k > |\kappa|$, and $r > 0$—the reflected wave suffers no inversion. This is in contrast to the ''hard wall'' case of Eqs. (2.111), where as $V_0 \longrightarrow \infty$ at fixed E, $r \longrightarrow -1$ and $\tau \longrightarrow 0$, and so the reflected wave is flipped.

On the other hand, if we consider a ''down-step'' ($V_0 < 0$), then $|\kappa| > k$ and again $r < 0$, with $r \longrightarrow -1$ as $V_0 \longrightarrow -\infty$. The change in sign as V_0 crosses through zero (with $E > V_0$) is a bit counterintuitive on its own. However, it's a bit more intuitive to look at the behavior of τ, which crosses through unity when V_0 crosses through zero. The case $\tau < 1$ corresponds to $r < 0$ (so that on the input side, the reflected wave cancels some of the incoming wave to match the transmitted wave at the boundary), and the case $\tau > 1$ corresponds to $r > 0$ (so that the reflected wave *adds* to the incoming wave to form a larger-than-incident transmitted wave). A transmission coefficient larger than unity may seem a bit counterintuitive as well, and we're just about to address this.

Given the amplitude reflection and transmission coefficients, it's tempting to define *probabilities* of reflection and transmission to be $|r|^2$ and $|\tau|^2$, respectively, particularly in the $E > V_0$ case where we are just comparing the amplitudes of plane waves. However, it's easy to see that

$$|r|^2 + |\tau|^2 \neq 1. \tag{2.114}$$

Of course, we already knew it couldn't work out, since we saw that it's possible for $\tau > 1$. And so we see that we need to be more careful about how we define probabilities of reflection and transmission.

2.6.1.2 Probability Current

In physics, we deal with lots of "stuff"—charge, mass, probability, etc. Suppose we represent a **density of stuff** as $\rho(\mathbf{r})$. This means that if we want to count the total amount of stuff in a volume V, we should just integrate the density over the volume:

$$\text{(stuff)} = \int_V d^3r\, \rho(\mathbf{r}). \tag{2.115}$$
(stuff)

Now let's denote the **current density of stuff** by $\mathbf{j}$, which represents how stuff gets around. More specifically, the rate at which stuff leaves V is

$$\text{(rate of losing stuff)} = \int_{\partial V} d\mathbf{S} \cdot \mathbf{j}(\mathbf{r}), \tag{2.116}$$

where "∂V" denotes the bounding surface of V. This says that the flux of stuff through an element dS of the surface is the normal component of the current density at that location. By the divergence theorem, we can change this surface integral into a volume integral as

$$\text{(rate of losing stuff)} = \int_V d^3r\, \nabla \cdot \mathbf{j}(\mathbf{r}). \tag{2.117}$$

Intepreting the words so far, we can write this all mathematically as

$$-\partial_t \int_V d^3r\, \rho(\mathbf{r}) = \int_V d^3r\, \nabla \cdot \mathbf{j}(\mathbf{r}). \tag{2.118}$$

Noting that the integration volume is arbitrary, we may equate integrands to arrive at the **continuity equation**

$$\partial_t \rho(\mathbf{r}) = -\nabla \cdot \mathbf{j}(\mathbf{r}). \tag{2.119}$$
(continuity equation for stuff)

This equation is quite general, and is useful in continuum mechanics (for the mass density) and in electromagnetism for the charge density.

In quantum mechanics the continuity equation is useful when applied to the *probability* density, so we set

$$\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2. \tag{2.120}$$

Differentiating and performing some manipulations,

$$\begin{aligned}
\partial_t \rho(\mathbf{r}) &= \partial_t |\psi(\mathbf{r})|^2 \\
&= \psi^* \partial_t \psi + \psi \partial_t \psi^* \\
&= \frac{1}{i\hbar}\Big(\psi^* H\psi - \psi H\psi^*\Big) \\
&= \frac{1}{2mi\hbar}\Big(\psi^* p^2\psi - \psi p^2\psi^*\Big) \\
&= -\frac{\hbar}{2mi}\Big(\psi^* \nabla^2\psi - \psi \nabla^2\psi^*\Big) \\
&= -\frac{\hbar}{2mi}\nabla \cdot \Big(\psi^* \nabla\psi - \psi \nabla\psi^*\Big),
\end{aligned} \tag{2.121}$$

where we assumed a Hamiltonian of the form $H = p^2/2m + V(\mathbf{r})$. Comparing to the continuity equation (2.119) allows us to identify a **probability current density**

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{2mi}\Big(\psi^*\nabla\psi - \psi\nabla\psi^*\Big). \qquad \text{(probability current density)} \tag{2.122}$$

The probability current density is a real quantity, which we can see by rearranging this expression to read

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{2mi}\psi^*\big(\nabla - \nabla^\dagger\big)\psi. \tag{2.123}$$

We can go further, and write the current density in the suggestive forms

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{m}\mathrm{Im}\big[\psi^*\nabla\psi\big] = \frac{1}{m}\mathrm{Re}\big[\psi^*\mathbf{p}\psi\big], \qquad \text{(probability current density)} \tag{2.124}$$

after using $\mathbf{p} = -i\hbar\nabla$. The latter form is fairly intuitive in terms of a ''velocity density,'' being the integrand of the expectation value $\langle\psi|\mathbf{p}/m|\psi\rangle$.[3] The current is driven by the phase variation in the wave function; for example, writing the wave function in the polar form $\psi(\mathbf{r}) = R\,e^{i\varphi}$ in terms of the real fields $R(\mathbf{r})$ and $\varphi(\mathbf{r})$, the probability density is (Problem 2.26)

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar|\psi|^2}{m}\nabla\varphi. \tag{2.125}$$

The probability current density is analogous to the Poynting vector in electromagnetism, which represents the flow of *energy*; the present quantity represents the flow of *probability density*.

2.6.1.3 Probability Current in the Step-Potential Problem

Applying the probability current to the step-potential wave function (2.108), we will compute separate probability current densities for each of the incoming, reflected, and transmitted waves, *still* in the case of a propagating transmitted wave ($E > V_0$), to pick up where we left off in Section 2.6.1.1. For the incident wave e^{ikx}, from Eq. (2.125) the probability current density is

$$\mathbf{j}_\mathrm{i} = \frac{\hbar k}{m}\hat{x}. \tag{2.126}$$

This makes a lot of sense, since thinking of this incoming wave as a momentum eigenstate $e^{ipx/\hbar}$, the momentum is $p = \hbar k$, and thus the velocity is $v = p/m = \hbar k/m$, which is precisely the probability current density. (In general the probability current density is the squared amplitude times the velocity, but the amplitude is unity here.) The calculations of the reflected and transmitted probability currents follow in the same way, with results

$$\mathbf{j}_\mathrm{r} = -|r|^2\frac{\hbar k}{m}\hat{x}, \qquad \mathbf{j}_\mathrm{t} = |\tau|^2\frac{\hbar\kappa}{m}\hat{x}. \tag{2.127}$$

Now given the coefficients (2.113), we can compute

$$|\mathbf{j}_\mathrm{r}| + |\mathbf{j}_\mathrm{t}| = \frac{\hbar k}{m}\left(|r|^2 + \frac{\kappa}{k}|\tau|^2\right) = \frac{\hbar k}{m}\left[\left(\frac{k-|\kappa|}{k+|\kappa|}\right)^2 + \frac{4k\kappa}{(k+|\kappa|)^2}\right] = \frac{\hbar k}{m} = |\mathbf{j}_\mathrm{i}|. \tag{2.128}$$

Thus, defining **probability reflection and transmission coefficients**

$$R := \frac{|\mathbf{j}_\mathrm{r}|}{|\mathbf{j}_\mathrm{i}|}, \qquad T := \frac{|\mathbf{j}_\mathrm{t}|}{|\mathbf{j}_\mathrm{i}|}, \qquad \text{(probability reflection, transmission coefficients)} \tag{2.129}$$

[3] There is a more precise interpretation here. Suppose that we try to construct something like a local velocity operator, which would be the product of the velocity operator $\mathbf{p}/m$ and a position projector $|\mathbf{r}\rangle\langle\mathbf{r}|$. Because these operators do not commute, a simple product of these operators is not Hermitian; however a symmetrized product is. Then $\mathbf{j}(\mathbf{r})$ can be understood as the expectation value of this symmetrized product.

where for the potential step, we have already calculated these to be reflection and transmission probabilities

$$R = \left(\frac{k - |\kappa|}{k + |\kappa|}\right)^2, \qquad T = \frac{4k\kappa}{(k + |\kappa|)^2}.$$

(reflection, transmission coefficients, potential step) (2.130)

We have also shown that the coefficients in this case satisfy

$$R + T = 1, \tag{2.131}$$

which is indeed a sensible check for reflection and transmission probabilities.

The reason that the previous attempt (2.114) to define reflection and transmission probabilities didn't work out is that the speed of the wave function is modified by the potential in region II. The probability flow must account for both the amplitude and velocity of the wave function; the probability current properly accounts for both of these aspects. On the other hand, for the square-barrier problem, the potential is asymptotically $V(x) = 0$ for large $\pm x$, so in that case there is no problem defining the reflection and transmission probabilities directly as $R = |r|^2$ and $T = |\tau|^2$.

Before moving on, let's point out one odd feature of our treatment above. It's perfectly sensible to treat the transmitted wave separately from the incoming and reflected waves, because it occurs in a completely different region of space. However, the incoming and reflected waves overlap, so it seems like we should be treating them together. In particular, the probability current (2.122) is a quadratic function of ψ, so it seems like there are cross-terms between the incident and reflected waves that we might be missing. So what gives, is the above analysis invalid?

There are a couple of ways of justifying the above treatment. One is to say that we aren't really dealing with plane waves, which aren't physical anyway. Rather, we are dealing with an incident wave packet, which is somewhat spatially localized (say, a Gaussian wave packet). If we start the wave packet at very large $-x$, then by the time its reflection returns, it won't overlap the incident wave packet. If there is a very small spread in incident k (i.e., in incident momenta), then the plane-wave treatment should be accurate (the incident and reflected waves will still be temporally separated, no matter how small the spread in k, provided we look far enough away from $x = 0$). This issue arises with reflections at a dielectric interface in optics, where the analogous justification is that the incoming and reflected waves must have some transverse localization, and thus they must be spatially separated if we look far enough away from the interface.[4] The other justification is that you *can* go ahead and compute a probability current for both waves together, in which case there should be a net current of $(1 - |r|^2)(\hbar k/m)$ to the right in the example above. There will also be oscillating, localized currents due to the aforementioned cross terms, but these will vanish under a time average, and thus do not represent a steady transport of probability. The analogy in optics is that reflection and transmission coefficients are defined in terms of intensity, which is the time average of the Poynting vector. The fast oscillations in the optical case are so fast that they can't even be detected on a conventional photodetector or eyeball, so it's best to discard them.

2.6.1.4 The Evanescent Wave in the Step-Potential Problem

In our original setup of the solution (2.108) for the step potential (where $V_0 > 0$ and $E < V_0$), the exponentially damped solution in region II, or the evanescent wave is worth some more consideration. It does not correspond to a propagating wave, as it lacks the oscillatory character of the momentum eigenstates in region I. In fact, we can just calculate the probability current,

$$\mathbf{j}_t = \frac{\hbar}{2mi}\Big((-\kappa) - (-\kappa)\Big)\hat{x} = 0, \tag{2.132}$$

to see that the evanescent wave transports no probability density. Nevertheless, it represents some nonzero probability density of finding the particle in the forbidden region. However, it seems that the overall probability must be infinitesimal compared to the unnormalizable, propagating component. So: What does it

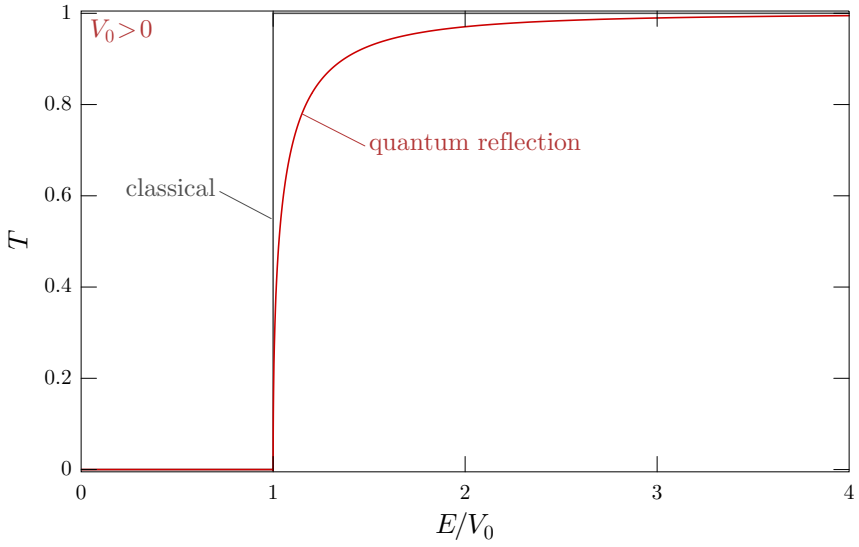
[4] Daniel Adam Steck, *Classical and Modern Optics*, available online at `http://steck.us/teaching` (2006).

really represent? Is there some substantial probability for finding the particle in the forbidden region? How did it get there? What does it want from us?

To answer this, we should step back and recall that plane-wave-like propagating solutions, as in region I, are nonphysical idealizations. A more realistic incoming wave would be a more-or-less-localized wave packet—a superposition of the solutions we have constructed, covering some (possibly narrow) range of E—coming in to collide with the potential step. This wave packet *transiently* enters the forbidden region, and occupies it only during the actual collision. When the wave packet moves away from the step, the evanescent wave will correspondingly be gone. This does not contradict the lack of a probability current in the eigenstate, because the eigenstate represents only *steady* behavior. But an entrance followed by an exit represents no net, steady current, and thus is not captured by an eigenstate (at least, not by any *single* eigenstate). During the collision with the step, the magnitude of the evanescent wave will be of order $\psi_{\max}\tau$, where $\psi_{\max}$ is the largest magnitude of the wave packet. This means that the probability of finding the particle in the forbidden region at any instant of time becomes vanishingly small as the width σ_x of the wave packet becomes large. However, the *duration* of the collision becomes correspondingly large, and so there is more "opportunity" to find the particle in the forbidden region. (Note, however, that it's tempting to say something like the *time-integrated* probability for finding the particle in the forbidden region is invariant, but continuously *watching* the forbidden region is a kind of measurement that drastically changes the nature of this problem.)

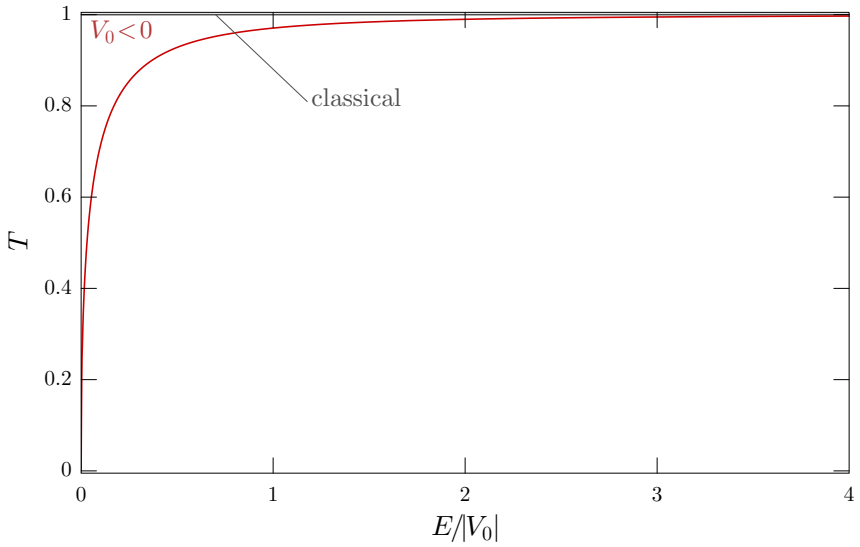
2.6.1.5 Quantum Reflection

Going back to the coefficients (2.111) in the case $V_0 > 0$ for the potential step, we can visualize these in the form of the transmission probability T as defined in Eqs. (2.129). The result is shown below.



Again, for $E < V_0$, the transmission probability is zero, because the wave can't propagate in the energetically forbidden region. For larger energies $E > V_0$, the transmission coefficient (2.130) no longer vanishes. Classically, the prediction is that the particle should go on through if it has sufficient energy (i.e., $T = 1$ if $E > V_0$), but quantum mechanics says there is still some probability for reflection. This phenomenon is called **quantum reflection**, and is a distinctly nonclassical manifestation of the wave nature of quantum particles.

Quantum reflection also occurs when $V_0 < 0$, for a *negative* potential step, as illustrated by the plot of the transmission probability below.



We can make some overall observations.

1. The largest quantum reflection occurs when the particle has *just* enough energy to transmit. For $V_0 < 0$, this is when $E \approx 0$; for $V_0 > 0$, this is when $E \approx V_0$. The reflection probability in either case approaches unity. This also occurs, by the way, if the incident energy is fixed, but the particle encounters an arbitrarily large, *negative* step ($V_0 \longrightarrow -\infty$).

2. The reflection probability drops to zero in the limit of large incident energy. In this limit, the particle has so much energy that it doesn't "notice" the potential step.

3. Generally speaking, quantum reflections occur at large, steep changes in the potential $V(x)$.

A nice example of quantum reflections observed experimentally comes from cold atoms slowly approaching a surface. In this case, the Casimir–Polder potential (an attractive potential between a neutral atom and a surface due to quantum fluctuations) is a purely attractive potential, and one might expect the atoms to simply fall into this potential and become stuck. Many atoms do this, in fact, but with sufficiently slow atoms, reflections from this attractive potential (of the form $V(z) \sim \alpha z^{-3}$ at small z) have been observed.[5] Further, if the surface is modified to reduce the effective density of the material, this weakens the force (in the sense of reducing the constant α, but maintaining the z^{-3} dependence of the potential). The weaker potential allows the atoms to proceed farther into the potential, and reflect from a region with a sharper potential gradient. Thus, the experimental reflection probability from the "weaker" potential is in fact dramatically enhanced.[6]

2.6.2 Quantum Tunneling and Reflection: Square Barrier

Now, at last we can return to the square-barrier problem. Recall that the solution has the form of Eq. (2.104) for low incident energy, $E < V_0$. Matching the boundaries according to

$$\psi_E(\pm L/2 + 0^+) = \psi_E(\pm L/2 + 0^-), \qquad \psi'_E(\pm L/2 + 0^+) = \psi'_E(\pm L/2 + 0^-), \tag{2.133}$$

[5] Fujio Shimizu, "Specular Reflection of Very Slow Metastable Neon Atoms from a Solid Surface," *Physical Review Letters* **86**, 987 (2001) (doi: 10.1103/PhysRevLett.86.987).

[6] Fujio Shimizu and Jun ichi Fujita, "Giant Quantum Reflection of Neon Atoms from a Ridged Silicon Surface," *Journal of the Physical Society of Japan* **71**, 5 (2002) (doi: 10.1143/JPSJ.71.5). T. A. Pasquini, M. Saba, G.-B. Jo, Y. Shin, W. Ketterle, D. E. Pritchard, T. A. Savas, and N. Mulders, "Low Velocity Quantum Reflection of Bose-Einstein Condensates," *Physical Review Letters* **97**, 093201 (2006).

and solving the resulting four equations (Problem 2.27), the resulting amplitude transmission and reflection coefficients are

$$\tau = \frac{\tau_1 \tau_1' e^{-\kappa L} e^{-ikL}}{1 - r_1^2 e^{-2\kappa L}}$$
$$r = \frac{r_1 (1 - e^{-2\kappa L})\, e^{-ikL}}{1 - r_1^2 e^{-2\kappa L}}, \qquad (2.134)$$

(square barrier, $E < V_0$)

where τ_1 and r_1 are the potential-step transmission and reflection coefficients

$$\tau_1 = -\frac{2ik}{\kappa - ik}, \qquad r_1 = -\frac{\kappa + ik}{\kappa - ik}, \qquad (2.135)$$

as in Eqs. (2.111), and τ_1' is obtained from τ_1 by interchanging k and κ and then taking the complex conjugate of the result:

$$\tau_1' = \frac{2\kappa}{\kappa - ik}. \qquad (2.136)$$

The same results apply to the higher-energy case $E > V_0$ (including the case of the square potential well, $V_0 < 0$), under the same substitution $\kappa \longrightarrow -i|\kappa|$ as in the potential step. Then the transmission and reflection coefficients become

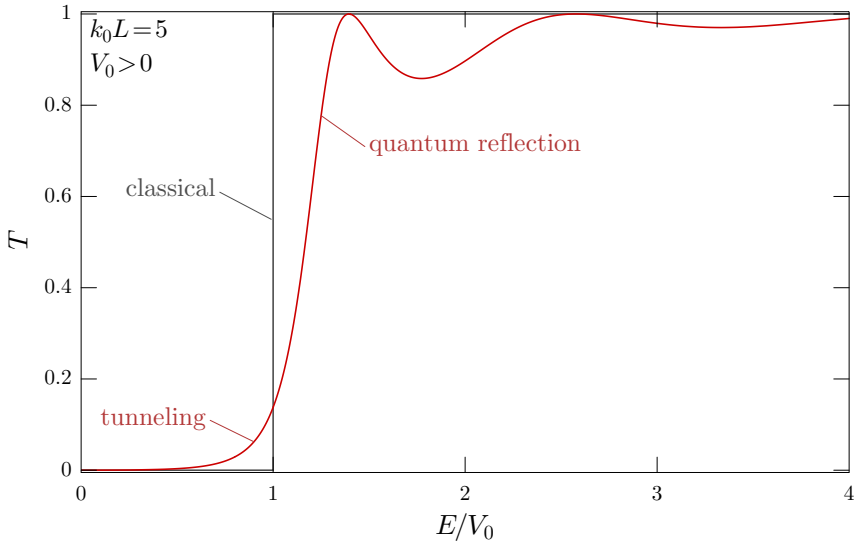
$$\tau = \frac{\tau_1 \tau_1' e^{i|\kappa|L} e^{-ikL}}{1 - r_1^2 e^{i2|\kappa|L}}$$
$$r = \frac{r_1 (1 - e^{i2|\kappa|L})\, e^{-ikL}}{1 - r_1^2 e^{i2|\kappa|L}}, \qquad (2.137)$$

(square barrier, $E > V_0$)

with

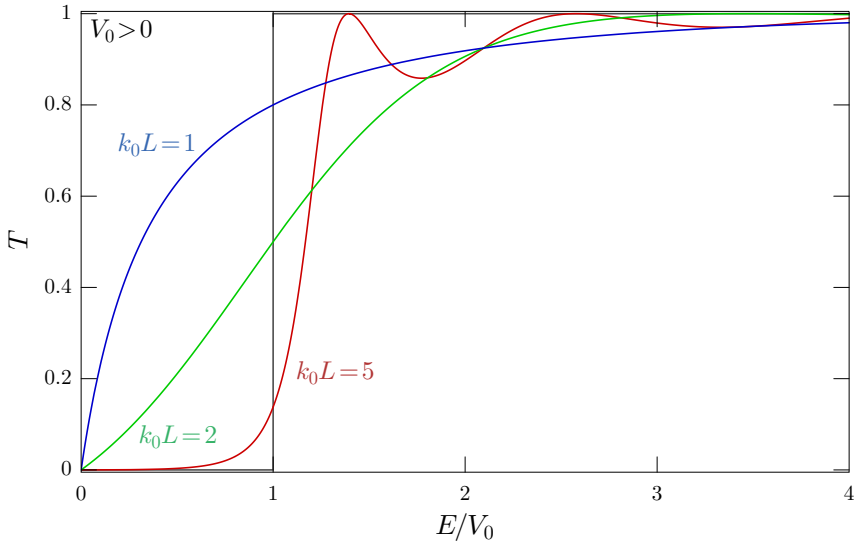
$$\tau_1 = \frac{2k}{k + |\kappa|}, \qquad \tau_1' = \frac{2|\kappa|}{k + |\kappa|}, \qquad r_1 = \frac{k - |\kappa|}{k + |\kappa|}. \qquad (2.138)$$

We can then visualize these results by plotting the transmission probability ($T = |\tau|^2$, according to our discussion above of the probability current) as follows. First, V_0 defines a wave number according to $k_0 = \sqrt{2mV_0}/\hbar$. Then both k/k_0 and κ/k_0 are determined solely by the normalized energy E/V_0, and these two quantities in turn determine all the one-step reflection and transmission coefficients. The remaining parameter in the square-barrier problem is the thickness L, which can be expressed in dimensionless form as $k_0 L$. The exponential arguments can be expressed in terms of $k_0 L$ and either k/k_0 or κ/k_0. Thus, the only two free parameters in this problem are E/V_0 and $k_0 L$. A typical result is plotted below.

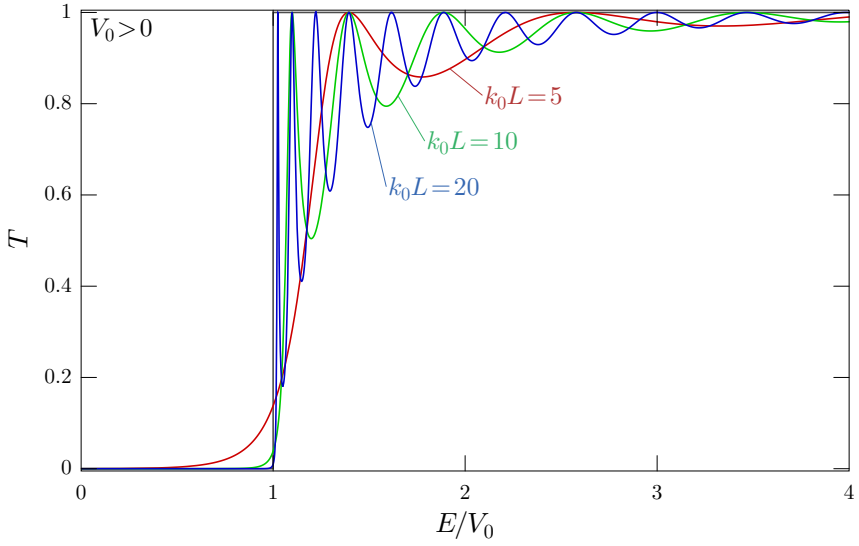


As in the potential step, quantum reflection again occurs in this problem for $E > V_0$. However, the dependence of the transmission probability on E is more complicated, with oscillations that we will return to below. For $E < V_0$, the transmission probability is nonzero, unlike the solution in the potential-step problem. This nonzero transmission represents **quantum tunneling**, which is the penetration of the barrier even when energetically forbidden in the classical case.[7]

To show some other representative cases, the transmission curve from the previous plot is shown with two other transmission curves, corresponding to thinner barriers. The tunneling probability is enhanced in these two cases.



The same reference transmission curve is shown with two other curves corresponding to *thicker* barriers in the plots below. These are more "classical" in that tunneling is suppressed. There is still a significant quantum reflection, though depending on the exact energy. Note that the oscillations become more rapid with E as the barrier becomes thicker.



In the true classical limit, tunneling is of course suppressed, and we see this happening in the plots above. The suppression of quantum reflection is a little less obvious, because the envelope of the oscillations seems

[7] The optical analogue of this effect is called **frustrated total internal reflection**. See Daniel Adam Steck, *op. cit.* An example is a pair of 45-45-90 prisms, placed together to form a cube, but with a tiny gap in between. A laser beam entering one face of the cube internally reflects from one side of the gap; the other side "interrupts" the evanescent wave in the gap and allows the optical wave to propagate again to the other side of the cube. By varying the gap, it is possible to make an adjustable-ratio beam splitter.

to be the same; it's just that the oscillations are becoming more dense. In the limit of a classically thick barrier, the oscillations would become incredibly dense, and anything that tends to disturb the positions of the oscillations would cause them to wash out, and the oscillations would be replaced by their average value—this is just the transmission plot for the potential step on p. 139, corresponding to a square barrier with $L \longrightarrow \infty$. The other aspect of the classical limit is that on a macroscopic scale it is difficult to make an object move slowly enough to get into the quantum reflection regime. That is, on a classical scale this whole transmission plot is effectively "squished" in the horizontal direction, such that the quantum-reflection regime corresponds to an unattainably narrow range of incident energy.

2.6.2.1 Virtual States and Transmission Resonances

Now to address the transmission-probability oscillations in the quantum-reflection regime, $E > V_0$. Again, these apply to high-energy particles incident on a barrier, or to any particles incident on a square well. In this case the amplitude coefficients (2.137) apply. Let's compute the transmission probability explicitly. First, noting that

$$\tau_1 \tau_1' = \frac{4k|\kappa|}{(k + |\kappa|^2)^2} = 1 - r_1^2, \tag{2.139}$$

we can write

$$T = |\tau|^2 = \left| \frac{1 - r_1^2}{1 - r_1^2 e^{-i2|\kappa|L}} \right|^2, \tag{2.140}$$

noting that the phase factors in the numerator of τ in Eqs. (2.137) simply goes away. Now it should be reasonably obvious that the oscillatory dependence of T is due to the L-dependent phase in the denominator of Eq. (2.140). In particular, the transmission probability is unity provided that

$$e^{-i2|\kappa|L} = 1. \tag{2.141}$$

Notice that the reflection coefficient r in Eqs. (2.137) also vanishes under the same condition. The equality here is satisfied when the argument of the phase factor is an integer multiple of 2π:

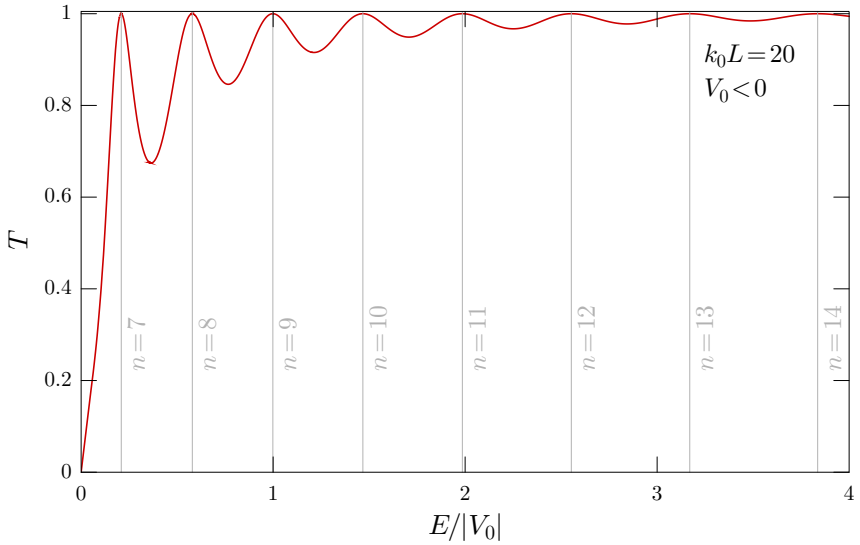
$$2|\kappa|L = 2\pi n, \qquad n \in \mathbb{Z}^+. \tag{2.142}$$

We exclude $n = 0$ to avoid a trivial solution where either L or the wave number must be zero. Using Eqs. (2.106) for κ, we can rewrite this condition as

$$E_n - V_0 = \frac{n^2 \pi^2 \hbar^2}{2mL^2}. \tag{2.143}$$
(virtual energy levels)

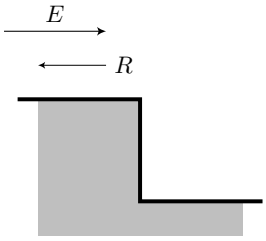
Harkening back to the infinite square well, we can see that, except for the offset V_0, these are just the eigenenergies of that problem.

These are not proper energy levels, as they correspond to energies within a continuum of allowed energies. They are thus sometimes called **virtual energy levels** or **virtual states**. To visualize these again, let's consider a particle incident on a finite square well ($V_0 < 0$). The transmission probability is plotted below, along with some of the virtual energies from Eq. (2.143).

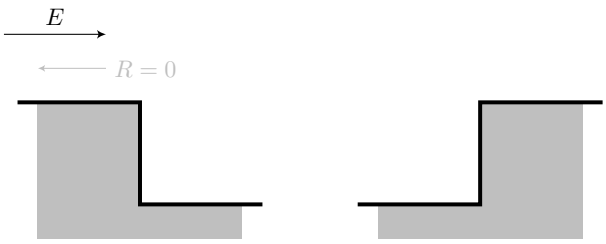


The lower-energy levels that are not shown ($n = 1$ to 6) correspond to true bound states of the potential well [and they have somewhat different energies than what would be predicted by Eq. (2.143)]. Of course, the virtual energies line up precisely with the transmission maxima, as these were how the energies were defined. Again, even though these energy levels don't exist as bound states, because they are above the height of the potential well, if the incoming wave "resonates" with one of these levels, its transmission is enhanced.

This is a very strange thing indeed. Let's say this in the following way. If we consider a particle incident on a potential step, with a reasonable choice of the step, the particle will have some probability of reflecting.



Without changing this step, it is possible to introduce a *second* step, *behind* the first one (as seen by the particle), in such a way that the reflection from the first step is *completely suppressed*.



How can this be? The key is to remember that the wave reflects from either potential step. Consider the wave "rattling around" in the region of the potential well. The effect of going around one round trip is

$$\psi_{n+1} = \psi_n r_1^2 e^{-i2|\kappa|L}, \tag{2.144}$$

including the reflection coefficients for both steps, as well as the phase associated with two passes through the well (one in each direction). Summing all these reflected wave components gives

$$\psi_0 + \psi_1 + \psi_2 + \cdots = \psi_0 + \left(r_1^2 e^{-i2|\kappa|L}\right)\psi_0 + \left(r_1^2 e^{-i2|\kappa|L}\right)^2 \psi_0 + \cdots = \frac{\psi_0}{1 - r_1^2 e^{-i2|\kappa|L}}, \tag{2.145}$$

where we have used $1 + x + x^2 + \cdots = 1/(1-x)$ for $|x| < 1$. The result here reproduces the denominators in Eqs. (2.137), which is the salient part. (The other factors in the numerators may be justified by a more careful argument that generalizes the reflection and transmission coefficients to be widely applicable; see Problem 2.32.)

The main point of all this is that there is the possibility for the wave in region II to build up to large amplitude if it constructively interferes with itself after one round trip. That is, an integer number of half-wavelengths should fit into region II, which is exactly the virtual-energy condition (2.143). These virtual energies do represent states, but *metastable* ones, since they will leak away quickly by transmission through the potential steps. But to answer the question about the suppressed reflection, consider the wave at first incident from the left. Part reflects, but part enters region II. The part in region II will rattle around and some will go back into region I. The point is that on resonance, the phase will be such that the transmission from region II to region I will partially cancel the "direct" reflection of the incident wave from the first potential step. This means less reflected, so more of the incident wave makes it into region II. This process continues until the component from region II *completely* cancels the reflected part of the incident wave. At this point, no more of the wave can enter region II, and steady state is achieved—and remember that the steady state is the *only* thing captured by an energy eigenstate.

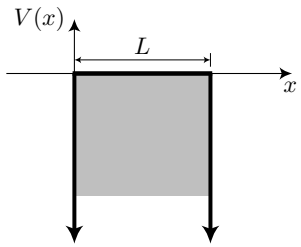
This scattering by a potential well (or a shallow potential barrier) has a few analogues in optics: a (planar) Fabry–Perot resonator, an etalon (planar slab of glass that acts as a resonator), and reflection by a thin dielectric film.

2.6.2.2 A Crazy Potential

Based on the analysis from the previous section, and from the discussion on quantum reflection, you should now be able to analyze the potential

$$V(x) = \begin{cases} 0, & x \in (0, L) \\ -\infty, & x \notin (0, L), \end{cases} \tag{2.146}$$

as illustrated below.



Let's call this the **infinite pedestal** potential. Based on what you now know, does this potential have bound states associated with the top of the pedestal?

2.6.2.3 Delta-Function Limit: Tunneling through a Delta Barrier

As in the solution for the delta-function potential well in Section 2.5.3, we can find the delta-function limit of the square barrier to find the scattering properties of the delta-function *barrier*

$$V(x) = \beta\,\delta(x) \qquad (\beta > 0). \tag{2.147}$$

As before, we can set

$$\beta = V_0 L, \tag{2.148}$$

and consider the limit $L \longrightarrow 0$ at fixed β (such that $V_0 \longrightarrow \infty$ as $1/L$). We can start with the setup of the square barrier as in Eq. (2.104) for the case of low incident energy $E < V_0$. The incident wave vector k and the interior wave vector κ are given as in Eqs. (2.106) as

$$k = \frac{\sqrt{2mE}}{\hbar}, \qquad \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{2.149}$$

Thus, the $V_0 \longrightarrow \infty$ limit implies $\kappa \longrightarrow \infty$. Then starting with the potential-step coefficients (2.135)–(2.136),

$$\tau_1 = -\frac{2ik}{\kappa - ik}, \qquad \tau_1' = \frac{2\kappa}{\kappa - ik}, \qquad r_1 = -\frac{\kappa + ik}{\kappa - ik}, \tag{2.150}$$

in this limit we then have

$$\tau_1 \longrightarrow 0, \qquad \tau_1' \longrightarrow 2, \qquad r_1 \longrightarrow -1. \tag{2.151}$$

However, in this limit these coefficients lead to an ill-defined result for the barrier transmission coefficient in Eqs. (2.134),

$$\tau = \frac{\tau_1 \tau_1' e^{-\kappa L} e^{-ikL}}{1 - r_1^2 e^{-2\kappa L}}, \tag{2.152}$$

which takes the form $0/0$ if we also take $L \longrightarrow 0$.

Thus, to take the delta-function limit more carefully, we should keep the next-order term in κ^{-1} (more properly, in the dimensionless quantity k/κ):

$$\tau_1 = -\frac{2ik}{\kappa} + O(\kappa^{-2}), \qquad \tau_1' = 2 - \frac{2ik}{\kappa} + O(\kappa^{-2}), \qquad r_1 = -1 - \frac{2ik}{\kappa} + O(\kappa^{-2}). \tag{2.153}$$

More specifically, we will need the following quantities to the same order of approximation:

$$\tau_1 \tau_1' = -\frac{4ik}{\kappa} + O(\kappa^{-2}), \qquad r_1^2 = 1 + \frac{4ik}{\kappa} + O(\kappa^{-2}). \tag{2.154}$$

These last two expressions take care of everything but the exponential factors in Eq. (2.152). So what happens to those? Clearly $e^{-ikL} \longrightarrow 1$ as $L \longrightarrow 0$, but the $e^{-\kappa L}$ factors are a bit trickier. Noting that $\kappa L \sim \sqrt{V_0} L \sim \sqrt{\beta L} \longrightarrow 0$, it seems like these exponential factors should also be replaced by unity. But this doesn't seem right, because the result wouldn't depend on β, and the result *really should* depend on β. The trick to getting this to work out without going crazy with Taylor expansions is to realize that terms of the form $\kappa^2 L \sim \beta$ will survive the delta-function limit, so we should look for these. Such a term is only possible in the *denominator* of Eq. (2.152), where we will get a κL from the exponential, and another factor of κ will come from $\tau_1 \tau_1'$. Thus we can set $e^{-\kappa L} = 1$ in the numerator of Eq. (2.152), and $e^{-2\kappa L} = 1 - 2\kappa L$ in the denominator. The denominator will have the form

$$1 - r_1^2 e^{-2\kappa L} = 1 - \left(1 + \frac{4ik}{\kappa}\right)(1 - 2\kappa L) = -\frac{4ik}{\kappa} + 2\kappa L + 8ikL. \tag{2.155}$$

The last kL term will vanish in the limit $L \longrightarrow 0$, so we can discard it now. Putting all these pieces together, Eq. (2.152) becomes

$$\tau = \frac{-4ik/\kappa}{-4ik/\kappa + 2\kappa L} = \frac{1}{1 + i\kappa^2 L/2k}. \tag{2.156}$$

Now being more precise about the quantity

$$\kappa^2 L = \frac{2m(V_0 - E)L}{\hbar^2} = \frac{2m\beta}{\hbar^2} - \frac{2mEL}{\hbar^2} \longrightarrow \frac{2m\beta}{\hbar^2} \tag{2.157}$$

in the delta-function limit, we can finish taking the limit in Eq. (2.156) to find

$$\tau = \frac{1}{1 + im\beta/\hbar^2 k}. \tag{2.158}$$

The reflection coefficient from Eqs. (2.134),

$$r = \frac{r_1(1 - e^{-2\kappa L})\, e^{-ikL}}{1 - r_1^2 e^{-2\kappa L}}, \tag{2.159}$$

goes over to the delta-function limit in a similar way. In this case, we again seek to keep terms of the form $\kappa^2 L$. We can do this by setting $r_1 = -1$, $(1 - e^{-2\kappa L}) = 2\kappa L$, and $e^{ikL} = 1$ in the numerator, while treating the denominator in the same way as before. The result is

$$r = \frac{-2\kappa L}{-4ik/\kappa + 2\kappa L} = \frac{1}{2ik/\kappa^2 L - 1}. \tag{2.160}$$

Again with Eq. (2.157), we can finish the delta limit to obtain

$$r = \frac{1}{i\hbar^2 k/m\beta - 1}. \tag{2.161}$$

This yields a reflection probability

$$R = |r|^2 = \frac{1}{1 + \hbar^4 k^2/m^2\beta^2} = \frac{1}{1 + 2\hbar^2 E/m\beta^2},$$

(reflection probability δ barrier) (2.162)

after using $k^2 = 2mE/\hbar^2$ from Eqs. (2.149). Similarly, we can write the transmission probability as

$$T = |\tau|^2 = 1 - |r|^2 = \frac{1}{1 + m^2\beta^2/\hbar^4 k^2} = \frac{1}{1 + m\beta^2/2\hbar^2 E}.$$

(transmission probability, δ barrier) (2.163)

In particular, we can see that $R > 0$ and $T < 1$ for any $E > 0$. Furthermore, despite having an arbitrarily high barrier, a perfect reflection ($R = 1$) is only achieved at fixed E for $\beta \longrightarrow \infty$ (assuming also fixed mass). Thus, unlike the wall of the infinite square well, a delta barrier only imposes a Dirichlet boundary condition when $\beta \longrightarrow \infty$.

2.6.2.4 Scattering from a Delta Well

The above analysis is also amenable to describing the delta well,

$$V(x) = -\beta\,\delta(x) \qquad (\beta > 0). \tag{2.164}$$

This is of course the same potential as in Section 2.5.3, but the goal there was to examine the (lone) bound state, whereas here we are finally returning to handle the unbound (continuum states). The analysis here is identical to the above analysis with the replacements

$$V_0 \longrightarrow -V_0, \qquad \kappa \longrightarrow -i|\kappa|, \tag{2.165}$$

which amounts to replacing $\beta \longrightarrow -\beta$. Then the coefficients from Eqs. (2.158) and (2.161) become

$$r = -\frac{1}{1 + i\hbar^2 k/m\beta}, \qquad \tau = \frac{1}{1 - i\kappa^2 L/2k}. \tag{2.166}$$

Note that the *magnitudes* of the coefficients are the same as before, it is just the *phases* that differ. Thus, the reflection probability

$$R = |r|^2 = \frac{1}{1 + \hbar^4 k^2/m^2\beta^2} = \frac{1}{1 + 2\hbar^2 E/m\beta^2},$$

(reflection probability, δ well) (2.167)

as well as the transmission probability

$$T = |\tau|^2 = 1 - |r|^2 = \frac{1}{1 + m^2\beta^2/\hbar^4 k^2} = \frac{1}{1 + m\beta^2/2\hbar^2 E},$$

(transmission probability, δ well) (2.168)

are the same as for the delta barrier of the same amplitude. Recalling that a more direct derivation would seek to calculate the kink in the wave function due to the delta potential, it evidently doesn't matter which way the kink goes.

2.6.3 Semiclassical Approximation for the Tunneling Probability

Now let's consider a thin-barrier limit, but *without* the corresponding $V_0 \longrightarrow \infty$ divergence in the delta-function limit of Section 2.6.2.3. Let's replace L by a small width Δx in the transmission coefficient (2.152)

$$\tau = \frac{\tau_1 \tau_1' e^{-\kappa\,\Delta x} e^{-ik\,\Delta x}}{1 - r_1^2 e^{-2\kappa\,\Delta x}}, \tag{2.169}$$

keeping in mind that we are still considering the tunneling case of $E < V_0$. Then suppose that, in the *denominator*, we make the approximation $e^{-2\kappa\Delta x} \approx 1$. We can then use the relation (2.139),

$$\tau_1 \tau_1' = 1 - r_1^2, \tag{2.170}$$

so that Eq. (2.169) reduces to

$$\tau = e^{-\kappa\,\Delta x} e^{-ik\,\Delta x}. \tag{2.171}$$

Hang on, though—that argument was just a little *too* slippery. The difference between $e^{-2\kappa\Delta x}$ and unity should lead to corrections of the form $\kappa\Delta x$ to a similar order as $e^{-\kappa\Delta x}$ in the numerator. To properly justify Eq. (2.171), we should *also* assume that r_0^2 is small, and thus that $\tau_1\tau_1'$ is close to unity. This extra assumption suppresses any extra contribution from the damping factor in the denominator. The remaining phase factor won't be so useful in the discussion to follow, so let's consider the transmission probability

$$T \approx e^{-2\kappa\,\Delta x} \tag{2.172}$$

through a thin barrier.

Of course, it's also useful to compare the solution here to the delta-barrier transmission coefficient (2.163), in case that could be adapted to obtain the same result. However, referring back to the expansions (2.153) of the reflection and transmission coefficients for the potential step, the approximations in that case are not compatible with the approximations here: Here we needed to assume almost no reflection ($|r_1| \ll 1$), but in the delta-barrier case the reflection coefficient turned out to be close to unity. In the delta barrier, reflection is dominated by the sharp change in the background potential, but the semiclassical approximation relies on a smooth change in the potential, so that the tunneling probability is dominated by the exponential decay inside the barrier rather than reflections at the barrier interface.

2.6.3.1 Stacks of Thin Layers

Now consider a more general barrier, where $V(x)$ has some more complicated shape than a single, square bump. In fact, we'd like to consider the case where $V(x)$ rises and falls *smoothly* to form a barrier. We can approximate any such barrier by a ''stack'' of thin, constant pieces, each of width Δx. Suppose we write down

$$T \approx T_1 T_2 T_3 \cdots = e^{-2\kappa_1\,\Delta x} e^{-2\kappa_2\,\Delta x} e^{-2\kappa_3\,\Delta x} \cdots \tag{2.173}$$

as an *approximate* expression for the total transmission probability through the stack. While it is reasonable to express the total transmission probability as a product of individual probabilities (since the particle must tunnel through barrier 1 *and* barrier 2 *and* so on), the approximation involves ignoring the multiple reflections between layers—recall that anything reflected from any particular layer may still get a chance to transmit if it reflects from another, ''earlier'' layer. To the extent we can do this, we can collect all factors to write

$$T \approx \prod_j e^{-2\kappa_j\,\Delta x} = \exp\left(-2\sum_j \kappa_j\,\Delta x\right) = \exp\left(-2\int_{x_1}^{x_2} \kappa(x)\,dx\right) \tag{2.174}$$

where we have taken the continuum limit $\Delta x \longrightarrow 0$ in the last expression, and x_1 and x_2 are the two points where $V(x) = E$ (respectively, the ''entrance'' and ''exit'' points of the barrier-tunneling process). Again, we are being a little slippery here: Since the potential is potentially different (very punny, har har) at each point, we should really be talking about probability currents, and not just $|\tau|^2$s. The transmission probabilities are then weighted by factors like κ_{j+1}/κ_j. But because we will assume that the initial and final potentials are

the same for the tunneling wave, these factors will ultimately end up cancelling out, and we'll end up with the same expression. Finally, using

$$\kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}, \tag{2.175}$$

the transmission coefficient becomes

$$T \approx \exp\left(-\frac{2\sqrt{2m}}{\hbar}\int_{x_1}^{x_2} dx\sqrt{V(x) - E}\right). \tag{2.176}$$

(tunneling probability, semiclassical approximation)

This result is said to be a **semiclassical approximation** for the tunneling probability, the "classical" part being that we are ignoring the multiple wave reflections (i.e., ignoring coherence between the wave at different locations in the barrier potential).

The semiclassical approximation is justified if the reflection coefficients of any of the thin barriers are small—this returns to the small-r_1 approximation above. Recalling that reflections occur with large differences in the wave vector κ between different regions, we are essentially assuming that $\kappa(x)$ varies slowly, and thus that $V(x)$ varies slowly, which means $\delta V \ll V$. A typical length scale over which we should measure the variation of the potential is $\delta x \sim \kappa^{-1}$. Combining this with the small-variation condition leads to the condition

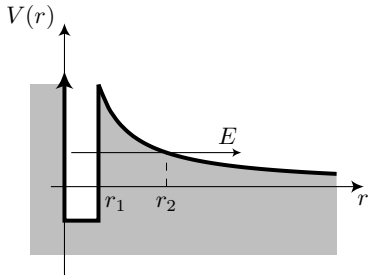
$$\frac{\delta V}{\delta x} = \frac{dV}{dx} \ll \kappa(x)V(x) \tag{2.177}$$

(semiclassical condition)

for Eq. (2.176) to be accurate. Typically, this means "long-distance" tunneling, for which we expect T to be small. However, this expression gives a powerful analytical tool to estimate the tunneling probability in the presence of a complicated potential that is resistant to direct analytical calculations.

2.6.3.2 Application to α-Decay

A classic application of the semiclassical approximation to the tunneling rate is Gamow's estimate of the rate of nuclear decay by α-particle emission.[8] The model is a particle in the potential $V(r)$, as shown below.



The large-r part of the potential is electrostatic repulsion between the α particle (of charge $q_\alpha = 2e$, where e is the fundamental charge), and the nucleus (of charge $q_\mathrm{n} = Ze$, where Ze is the charge of the nucleus *after* emitting the α particle):

$$V(r) = \frac{1}{4\pi\epsilon_0}\frac{q_\alpha q_\mathrm{n}}{r} = \frac{1}{4\pi\epsilon_0}\frac{2Ze^2}{r} \qquad (r > r_1). \tag{2.178}$$

The "inner" part of the potential is a square well, representing the nuclear binding force. This force acts at short range ($r < r_1$, where r_1 is the nuclear radius), which in part justifies modeling the force in terms of a sharp wall at the edge of the nucleus. There is also an effective hard wall at $r = 0$. Since this is a fully three-dimensional potential and we are only looking at the radius $r = |\mathbf{r}|$, a particle crossing through $r = 0$ appears to reflect from the origin, which justifies this hard wall. The wall is there simply to give a conceptual completion of the potential well; it won't directly enter the calculation.

[8] G. Gamow, "Zur Quantentheorie des Atomkernes," *Zeitschrift für Physik* **51**, 204 (1928) (doi: 10.1007/BF01343196). English translation at `http://web.ihep.su/dbserv/compas/src/gamow28/eng.pdf`.

Thus, we can view the nuclear decay by α emission as a tunneling process, where the particle escapes by tunneling through the electrostatic barrier. The particle energy E is the asymptotic particle kinetic energy after emission; the depth of the potential well (more specifically the particle energy relative to the bottom of the potential well) will be ignorable in this calculation.

This tunneling process is three-dimensional, however, and we have only considered tunneling in one dimension, so before proceeding we need to discuss the ramifications of this. The Schrödinger equation in three dimensions is

$$\nabla^2\psi(\mathbf{r}) = -\frac{2m}{\hbar^2}\big[V(\mathbf{r}) - E\big]\,\psi(\mathbf{r}). \tag{2.179}$$

Since the potential is spherically symmetric, let's assume for the moment that this also applies to the wave function, so that $\psi(\mathbf{r}) = \psi(r)$. Then

$$\nabla^2\psi(r) = -\frac{2m}{\hbar^2}\big[V(r) - E\big]\,\psi(r). \tag{2.180}$$

It turns out that in spherical symmetry, the Laplacian is

$$\nabla^2\psi(r) = \frac{1}{r}\partial_r^2\big[r\psi(r)\big], \tag{2.181}$$

something to be justified later when we return to problems in three dimensions (most notably, the hydrogen atom). Putting this into the Schrödinger equation and multiplying through by r,

$$\partial_r^2\big[r\psi(r)\big] = -\frac{2m}{\hbar^2}\big[V(r) - E\big]\,r\psi(r). \tag{2.182}$$

Thus, $r\psi(r)$ acts as an effective wave function that satisfies an equation that has the form of a one-dimensional Schrödinger equation. Plus, remember that $r^2|\psi|^2$ is the correct radial density, so $r\psi(r)$ is analogous to $\psi(x)$ in a one-dimensional calculation.

So to proceed, although it applies to tunneling in one dimension, we may adapt Eq. (2.176) for the tunneling probability:

$$T \approx \exp\!\left(-\frac{2\sqrt{2m}}{\hbar}\int_{r_1}^{r_2} dr\sqrt{V(r) - E}\right). \tag{2.183}$$

As before, r_1 is the nuclear radius, and r_2 is defined by $V(r_2) = E$, and thus

$$r_2 = \frac{Ze^2}{2\pi\epsilon_0 E}. \tag{2.184}$$

This also means that $V(r) = Er_2/r$, and thus the tunneling probability (2.183) becomes

$$T \approx \exp\!\left(-\frac{2\sqrt{2mE}}{\hbar}\int_{r_1}^{r_2} dr\sqrt{\frac{r_2}{r} - 1}\right). \tag{2.185}$$

As a further approximation, since $r_2 \gg r_1$ (i.e., the nuclear radius is much smaller than the atomic radius), it doesn't change the integral very much to simply set $r_1 = 0$. Then we are left with the integral

$$\int_0^{r_2} dr\sqrt{\frac{r_2}{r} - 1} = \frac{\pi r_2}{2}, \tag{2.186}$$

and Eq. (2.185) becomes

$$T \approx \exp\!\left(-\frac{\sqrt{2mE}\,\pi r_2}{\hbar}\right) = \exp\!\left(-\sqrt{\frac{2m}{E}}\frac{Ze^2}{2\epsilon_0\hbar}\right), \tag{2.187}$$

(Gamow factor)

Note that the factor $\sqrt{2E/m}$ has the form of a (nonrelativistic) velocity, but since the decay velocities are typically relativistic, this is probably not a useful identification. This exponential factor (the transmission

probability) is significant, and is called the **Gamow factor**. To see why this is useful, first we need to translate this into something observable, since the transmission probability itself is not directly measurable. However, the nuclear decay rate Γ is basically the product of the transmission probability and the rate at which the α particle ''collides'' with the potential barrier. This latter rate is also something that we don't directly know, as it depends on the details of the nucleus. However, as a scaling relation, we can simply note that Γ scales with the emission energy or velocity as the Gamow factor. Expressing this in terms of the logarithm of the decay rate, we can write

$$\log\Gamma = (\text{const}) - \sqrt{\frac{E_{\text{G}}}{E}}, \tag{2.188}$$
(Geiger–Nuttall Law)

where we have defined the Gamow energy

$$E_{\text{G}} := \frac{mZ^2e^4}{2\epsilon_0^2\hbar^2}, \tag{2.189}$$

Here again, the ''(const)'' is a constant that depends on details of the nucleus. This scaling relation, the **Geiger–Nuttall Law**,[9] says that a plot of the logarithm of the decay rate vs. $E^{-1/2}$ yields a straight line. The constant may vary somewhat among different groups of nuclei, but the slope is more or less *universal* (depending on Z, which does not vary much over the heavy α-emitting nuclei).

As an example of this scaling, let's consider the scaling among various isotopes of polonium.[10] Data for the decay energy and the half-life, defined as

$$t_{1/2} = \Gamma^{-1}\log 2, \tag{2.190}$$

are shown in the table below.[11]

Isotope	**half-life**	**decay energy (MeV)**
^{192}Po	34 ms	7.17
^{194}Po	0.39 s	6.84
^{196}Po	5.8 s	6.52
^{208}Po	2.898 y	5.213
^{210}Po	138.4 d	5.304
^{212}Po	0.298 μs	8.784
^{214}Po	163.7 μs	7.686
^{216}Po	0.145 s	6.778

This series is particularly nice as Z is constant among the isotopes; also isotopes with nuclear spin or significant alternate decay paths are excluded, since neither effect is accounted for in the above theory. With $Z = 82$ after the α-particle emission, the Gamow energy is $E_{\text{G}} \approx 110\,\text{GeV}$. Plotting $t_{1/2}$ vs. $E^{-1/2}$ also yields a straight line, since we have

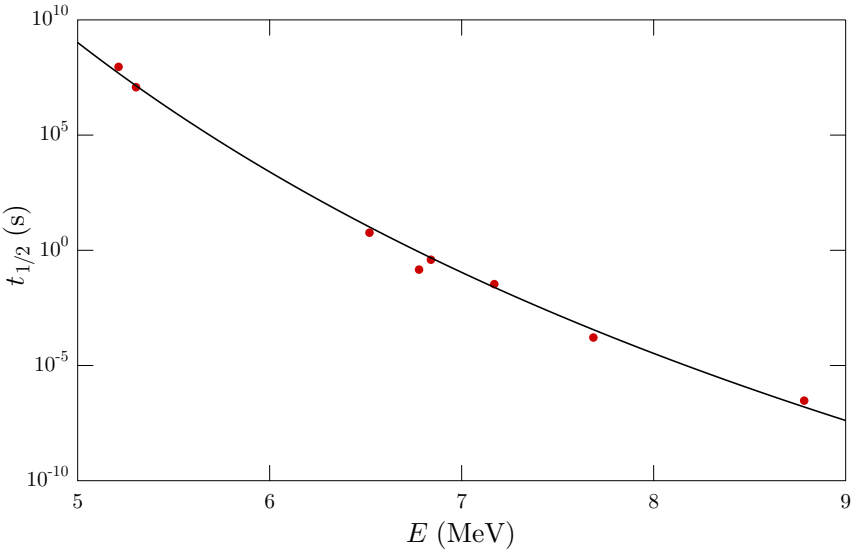
$$\log t_{1/2} = (\text{const}) + \sqrt{\frac{E_{\text{G}}}{E}}, \tag{2.191}$$

where the ''(const)'' is different, but still unimportant. However, we can still see this dependence by plotting the logarithm of the half-life vs. E, as in the plot below.

[9] after H. Geiger and J. M. Nuttall, (1911) ''The ranges of the α particles from various radioactive substances and a relation between range and period of transformation,'' *Philosophical Magazine* Series 6 **22**, 613 (1911) (doi: 10.1080/14786441008637156).

[10] This example from John R. Taylor and Chris D. Zafiratos, *Modern Physics for Scientists and Engineers* (Prentice Hall, 1991), p. 365.

[11] Data from Norman E. Holden, ''Table of the Isotopes,'' in *CRC Handbook of Chemistry and Physics*, David R. Lide, Ed., 82nd ed. (2001) (ISBN: 0849304822); polonium data on pp. 11-171–11-172.



The plot also shows the curve $\sqrt{E_G/E}$, shifted by an arbitrary amount designed to make the curve overlap the data. Given the relatively crude nature of Gamow's estimate, the scaling behavior matches the data quite well.

2.7 Exercises

Problem 2.1

A rite of passage in the training of every physicist is ‘‘completing the square’’ for the first time. You'll have to do this essentially every time you work with a Gaussian state in quantum mechanics, so let's just get this out of the way once and for all. That is, using the integral formula

$$\int_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{\frac{\pi}{a}} \qquad (a \in \mathbb{C},\ \mathrm{Re}[a] > 0), \tag{2.192}$$

prove the more general formula

$$\int_{-\infty}^{\infty} e^{-(\alpha x^2+\beta x+\gamma)}\,dx = \sqrt{\frac{\pi}{\alpha}}\,\exp\!\left(\frac{\beta^2}{4\alpha}-\gamma\right) \qquad (\alpha,\beta,\gamma \in \mathbb{C},\ \mathrm{Re}[\alpha] > 0). \tag{2.193}$$

Problem 2.2

We showed that the propagator for the free particle can be written

$$K(x,t;x_0,t_0) = \frac{1}{2\pi\hbar}\int dp\, e^{-ip^2(t-t_0)/2m\hbar} e^{ip(x-x_0)/\hbar}. \tag{2.194}$$

Carry out the integral to show that

$$K(x,t;x_0,t_0) = \sqrt{\frac{m}{i2\pi\hbar(t-t_0)}}\,\exp\left[\frac{im(x-x_0)^2}{2\hbar(t-t_0)}\right]. \tag{2.195}$$

But be careful! Note that the integral in Eq. (2.194) is *not* of the form (2.193), nor is the integral even well defined. Carefully (and *explicitly*) regularize the integral (or otherwise show that it gives a sensible result) and then carry it out to prove the result.

Problem 2.3

Consider the free quantum particle with initial state

$$\psi(x,t=0) = \frac{1}{(2\pi)^{1/4}\sigma^{1/2}}\,e^{-x^2/4\sigma^2}\,e^{ikx}. \tag{2.196}$$

(a) Show that the solution for all t may be written compactly as

$$\psi(x,t) = \frac{1}{(2\pi)^{1/4}}\sqrt{\frac{\zeta(0)}{\sigma\zeta(t)}}\,\exp\!\left(\frac{i\tau_0(x-vt)^2}{4\sigma^2\zeta(t)}\right)e^{ik(x-vt/2)}, \tag{2.197}$$

where

$$\zeta(t) := t - i\tau_0, \qquad \tau_0 := \frac{2m\sigma^2}{\hbar}, \qquad v := \frac{\hbar k}{m}. \tag{2.198}$$

Try to stay organized and not let your calculation get out of control!

(b) This expression (2.197) is elegant, but because of the complex functions in odd places, it's a bit hard to get a sense of what is going on. To get a better handle on the Gaussian free particle, eliminate $\zeta(t)$ in Eq. (2.197) to obtain the equivalent expression

$$\psi(x,t) = \frac{1}{(2\pi)^{1/4}\sqrt{\sigma_x(t)}}\exp\left[-\frac{(x-vt)^2}{4\sigma_x^2(t)}\right]\exp\left[i\frac{t(x-vt)^2}{4\tau_0\sigma_x^2(t)}\right]\exp\left[ik\left(x-\frac{vt}{2}\right)-\frac{i}{2}\tan^{-1}\left(\frac{t}{\tau_0}\right)\right], \tag{2.199}$$

where

$$\sigma_x(t) = \sigma\sqrt{1 + \frac{t^2}{\tau_0^2}} = \sigma\sqrt{1 + \frac{\hbar^2 t^2}{4m^2\sigma^4}}. \tag{2.200}$$

(c) Now, to make sure we're all on the same page, what is the position uncertainty as a function of time for the Gaussian free particle? (You can read it off of the solution, but justify your reading.) What are physical interpretations of τ_0 and v?

Also, try your hand at giving a physical interpretation to each of the factors in Eq. (2.199). At minimum you should be able to handle the prefactor and first exponential factor, but give the last two factors a try too. Actually, I'll do one of the least obvious for you—the arctangent part of the last factor is called a **Gouy phase** (rhymes with "chewy maze") in optics, and it is a slow phase variation associated with the focusing of the wave packet (for $t < 0$) and the dispersal of the wave packet (for $t > 0$). Actually, it has the form of a slight effective *increase* in energy, especially around $t = 0$.

Problem 2.4

For the time-dependent Gaussian state (2.197) in Problem 2.3, show explicitly that, in terms of the canonical operators p and x, it is consistent with:

(a) the standard uncertainty relation [Eq. (1.43)]

$$V_P V_Q \geq \frac{1}{4}\Big|\big\langle [P,Q] \big\rangle\Big|^2, \tag{2.201}$$

which in this case reduces to

$$V_x V_p \geq \frac{\hbar^2}{4}. \tag{2.202}$$

(b) the generalized (stronger) uncertainty relation [Eq. (1.51)]

$$V_P V_Q \geq \frac{1}{4}\Big|\big\langle [P,Q] \big\rangle\Big|^2 + \frac{1}{4}\Big|\big\langle [P,Q]_+ \big\rangle - 2\langle P\rangle\langle Q\rangle\Big|^2. \tag{2.203}$$

which may be rewritten

$$V_x V_p - C_{xp}^2 \geq \frac{\hbar^2}{4} \tag{2.204}$$

in terms of the **symmetrized covariance**

$$C_{xp} := \frac{1}{2}\big\langle [x,p]_+ \big\rangle - \langle x\rangle\langle p\rangle\,. \tag{2.205}$$

In fact, you should find that the equality is satisfied for the Gaussian state, something that turns out to be unique to Gaussian wave functions.

Problem 2.5

A **convolution integral** has the form

$$\psi_{\rm C}(x) = \int_{-\infty}^{\infty} dx'\, K(x - x')\, \psi(x'), \tag{2.206}$$

where $K(x)$ is called the **convolution kernel**, and the convolution integral here is often abbreviated as $\psi_c = K * \psi$. (Think of the convolution kernel "smearing" $\psi(x)$ to make $\psi_{\rm C}(x)$; for example, if $K(x)$ is a Gaussian function, this would be a "Gaussian blur" in photo-editing software.) The **convolution theorem** says that in momentum space,

$$\phi_{\rm C}(p) = \sqrt{2\pi\hbar}\,\tilde{K}(p)\,\phi(p), \tag{2.207}$$

where $\phi(p)$ and $\phi_{\mathrm{C}}(p)$ are the momentum-representation forms of the wave functions, and $\tilde{K}(p)$ is defined in the analogous way:

$$\tilde{K}(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx\, K(x)\, e^{-ipx/\hbar}. \tag{2.208}$$

That is, convolution in the position representation is just multiplication in the momentum representation (up to an overall factor, which is an artifact of the normalization of the momentum eigenstates).

(a) Prove the convolution theorem, Eq. (2.207).

(b) Write down the analogous "reverse" convolution theorem for the momentum convolution

$$\phi_{\mathrm{C}}(p) = \int_{-\infty}^{\infty} dp'\, \tilde{L}(p-p')\, \phi(p') = \big(\tilde{L} * \phi\big)(p). \tag{2.209}$$

(c) Given that $\psi(x)$ is a normalized wave function, what is required of $K(x)$ for $\psi_{\mathrm{C}}(x)$ to also be normalized? (That is, derive an integral equation that must be satisfied by $K(x)$ in order for the convolution to preserve normalization.) Try to give an interpretation of the condition on $K(x)$.

Problem 2.6

Consider a free quantum particle, with position operator $x(t)$ in the Heisenberg picture. Derive an expression for the commutator $[x(t), x(0)]$.

Problem 2.7

Let $\psi(x,t)$ be a (normalized) solution to the free-particle Schrödinger equation in one dimension. Show that

$$\check{\psi}(x,t) := \eta \sum_{j=-\infty}^{\infty} \Big[\psi(x+2jL,t) - \psi(2jL-x,t)\Big] \tag{2.210}$$

is a solution to the infinite-square-well problem on $[0,L]$, where η is a normalization factor. Note that if $\psi(x,t)$ is even about $2Ln$ for some integer n, then the above solution is trivial; so you may assume this isn't an issue.

Problem 2.8

Consider a one-dimensional particle ($H = p^2/2m$) confined to a box with periodic boundary conditions; that is, any solution $\psi_{\mathrm{p}}(x,t)$ must satisfy

$$\psi_{\mathrm{p}}(x+2\pi,t) = \psi_{\mathrm{p}}(x,t), \qquad x \in \mathbb{R} \tag{2.211}$$

at any time t. Suppose $\psi(x,t)$ is a solution to the standard free-particle problem ($H = p^2/2m$, no boundary conditions except at infinity). Show how to modify $\psi(x,t)$ so that it is *still* a solution to the free-particle problem, but *also* is a solution to the problem with periodic boundary conditions.

If it helps, you can think of x as an angular variable, so the problem with periodic boundary conditions is equivalent to a free rigid rotor of inertial moment m.

Problem 2.9

A particle is in the ground state of an infinite square well of length L.

(a) Suddenly, the walls are taken away. What is the new momentum (probability) distribution?

(b) Compute the new expected energy using the momentum distribution. Does it make sense?

(c) Suppose instead the walls are moved suddenly to a separation L', with $L' > L$ (*the center of the well is not shifted*). What is the probability of finding the particle in the first excited state (second energy level)?

Problem 2.10

Consider a particle in one dimension in a potential $V(x)$. Let $\psi(x)$ be the energy eigenfunction corresponding to energy E, also satisfying $\psi \longrightarrow 0$ as $|x| \longrightarrow \infty$. Show that this eigenstate is nondegenerate.

Hint: you will want to assume that there are two eigenfunctions corresponding to the same energy, and show that they are in fact equivalent.

Problem 2.11

For each of the energy eigenstates of the infinite square well, compute the position variance V_x. Show that as $n \longrightarrow \infty$ (i.e., large-energy limit), these are consistent with a *classical* interpretation of the infinite square well.

Problem 2.12

Consider a particle of mass m in an infinite square well, with the well occupying $(-L/2, L/2)$. Now consider the initial condition

$$\psi(x,0) = \begin{cases} \sqrt{2/L} & (-L/2 < x < 0) \\ 0 & (0 < x < L/2), \end{cases} \tag{2.212}$$

That is, initially the particle uniformly occupies $(-L/2, 0)$. At some later time τ, the state is (up to an overall phase factor)

$$\psi(x,\tau) = \begin{cases} 0 & (-L/2 < x < 0) \\ \sqrt{2/L} & (0 < x < L/2), \end{cases} \tag{2.213}$$

or that is, at time τ the particle uniformly occupies $(0, L/2)$. What is the first time τ that this occurs?

Problem 2.13

As in Problem 2.12, consider a particle of mass m in an infinite square well, with the well occupying $(-L/2, L/2)$. Show that the expectation value $\langle x^{10} p^{51} x^{10} \rangle$ vanishes with respect to any energy eigenstate $|E_n\rangle$.

Problem 2.14

(a) Let $\mathscr{F}$ denote the Fourier-transform operator, which is defined by the integral transformation

$$\langle p|\mathscr{F}|\psi\rangle = \int dx\, \langle p|\mathscr{F}|x\rangle\langle x|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, \psi(x)\, e^{-ipx/\hbar}, \tag{2.214}$$

as expressed in the momentum representation, or more directly,

$$\langle x|\mathscr{F}|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{-ipx/\hbar} = \langle p|\mathscr{F}|x\rangle. \tag{2.215}$$

Write down an explicit expression for $\langle p|\mathscr{F}^{-1}|\psi\rangle$, where $\mathscr{F}^{-1}$ is the operator representing an inverse Fourier transform.

(b) Is $\mathscr{F}$ unitary? Give a (simple) justification for why or why not.

(c) Show that

$$\Pi = \mathscr{F}^2. \tag{2.216}$$

Problem 2.15

Consider the complex-conjugation operators C_x and C_p, defined in their respective natural representations by

$$\langle x|C_x|\psi\rangle = \langle x|\psi\rangle^*, \qquad \langle p|C_p|\psi\rangle = \langle p|\psi\rangle^*. \tag{2.217}$$

(a) Show that $C_x = \Pi C_p$, where Π is the parity operator.

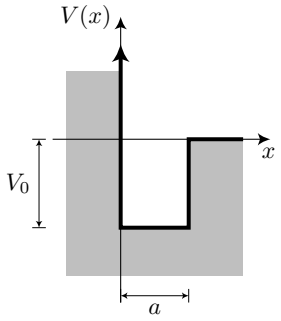
(b) What are the eigenvalues of C_x and C_p? Describe qualitatively the corresponding eigenvectors.

Problem 2.16

Consider a potential well with one hard barrier and one finite step, given by

$$V(x) = \begin{cases} \infty, & x < 0 \\ -V_0, & 0 < x < a \\ 0, & x > a, \end{cases} \tag{2.218}$$

(for $V_0 > 0$), and as shown schematically below.



(a) Derive an equation that determines the eigenenergies for bound states of this potential.

(b) Derive an expression for the smallest value of V_0 for which a bound state exists in the well.

Note: if you were to relate this problem to one where you know the solution, you wouldn't need to rederive the known solution.

Problem 2.17

Consider a free quantum particle on the line $[0, L]$, subject to a Dirichlet boundary condition at $x = 0$ and a Neumann boundary condition at $x = L$. That is,

$$\psi(x = 0) = 0, \qquad \psi'(x = L) = 0. \tag{2.219}$$

Find all the energy eigenvalues and eigenfunctions for this system.

Also, what kind of potential would impose such boundary conditions on a particle?

Problem 2.18

In Problem 2.17, you considered a free quantum particle on the line $[0, L]$, subject to a Dirichlet boundary condition at $x = 0$ and a Neumann boundary condition at $x = L$. That is,

$$\psi(x = 0) = 0, \qquad \psi'(x = L) = 0. \tag{2.220}$$

You found the energy eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{(n - 1/2)\pi x}{L}. \tag{2.221}$$

and the eigenenergies

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{(n - 1/2)^2 \pi^2 \hbar^2}{2mL} \qquad (n \in \mathbb{Z}^+), \tag{2.222}$$

corresponding to the purely kinetic energies of the states.

(a) Compute the expectation value

$$\rho_n := \frac{\hbar}{i} \langle \partial_x \rangle_n \tag{2.223}$$

with respect to the state $\psi_n(x)$.

(b) Considering the eigenstates as superpositions of free-space momentum states, or by some other simple argument, calculate $\langle p \rangle_n$ in each eigenstate. Is it weird that this result is different from that of (a)? Just wait...

(c) Show that the operator $(\hbar/i)\partial_x$ is not even Hermitian in the Hilbert space spanned by the eigenstates.

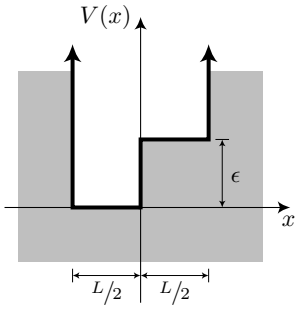
(d) Derive the proper expression for the momentum operator on this Hilbert space in the position representation. Recall that the momentum operator in the position representation follows from the commutator $[x, p] = i\hbar$; this admits an arbitrary additive function of position. Before, we argued it away. Now you'll need it, and it will involve a delta function.

Problem 2.19

Consider a particle in the potential

$$V(x) = \begin{cases} \infty, & |x| > L/2 \\ 0, & -L/2 < x < 0 \\ \epsilon, & 0 < x < L/2 \end{cases} \tag{2.224}$$

(for $\epsilon > 0$), shown schematically below.



(a) Derive an equation that determines the eigenenergies.

(b) Is it possible to choose ϵ such that there is a bound state whose wave function $\psi_E(x)$ is constant in the region $0 < x < L/2$?

Problem 2.20

Compute $\langle p^2 \rangle, \langle p^3 \rangle$, and $\langle p^4 \rangle$ for each energy eigenstate

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \tag{2.225}$$

of the infinite square well.

Problem 2.21

(a) Complete the derivation from Section 2.5.3, where we took the limit $L \longrightarrow 0$ at fixed $\beta = V_0 L$ of the square-well potential to derive the lone bound state of the potential

$$V(x) = -\beta\,\delta(x), \tag{2.226}$$

showing that the eigenenergy is

$$E = -\frac{m\beta^2}{2\hbar^2}, \tag{2.227}$$

and that the corresponding normalized wave function is

$$\psi(x) = \sqrt{\frac{m\beta}{\hbar^2}}\, e^{-m\beta|x|/\hbar^2}. \tag{2.228}$$

Hint: once you solve the eigenvalue condition $\chi \approx \sqrt{\alpha^2 - \chi^2}/\chi$, you can simplify the result by using a small-α approximation. However, if you end up with a trivial solution, it means that your approximation was too simple!

(b) Rederive these results using the "direct method," where the continuity condition is generalized to

$$\psi'_E(0^+) - \psi'_E(0^-) = -\frac{2m}{\hbar^2}\beta\psi_E(0) \tag{2.229}$$

due to the delta-function potential.

Problem 2.22

Write down the time-independent Schrödinger equation for a particle in a delta-potential well, $V(x) = -\beta\delta(x)$, but **in the momentum representation** (i.e., no reference to x). Then solve it (still in the p representation) to find the bound-state energy.

Problem 2.23

(a) For the finite square well in the deep-well limit ($E_n \ll V_0$) show that the energy (relative to the bottom of the well) is

$$E_n + V_0 \approx \frac{n^2\pi^2\hbar^2}{2mL^2}\left(1 - \frac{2}{\alpha}\right) \tag{2.230}$$

and the eigenfunctions are

$$\psi_n(x) \approx \begin{cases} (-1)^{\lfloor n/2\rfloor}\dfrac{n\pi}{\alpha\sqrt{2L}}e^{2\alpha(x+L/2)/L} & \text{(region I)} \\ \sqrt{\dfrac{2}{L}}\left(1 - \dfrac{1}{2\alpha}\right)\cos\left[\left(1 - \dfrac{1}{\alpha}\right)\dfrac{n\pi x}{L} - \dfrac{[1+(-1)^n]\pi}{4}\right] & \text{(region II)} \\ (-1)^{\lfloor (n-1)/2\rfloor}\dfrac{n\pi}{\alpha\sqrt{2L}}e^{-2\alpha(x-L/2)/L} & \text{(region III)}, \end{cases} \tag{2.231}$$

keeping only leading-order corrections in α^{-1}, where $\alpha^2 = mL^2V_0/2\hbar^2$.

(b) Show explicitly that $V(x)\,\psi_n(x) \longrightarrow 0$ in the classically forbidden regions in the limit $V_0 \longrightarrow \infty$, so that there is no contribution to the eigenstate energies from the forbidden regions.

Problem 2.24

The force operator in one dimension can be written $F = -\partial V/\partial x$ in terms of the potential $V(x)$. This comes form the Heisenberg equation of motion $\dot{p} = -\partial H/\partial x$, and so this force operator is appropriate

for a particle Hamiltonian of the form $H = p^2/2m + V(x)$. A particle in a potential well remains confined to the well because each "wall" of the well exerts a confining force on the particle.

(a) For a particle in the ground state $|0\rangle$ of a harmonic oscillator (Chapter 5), with $V(x) = m\omega^2 x^2/2$. Write down a sensible definition of the confining force (due to, say, the right-hand-side wall) in terms of an integral involving the wave function $\psi_0(x) = \langle x|0\rangle$ and F, and then compute it. We haven't studied the eigenstates yet, so you can use the expression

$$\psi_0(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}}\, e^{-m\omega x^2/2\hbar} \tag{2.232}$$

for the ground-state wave function.

(b) For the rest of this problem, consider the confining force for a particle of mass m in the ground state of the infinite-square-well potential of width L. The canonical derivation of the confinement force takes advantage of the well-defined wall position, and so it doesn't apply naturally to the case in (a). To work through the derivation, compute the change of the ground-state energy due to a change dL in the position of the right-hand wall, and then use the work-energy theorem to infer the force. You should obtain $F = dE/dL = -\pi^2\hbar^2/mL^3$.

(c) How do you alternately derive this confining force using the method from (a)? The problem is that it looks like the particle never "touches" the wall, because $V(x)\,|\psi(x)|^2 = 0$ everywhere. So set up a regularized force calculation in terms of the *finite*-square-well ground state, and compute the force in the infinite-square-well limit. Use the results of Problem 2.23 in setting up the calculation.

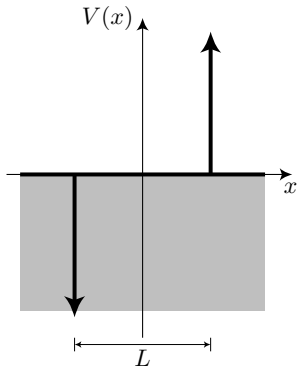
(d) Rederive the force in (b) by interpreting the ground-state eigenfunction as a superposition of left- and right-going plane waves, noting that in a time dt each wall transfers some of the particle's probability (and thus mass) density from one to the other plane wave.

Problem 2.25

Consider the delta well/barrier potential

$$V(x) = -\beta\,\delta(x + L/2) + \beta\,\delta(x - L/2), \qquad (\beta > 0), \tag{2.233}$$

as shown schematically below.



(a) Derive an equation whose solution determines the energies of bound states of this potential (i.e., an equation for the wave number k).

(b) Given some $\beta > 0$, how many bound states are there?

Problem 2.26

For the polar form

$$\psi(\mathbf{r}) = R\, e^{i\varphi} \tag{2.234}$$

of the wave function in terms of the real fields $R(\mathbf{r})$ and $\varphi(\mathbf{r})$, show that the probability current density is

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar|\psi|^2}{m}\nabla\varphi. \tag{2.235}$$

Thus, a phase gradient is required for a nonzero probability current.

Problem 2.27

Complete the derivation from Section 2.6.2 for the amplitude reflection and transmission coefficients of the square barrier of height V_0, width L, and incident energy $E < V_0$. Solve the continuity boundary-condition equations to derive the amplitude transmission coefficient

$$\tau = \frac{\tau_1\tau_1' e^{-\kappa L}e^{-ikL}}{1 - r_1^2 e^{-2\kappa L}} \tag{2.236}$$

as well as the amplitude reflection coefficient

$$r = \frac{r_1(1 - e^{-2\kappa L})\, e^{-ikL}}{1 - r_1^2 e^{-2\kappa L}}, \tag{2.237}$$

where

$$\tau_1 = -\frac{2ik}{\kappa - ik}, \qquad r_1 = -\frac{\kappa + ik}{\kappa - ik}, \qquad \tau_1' = \frac{2\kappa}{\kappa - ik} \tag{2.238}$$

are respectively the transmission and reflection coefficients for a potential step, and note that τ_1' is obtained from τ_1 as the complex conjugate of τ_1 after interchanging k and κ.

Hint: if you put the boundary-condition equations in matrix form, then with a couple of matrix manipulations you will be able to simplify matters by eliminating the wave-function amplitudes a and b for the barrier region. Also it may be handy to know the matrix-inversion formula

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix}^{-1} = \frac{1}{AD - BC}\begin{bmatrix} D & -B \\ -C & A \end{bmatrix}. \tag{2.239}$$

Problem 2.28

Consider the solution to a one-dimensional scattering potential at a single potential interface:

$$\psi(x) = \begin{cases} e^{ikx} + re^{-ikx} & (x < 0) \\ \tau e^{i\kappa x} & (x > 0). \end{cases} \tag{2.240}$$

We assume the incident energy to be large enough that all waves are propagating, with $k, \kappa > 0$. Note that the wave vector is k on the left-hand side of the interface, and κ to the right. This setup could correspond to a potential step, a delta-function potential, or other interfaces. The interface can even have finite thickness, provided its interior is excluded from the solution—that is, the plane waves in this setup need only refer to the *asymptotics* of the ingoing and outgoing waves at large $|x|$.

The reflection amplitude r and the transmission amplitude τ are not in general the same if the wave is incident on the other side of the interface. A solution impinging thusly on the interface can be written

$$\psi'(x) = \begin{cases} \tau' e^{-ikx} & (x < 0) \\ e^{-i\kappa x} + r' e^{i\kappa x} & (x > 0) \end{cases} \tag{2.241}$$

in terms of the incident-from-the-right reflection amplitude r' and the transmission amplitude τ'.

The wave functions $\psi(x)$ and $\psi'(x)$ here are solutions of the time-independent Schrödinger equation, and thus of the Helmholtz equation $(\nabla^2 + k^2)\psi(x) = 0$, with enforcement of the appropriate boundary condition. Complex conjugation of this equation shows that $\psi^*(x)$ and $\psi'^*(x)$ are also valid solutions (effectively, these correspond to time-reversed versions of the original solutions). Thus, for example, the conjugate

$$\psi'^*(x) = \begin{cases} \tau'^* e^{ikx} & (x < 0) \\ e^{i\kappa x} + r'^* e^{-i\kappa x} & (x > 0) \end{cases} \tag{2.242}$$

is a wave that has incident components from the left and from the right, but only has one outgoing component, to the right.

Note that an appropriate superposition of the solutions (2.240) and (2.241) has the same τ'^* and r'^* components as the conjugate solution (2.242). By requiring complete equivalence of the two expressions, derive the following relations among the coefficients:

$$r' = -r^* \frac{\tau}{\tau^*}, \qquad \tau'\tau^* = 1 - |r|^2. \tag{2.243}$$

(Stokes relations)

These are called the **Stokes relations** for the reflection and transmission amplitudes. Commonly, these are derived under the assumption that the amplitudes are real-valued, in which case they read $r' = -r$ and $\tau'\tau = 1 - |r|^2$. But in the general case it is useful to note that Eqs. (2.243) imply

$$|r'| = |r|, \qquad |\tau'| = |\tau| \frac{\kappa}{k} \tag{2.244}$$

for the relative magnitudes of the coefficients in each direction. (In fact it turns out that $\tau' = \tau(\kappa/k)$, something that comes up in the course of solving Problem 2.29.)

Problem 2.29

A useful way to recast the problem of scattering in one dimension is to reorganize the waves into *ingoing* waves

$$\psi_{\text{in}}(x) = \begin{cases} A_{\text{in}} e^{ikx} & (x < 0) \\ B_{\text{in}} e^{-i\kappa x} & (x > 0) \end{cases} \tag{2.245}$$

and *outgoing* waves

$$\psi_{\text{out}}(x) = \begin{cases} A_{\text{out}} e^{-ikx} & (x < 0) \\ B_{\text{out}} e^{i\kappa x} & (x > 0) \end{cases} \tag{2.246}$$

with respect to some scattering potential centered at $x = 0$. (Again, the scatterer may have some finite width, in which case the indicated waves refer to the asymptotic forms of the waves.) Then an arbitrary solution with some definite energy $E = \hbar^2 k^2 / 2m$ is a linear combination of these ingoing and outgoing waves with suitable choices of the coefficients to match the boundaries, just as it would be a linear combination of the modes (2.240) and (2.241) in Problem 2.28.

But by the definitions of the reflection and transmission coefficients in Problem 2.28, we know that the wave amplitudes must be related by

$$\begin{bmatrix} A_{\text{out}} \\ B_{\text{out}} \end{bmatrix} = \begin{bmatrix} r & \tau' \\ \tau & r' \end{bmatrix} \begin{bmatrix} A_{\text{in}} \\ B_{\text{in}} \end{bmatrix}, \tag{2.247}$$

where unprimed coefficients refer to incidence from the left, and primed coefficients refer to incidence from the right.

(a) Based on conservation of total probability current density, argue that the matrix in Eq. (2.247) is not unitary in general, but that the matrix

$$(U) = \begin{bmatrix} r & \tau'\sqrt{k/\kappa} \\ \tau\sqrt{\kappa/k} & r' \end{bmatrix} \tag{2.248}$$

should be unitary.

(b) Use the Stokes relations (2.243) of Problem 2.28 and the fact that total probability current density is conserved to prove explicitly that the matrix (2.248) is unitary. Thus the Stokes relations are essentially a statement of unitarity in the coupling of ingoing and outgoing waves.

Problem 2.30

The goal of this problem is to explore the Stokes relations of Problem 2.28 in the context of a potential step.

(a) The reflection and transmission amplitudes at a potential step [Eq. (2.138)] are

$$r = \frac{k - |\kappa|}{k + |\kappa|}, \qquad \tau = \frac{2k}{k + |\kappa|}, \tag{2.249}$$

in the case where the incident energy E is everywhere larger than the potential ($E > 0$ and $E > V_0$). Use the Stokes relations (2.243) to compute the amplitudes r' and τ' for incidence from the right, to obtain

$$r' = \frac{|\kappa| - k}{|\kappa| + k}, \qquad \tau' = \frac{2|\kappa|}{k + |\kappa|}. \tag{2.250}$$

Note that these are just the original amplitudes, but with k and $|\kappa|$ interchanged.

(b) Recall that he transmission and reflection amplitudes (2.135) for a rising potential step and a low incident energy ($E < V_0$, in the case $V_0 > 0$) are

$$r = -\frac{\kappa + ik}{\kappa - ik}, \qquad \tau = -\frac{2ik}{\kappa - ik}. \tag{2.251}$$

Recall that we made the replacement $\kappa \longrightarrow -i|\kappa|$ in order to adapt these amplitudes to the case of Eqs. (2.249). By reversing this replacement in Eqs. (2.250), derive the expressions

$$r' = \frac{\kappa + ik}{\kappa - ik} = -r, \qquad \tau' = \frac{2\kappa}{\kappa - ik}. \tag{2.252}$$

Note that these are also obtained from their counterparts (2.251) by exchanging $k \longleftrightarrow \kappa$, and conjugating the results.

(c) Now use the Stokes relations to derive expressions for r' and τ' based on the amplitudes (2.251). You should find results that are inequivalent to those of Eqs. (2.252). Why should the Stokes relations produce nonsensical results in this case?

Problem 2.31

Recall that the reflection and transmission coefficients for the delta-barrier potential (and the delta-well potential, in the case $\beta < 0$) are given by

$$r = \frac{1}{i\hbar^2 k/m\beta - 1}, \qquad \tau = \frac{1}{1 + im\beta/\hbar^2 k}. \tag{2.253}$$

(a) Compute the ''other-side'' coefficients r' and τ' from the Stokes relations for this potential. Explain why the resulting coefficients make sense.

(b) Demonstrate explicitly in this case that the coefficients induce a *unitary* transformation between the ingoing and outgoing modes of the form

$$(U) = \begin{bmatrix} r & \tau \\ \tau & r \end{bmatrix}. \tag{2.254}$$

Problem 2.32

The point of this problem is to finish up the discussion of the transmission resonances in the problem of scattering from a square well (Section 2.6.2.1), or from a square barrier with an above-the-barrier incident energy.

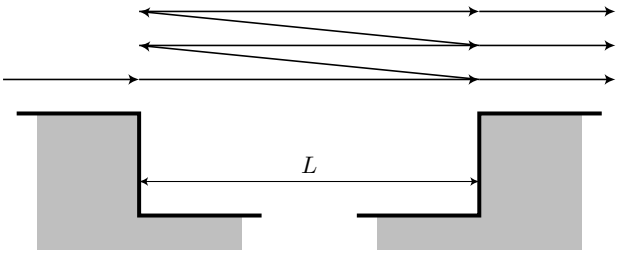
(a) The correct summation over the transmitted amplitudes is

$$\tau = e^{i(|\kappa|-k)L}\Big(\tau_1\tau_1' + \tau_1 r_1'^2\tau_1' e^{i2|\kappa|L} + \tau_1 r_1'^4\tau_1' e^{i4|\kappa|L} + \cdots\Big), \tag{2.255}$$

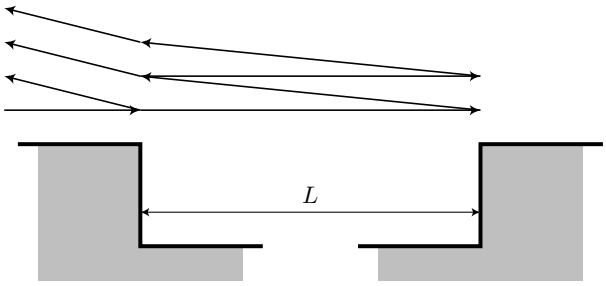
where r_1 and τ_1 are the respective reflection and transmission coefficient (amplitude) for a single potential step when the wave is *entering* the well, and r_1' and τ_1' are the coefficients when the wave is *exiting* the well. Similarly, the correct sum over all of the reflected amplitudes is

$$r = e^{-ikL}\Big(r_1 + \tau_1 r_1'\tau_1' e^{i2|\kappa|L} + \tau_1 r_1'^3\tau_1' e^{i4|\kappa|L} + \cdots\Big), \tag{2.256}$$

in terms of the same single-interface ampitudes. Justify all of the reflection and transmission amplitudes in these sums, along with all the phase factors. As a guide, you can use the diagram below of the first few transmitted amplitudes,



and the first few reflected amplitudes diagrammed below.



(b) Now sum the two series to obtain the expressions

$$\begin{aligned} \tau &= \frac{\tau_1\tau_1' e^{i(|\kappa|-k)L}}{1 - r_1'^2\, e^{i2|\kappa|L}} \\ r &= \frac{r_1 + r_1'(\tau_1\tau_1' - r_1 r_1')e^{i2|\kappa|L}}{1 - r_1'^2\, e^{i2|\kappa|L}}\, e^{-ikL}. \end{aligned} \tag{2.257}$$

These expressions are quite generally valid, they are not specific to a potential well. For example, see Problem 2.33 for the example of a pair of delta barriers; but they are even valid for *thick* interfaces, provided the phases are properly accounted for in defining r_1 and τ_1.

(c) Finally, apply the Stokes relations (2.243), under the assumption that r_1 and τ_1 are real, to show that Eqs. (2.257) can be written as in Eqs. (2.137):

$$\begin{aligned} \tau &= \frac{\tau_1 \tau_1' e^{i|\kappa|L} e^{-ikL}}{1 - r_1^2 e^{i2|\kappa|L}} \\ r &= \frac{r_1 (1 - e^{i2|\kappa|L})\, e^{-ikL}}{1 - r_1^2 e^{i2|\kappa|L}}. \end{aligned} \tag{2.258}$$

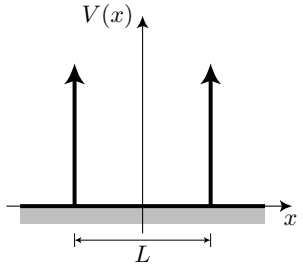
(d) Sum the amplitudes inside the potential well to obtain an expression for the amplitude a for the right-going component and the amplitude b for the left-going component (recalling that the eigenfunction inside the well has the form $ae^{i|\kappa|x} + be^{-i|\kappa|x}$). Make sure to include any appropriate phase factors.

Problem 2.33

Consider the symmetric double-delta barrier potential, given by

$$V(x) = \beta\, \delta(x - {}^{L}\!/_{2}) + \beta\, \delta(x + {}^{L}\!/_{2}), \tag{2.259}$$

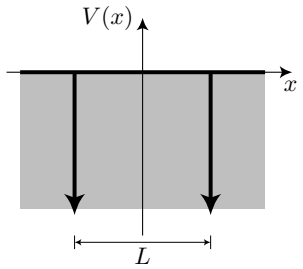
as shown schematically below.



Note that for $\beta < 0$, this potential also corresponds to the symmetric double delta well,

$$V(x) = -|\beta|\, \delta(x - {}^{L}\!/_{2}) - |\beta|\, \delta(x + {}^{L}\!/_{2}), \tag{2.260}$$

as shown schematically below.



(a) Treat this system as a scattering problem (with an incident energy $E > 0$), and use the boundary-matching method show that the condition for the scattering resonances is

$$\tan kL = \frac{\hbar^2 k}{m\beta}. \tag{2.261}$$

That is, the transmission probability is unity whenever this condition is satisfied. Also show that the transmission and reflection coefficients may be written

$$\begin{aligned} \tau &= \frac{{\tau_1}^2}{1 - r_1^2 e^{i2kL}} \\ r &= \frac{2r_1[1 + (\tau_1^2 - r_1^2)\, e^{i2kL}]\, e^{-ikL}}{1 - r_1^2 e^{i2kL}} \end{aligned} \tag{2.262}$$

in terms of the transmission and reflection coefficients τ_1 and r_1, respectively, of a single delta-potential reflector (see Problem 2.31).

(b) Show that the coefficients (2.262) can be reproduced by summing over all the appropriate reflected and transmitted components of the incident wave.

Problem 2.34

Consider a particle incident (from $x < 0$) on an *imaginary* potential step,

$$V(x) = iV_0\Theta(x), \qquad \Theta(x) = \begin{cases} 1, & x > 0 \\ 0, & x < 0, \end{cases} \tag{2.263}$$

with $V_0 \in \mathbb{R}$, in terms of the Heaviside step function $\Theta(x)$.

(a) By deriving an equation of motion for the norm of the wave function, show that time evolution in the presence of this potential is not norm-preserving. Does the norm increase or decrease with time?

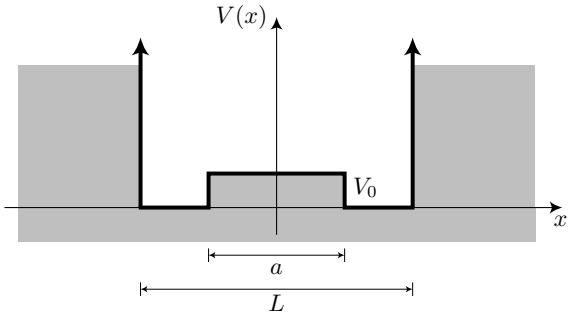
(b) Compute the amplitude reflection coefficient for this potential, writing your result (only) in terms of E and V_0.

Problem 2.35

Consider a double-well potential of the form

$$V(x) = \begin{cases} V_0, & |x| < a/2 \\ 0, & a/2 < |x| < L/2 \\ \infty, & |x| > L/2, \end{cases} \tag{2.264}$$

where $L > a > 0$ and $V_0 > 0$, as illustrated below.

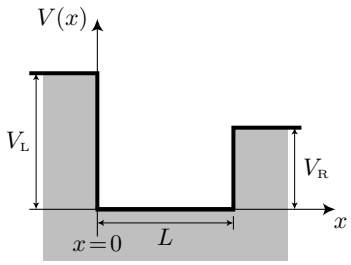


Derive an equation that determines the ground-state energy E_0. You may assume that V_0 is small, so that $E_0 > V_0$.

Problem 2.36

Consider the asymmetric finite potential well, shown below.[12]

[12] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory*, 2nd ed. (Pergamon, 1965) Problem 2, pp. 65-7 (ISBN: 0080209408).



(a) Derive an equation that determines the bound-state energy levels for $V_{\text{L}} > 0$ and $V_{\text{R}} > 0$. *Hint:* Set up the wave function in the middle region as $a\sin(kx + \delta)$.

(b) Show how the infinite-square-well limit comes about from your condition from (a).

(c) Suppose $V_{\text{L}} > V_{\text{R}} > 0$. What is the condition to have a single state in the well?

Problem 2.37

(a) Recall that for any set of basis states, the completeness of the basis [see Eq. (1.35)], expressed in the position representation in one dimension, reads

$$\sum_n \psi_n^*(x)\,\psi_n(x') = \delta(x - x'). \tag{2.265}$$

In terms of the infinite-square-well eigenfunctions, completeness reads

$$\frac{2}{L}\sum_n \sin(n\pi x)\sin(n\pi x') = \delta(x - x'), \tag{2.266}$$

while for the momentum eigenstates, completeness reads

$$\frac{1}{2\pi\hbar}\int dp\, e^{-ip(x-x')/\hbar} = \delta(x - x'). \tag{2.267}$$

These are two different representations for the delta function. Are they equivalent? If so, show this explicitly. If not, explain why not.

(b) We showed that the eigenstates of any symmetric potential has eigenfunctions that are either even or odd. However, for the free particle, we were using eigenstates of the form $e^{ipx/\hbar}$ that are neither odd nor even. Is this a contradiction? (Obviously not, so explain why not.)

Problem 2.38

When you're doing quantum mechanics, you're not *just* doing quantum mechanics. You're also doing, for example, *statistical* mechanics. The point of this problem is to explore this idea, from escaping random walks to geophysics, based on what we've covered so far.

(a) The free-particle Schrödinger equation

$$i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\partial_x^2\psi, \tag{2.268}$$

under the imaginary-time replacement $t \longrightarrow -it$ (along with the replacement $\hbar \longrightarrow m$ to get rid of extra constants), becomes the **diffusion equation**

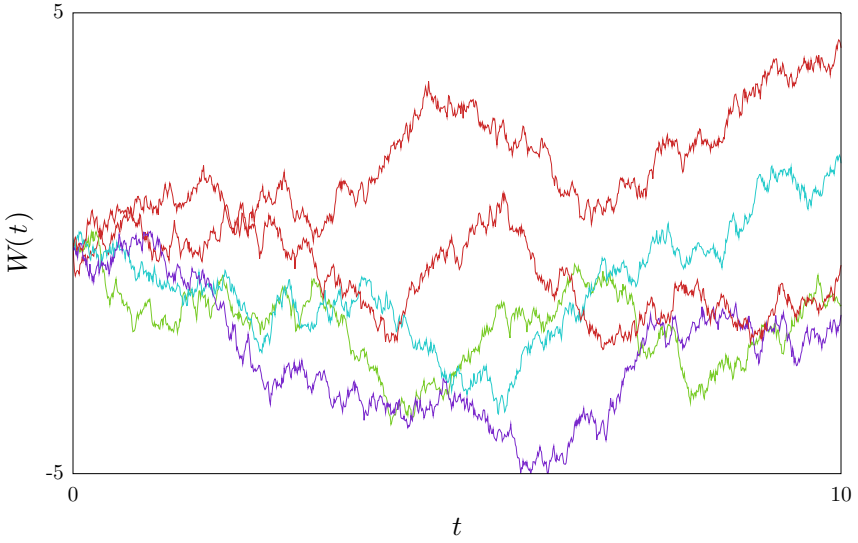
$$\partial_t\psi = \frac{1}{2}\partial_x^2\psi. \tag{2.269}$$

Make the same replacements in the free-particle propagator to show that the solution to the diffusion equation may be written

$$\psi(x,t) = \frac{1}{\sqrt{2\pi(t-t_0)}}\, e^{-(x-x_0)^2/2(t-t_0)}, \tag{2.270}$$

given the initial condition $\psi(x,t_0) = \delta(x-x_0)$. (Note that this solution only makes sense for $t \geq t_0$.)

(b) As the solution of the diffusion equation, the appropriately normalized $\psi(x,t)$ acts as a probability density for an ensemble of diffusing particles (*not* $|\psi(x,t)|^2$, as in quantum mechanics). The diffusing particles are said to undergo **Brownian motion**. We can take Eq. (2.270) to be the definition of Brownian motion, but more intuitively, you can think of a Brownian motion as a random walk, taking a random, independent step of variance Δt during every time step Δt, but in the continuous limit $\Delta t \longrightarrow 0$. The resulting paths are a bit complicated to handle, because they turn out to be continuous but everywhere nondifferentiable functions of time. Thus, we'll only treat them mathematically via the diffusion equation, although it's good to have some underlying mental picture of what the individual, diffusing particles are up to. For illustration, five different realizations of Brownian motion are plotted below [here $W(t)$ is a standard notation for Brownian motion].



One nice application of the result of part (a) is to ask, given that a Brownian particle starts at some position $d > 0$, what is the probability that it will cross the origin, and how long does it take? To set this up, note that the Schrödinger equation with a potential

$$i\hbar\partial_t\psi = -\frac{\hbar^2}{2m}\partial_x^2\psi + V(x)\psi \tag{2.271}$$

goes to the damped diffusion equation

$$\partial_t\psi = \frac{1}{2}\partial_x^2\psi - \frac{1}{m}V(x)\psi \tag{2.272}$$

under the same imaginary-time replacements as before. This means that where $V(x) > 0$, particles are disappearing (or "decaying") exponentially at a rate $V(x)/m$ [note that this is particle *creation* if $V(x) < 0$].

A good way to set up this boundary-crossing problem is to make the region $x < 0$ completely absorbing—that is, $V(x) = \infty$ for $x < 0$, and $V(x) = 0$ for $x > 0$. Then any particles from the ensemble that cross the origin are removed from the ensemble, and we can track the crossing probability by computing the (decaying) norm of the probability distribution. This potential is equivalent to a single, infinite barrier in quantum mechanics, and the potential here similarly imposes a Dirichlet

boundary condition on the probability distribution, $\psi(0,t) = 0$. It's easiest to satisfy this boundary condition by the method of images, which states that if $\psi(x,t)$ solves the diffusion equation (2.269), then

$$\check{\psi}(x,t) := \psi(x,t) - \psi(-x,t) \tag{2.273}$$

solves the diffusion equation with a Dirichlet boundary condition at $x = 0$. With the solution (2.270), starting at $x_0 = d$ at $t_0 = 0$, we have

$$\check{\psi}(x,t) = \frac{1}{\sqrt{2\pi t}}\left(e^{-(x-d)^2/2t} - e^{-(x+d)^2/2t}\right) \tag{2.274}$$

as the probability density for Brownian walkers starting at $x = d$ with a perfect absorber at $x = 0$.

Integrate this density over $x \in [0,\infty)$ to obtain the survival probability (i.e., the probability to *not* cross the origin) with time, then compute the crossing probability with time. Noting that the crossing probability $P_{\text{cross}}(t)$—which refers to the probability that, up to time t, the walker has *ever* touched the origin—and the probability density $f_{\tau_\text{d}}(x)$ for the *first*-crossing time τ_d are related by

$$P_{\text{cross}}(t) = \int_0^t d\tau\, f_{\tau_\text{d}}(\tau), \tag{2.275}$$

compute the first-passage density $f_{\tau_\text{d}}(\tau)$.

In your solutions, you should find that:

- The crossing probability converges to 1 as $t \longrightarrow \infty$ (that is, the Brownian walker will, with *certainty*, eventually hit the origin).
- The long-time tail of the first-crossing density scales as $x^{-3/2}$.

At this point, a gambling-related example might make this problem a little less abstract. Suppose you walk into a casino with an initial amount d of money. It's an idealized casino where on each game, you win or lose an amount δx of money, with equal probability of win or loss. The casino tosses you out in the event you go broke; so what is the probability density for being tossed out of the casino at time t? The above calculation models this situation (of **gambler's ruin**) in the limit where $\delta x \ll d$ and $\delta x \ll L$. It says that you will *definitely* get tossed out if you try to play for an arbitrarily long time. So quit while you're ahead!

(c) Lord Kelvin used a setup similar to that of (b) to estimate the age of the Earth. First, the **heat-conduction equation** is the same as the diffusion equation (2.269), but with the replacement $t \longrightarrow 2\alpha t$,

$$\partial_t \psi = \alpha \partial_x^2 \psi, \tag{2.276}$$

where α is the **thermal diffusivity**. Here, $\psi(x,t)$ represents the space- and time-dependent temperature profile of a thermally conductive medium. Kelvin's model of the Earth is that it started as a ball of uniform temperature, which then cooled with time due to radiation at the surface. To model this, assume that we are looking at a relatively shallow depth near Earth's surface, so we can treat Earth's surface as flat, and let $\psi(x,t)$ denote the temperature profile at depth $x > 0$. We will also assume constant diffusivity α with depth.

The initial condition is

$$\psi(x,0) = \psi_0, \tag{2.277}$$

where ψ_0 is a ''core temperature,'' as compared to the surface temperature (we'll reinterpret ψ_0 shortly). The temperature profile is subject to the Dirichlet boundary condition

$$\psi(0,t) = 0, \tag{2.278}$$

representing cooling at the surface (i.e., thermal contact with outer space). Now show that the solution

$$\psi(x,t) = \frac{\psi_0}{\sqrt{4\pi\alpha t}} \int_0^\infty dx' \left(e^{-(x-x')^2/4\alpha t} - e^{-(x+x')^2/4\alpha t}\right) \tag{2.279}$$

satisfies the initial condition and the boundary condition. Carry out the integration, and compute the temperature gradient at the surface

$$G := \left.\frac{\partial\psi}{\partial x}\right|_{x=0}. \tag{2.280}$$

Solving for t, you should find

$$t = \frac{\psi_0^2}{\pi\alpha G^2}. \tag{2.281}$$

The Earth's temperature gradient and thermal diffusivity can both be measured. For ψ_0, this can be taken to be the melting point of the Earth's crust (note that, handily, no *distance* appears, so the temperature at the edge of the region where α is constant will work nicely here). Lord Kelvin, using the measurements available at the time, gave an estimate[13] of 10^8 years for the age of the Earth, which is not too bad compared to the current estimate of 4.5×10^9 years.

(d) An interesting problem related to the boundary-crossing problem is that of a Brownian particle escaping from an interval $[0, L]$ in x. And, because we need to set up perfect absorbers at $x = 0$ and $x = L$, it's just the same as the infinite square well!

To revisit the casino analogy from before, this calculation models the case where you have an upper limit (goal) of money L, where you would quit when you reach your goal. Here you'll model the probability density for stopping (due either to getting tossed out or winning enough to buy that new car that you want). But it's easy to generalize the calculation to yield the probabilities of getting tossed out vs. winning your goal.

In Problem 2.7, you showed that, given a solution $\psi(x, t)$ to the free-particle problem, the image-laden version

$$\check{\psi}(x,t) := \sum_{j=-\infty}^{\infty}\Big[\psi(x + 2jL, t) - \psi(2jL - x, t)\Big] \tag{2.282}$$

is a solution to the infinite square well on $x \in [0, L]$ (note that we're skipping the normalization factor now, because we *want* the solution to become unnormalized).

Adapt this solution to the case of a Brownian walker starting at $x_0 \in [0, L]$, and show that probability of (first) escaping the interval $[0, L]$ in time t is

$$P_{\text{escape}}(t) = 1 - \sum_{j=-\infty}^{\infty}\left[\operatorname{erf}\!\left(\frac{x_0 + 2jL}{\sqrt{2t}}\right) - \frac{1}{2}\operatorname{erf}\!\left(\frac{x_0 + 2(j + 1/2)L}{\sqrt{2t}}\right) - \frac{1}{2}\operatorname{erf}\!\left(\frac{x_0 + 2(j - 1/2)L}{\sqrt{2t}}\right)\right]. \tag{2.283}$$

(e) The expression (2.283) is a bit complicated to read, but it is useful for obtaining the short-time escape behavior. Assume the centered initial condition $x_0 = L/2$, and then compute the probability density of first-escape times $f_{\text{escape}}(\tau)$, which is related to $P_{\text{escape}}(\tau)$ in the same way as in Eq. (2.275). At this point it should be clear that the short-time behavior is dominated by the $j = 0$ term, and thus given by

$$f_{\text{escape}}(\tau) \sim \frac{L}{\sqrt{2\pi\tau^3}}\, e^{-L^2/8\tau}. \tag{2.284}$$

Reconcile this solution with your result from part (b).

(f) Using the eigenstates of the infinite square well, we can even get an expression for the evolving probability density for the escaping ensemble of Brownian walkers in part (d). Using the quantum eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\frac{n\pi x}{L}, \tag{2.285}$$

[13] T. W. Körner, *Fourier Analysis* (Cambridge, 1988) Chapters 56-8 (ISBN: 0521389917).

recall that the time dependence is of the form $e^{-iE_n t/\hbar}$, where

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}. \tag{2.286}$$

With the imaginary-time replacements, we have

$$\frac{E_n}{\hbar} \longrightarrow \frac{n^2\pi^2}{2L^2}, \tag{2.287}$$

and a time-dependence factor of $e^{-iE_n t/\hbar} \longrightarrow e^{-n^2\pi^2 t/2L^2}$, or that is,

$$\psi_n(x,t) = \sqrt{\frac{2}{L}}\,\sin\Big(\frac{n\pi x}{L}\Big)\; e^{-n^2\pi^2 t/2L^2}. \tag{2.288}$$

Now starting with the initial condition

$$\psi(x,0) = \delta(x - x_0), \tag{2.289}$$

write this as a superposition of eigenstates to derive an expression for the decaying (unescaped) density $\psi(x,t)$. Use your result to derive the expression

$$P_{\text{escape}}(t) = 1 - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{[1-(-1)^n]}{n}\sin\Big(\frac{n\pi x_0}{L}\Big)\; e^{-n^2\pi^2 t/2L^2} \tag{2.290}$$

as an alternative to Eq. (2.283).

(g) Equation (2.290) is not obviously equivalent to Eq. (2.283); but the latter is useful for short-time asymptotics, while the former is better for long-time behavior. In this case the long-time behavior is dominated by the term with the smallest (i.e., ground-state) eigenvalue. Thus compute the long-time tail of the probability distribution of first-escape times, and show that the long-time decay is exponential.

This is much faster than the power-law decay of part (b). Essentially, the slow decay of the tail in (b) is due to diffusive trajectories that wander far away from the boundary before crossing it. In part (f), these trajectories don't happen because of the presence of a boundary on either side of the starting point.

Chapter 3

Double-Well Potentials and Two-State Dynamics

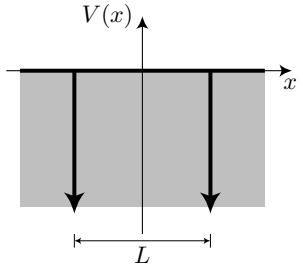
Previously, in Chapter 2, we studied barrier tunneling as a scattering-type problem, where an incoming plane wave partially penetrated and partially reflected from a barrier. The goal here is to study a related problem of barrier tunneling: This time, a particle starts in a potential well and moves into another well by tunneling through an intervening barrier. This problem is richer in a dynamical sense, and is a good example for studying transitions between two discrete states.

3.1 Prototype System: Particle in Two Delta-Function Wells

As a concrete example of two potential wells coupled by a potential barrier, consider the double delta well of the form

$$V(x) = -\beta\,\delta(x - L/2) - \beta\,\delta(x + L/2), \tag{3.1}$$

as shown schematically below.



This potential is a simple, toy model for a more general double-well problem, in the sense that we can ignore the internal structures of the wells and focus on the tunneling transport *between* the wells.

Recall that if we consider each well *separately* (e.g., in the limit $L \longrightarrow \infty$), then there is exactly one bound state per well, and the one-well state and energy are, respectively,

$$\psi_1(x) = \sqrt{\frac{m\beta}{\hbar^2}}\, e^{-m\beta|x|/\hbar^2} \tag{3.2}$$

and

$$E_1 = -\frac{m\beta^2}{2\hbar^2}, \tag{3.3}$$

from our previous treatment [see Eqs. (2.90)–(2.91)], where the coordinate x here is taken to be relative to the center of the well. Since the *double* well represented by Eq. (3.1) is symmetric, we expect definite-parity

eigenstates. Combining this intuition with the one-well solution, we can guess that there will be two bound states—one even, one odd. It turns out that this is true. Well, sort of.

The setup to solve this problem goes in the usual way, by assuming a piecewise solution

$$\psi_E(x) = \begin{cases} a_{\rm I} e^{\kappa x} & (x < -L/2) \\ a_{\rm II} e^{-\kappa x} + b_{\rm II} e^{\kappa x} & (-L/2 < x < L/2) \\ a_{\rm III} e^{-\kappa x} & (x > L/2), \end{cases} \tag{3.4}$$

where

$$\kappa = \frac{\sqrt{2m|E|}}{\hbar}, \tag{3.5}$$

and $E < 0$ for a bound state. Treating first the even solution ($a_{\rm III} = a_{\rm I}$, $b_{\rm II} = a_{\rm II}$), continuity of $\psi_E(x)$ at $x = -L/2$ gives

$$a_{\rm I} e^{-\kappa L/2} = 2a_{\rm II} \cosh \kappa L/2, \tag{3.6}$$

while at $x = -L/2$, $\psi'_E(x)$ suffers a discontinuity according to

$$\psi'_E(-L/2 + 0^+) = \psi'_E(-L/2 - 0^+) - \frac{2m\beta}{\hbar^2}\psi_E(-L/2), \tag{3.7}$$

which translates to

$$\kappa a_{\rm I} e^{-\kappa L/2} = -2\kappa a_{\rm II} \sinh \kappa L/2 + \frac{4m\beta}{\hbar^2} a_{\rm II} \cosh \kappa L/2. \tag{3.8}$$

Dividing this relation by Eq. (3.6), we find the energy condition

$$\kappa \left(\tanh \frac{\kappa L}{2} + 1 \right) = \frac{2m\beta}{\hbar^2}. \tag{3.9}$$
(even-state condition)

Notice that the left-hand side is a function of κ that increases monotonically from 0 to ∞. The right-hand side is nonnegative for nonnegative β, so given any nonnegative values of β and L, we are guaranteed a solution of this equation.

We can analyze the odd-parity bound state ($a_{\rm III} = -a_{\rm I}$, $b_{\rm II} = -a_{\rm II}$) in a similar way. Continuity of $\psi_E(x)$ at $x = -L/2$ gives

$$a_{\rm I} e^{-\kappa L/2} = 2a_{\rm II} \sinh \kappa L/2, \tag{3.10}$$

while at $x = -L/2$, the discontinuity condition for $\psi'_E(x)$ is

$$\kappa a_{\rm I} e^{-\kappa L/2} = -2\kappa a_{\rm II} \cosh \kappa L/2 + \frac{4m\beta}{\hbar^2} a_{\rm II} \sinh \kappa L/2. \tag{3.11}$$

Dividing these two conditions lead to

$$\kappa \left(\coth \frac{\kappa L}{2} + 1 \right) = \frac{2m\beta}{\hbar^2}. \tag{3.12}$$
(odd-state condition)

This condition is a little more subtle than the even-parity version. Schematically, we can view this condition in the form

$$x(\coth x + 1) = b, \tag{3.13}$$

where $x = \kappa L/2$, and $b = m\beta L/\hbar^2$. As $x \longrightarrow 0$, $\coth x \sim 1/x$. This means that $x(\coth x + 1)$ has a minimum value of 1 as $x \longrightarrow 0$. This function also rises monotonically with x without bound. Thus, there is a critical value of $b = 1$ that determines whether or not this condition has a solution. In particular, there is a solution if and only if $b \geq 1$. In terms of the original variables, this means $m\beta L/\hbar^2 > 1$, or at fixed β, the condition for an odd-parity solution

$$L \geq \frac{\hbar^2}{m\beta}. \tag{3.14}$$
(condition for odd-parity bound state)

That is, at fixed β, there is a *minimum distance* between the potential wells for an odd-parity bound state to exist. As we will see, the tunneling interaction between the wells shifts the bound-state energies away from the uncoupled value (3.3). For sufficiently small distances, the interaction between the wells is large enough to push the odd-parity energy above $E = 0$.

3.1.1 Lambert W Function

It is possible to write the solutions of Eqs. (3.9) in terms of a known special function, but since this is not one of the more famous functions among physicists, it's worth spending a moment to develop it a bit before proceeding.

The **Lambert W function** $W(z)$ is defined by the relation

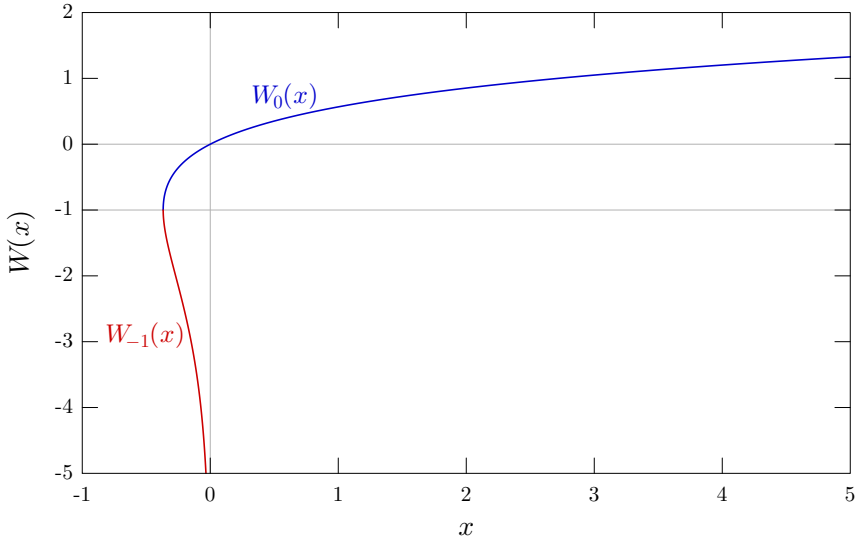
$$z = W(ze^z)\,. \qquad \text{(defining relation, Lambert } W \text{ function)} \tag{3.15}$$

It is a little easier to start by discussing the *inverse* of the function, which is

$$W^{-1}(y) = ye^y. \tag{3.16}$$

Notice that the inverse function has a minimum value at $e^y + ye^y = 0$, or $y = -1$, where $W^{-1}(-1) = -1/e$. The inverse function rises monotonically on either side of $y = 1$, which of course means that the *inverse* of this inverse function (i.e., $W(z)$ itself) is multi-valued. That is, the "Lambert W function" is, in fact, multi-valued, and thus not really a function.

However, $W(z)$ has at most two values for each real value of z, and thus we can think of it as a *pair* of functions, or **branches**. Since $W^{-1}(y) \longrightarrow \infty$ as $y \longrightarrow \infty$, we can regard one branch as defined on $z \in [-1/e, \infty)$, and it takes on values from $W(-1/e) = -1$ to $W(\infty) = \infty$—this branch is denoted $W_0(z)$. Since $W^{-1}(y) \longrightarrow 0$ as $y \longrightarrow -\infty$, the other branch is defined on $z \in [-1/e, 0)$, and it takes on values from $W(-1/e) = -1$ to $W(0) = -\infty$. The two branches of the W function are shown in the plot below.



For the purposes of derivation, it is often more convenient to let $z \longrightarrow W(z)$ in Eq. (3.15) to obtain

$$z = W(z)\, e^{W(z)}, \qquad \text{(alternate relation, Lambert } W \text{ function)} \tag{3.17}$$

as an alternate defining relation for the W function.

The W function doesn't come up much as a "textbook" special function in physics, although it does appear in electronics as part of the solution of a voltage "divider" of a resistor in series with a forward-biased, ideal diode.[1]

[1] Daniel A. Steck, *Analog and Digital Electronics*, available online at `http://steck.us/teaching` (2015).

3.1.2 Application to Double-Delta-Well Problem

To recast the double delta well in terms of the W function,[2] let's start by rewriting the even-party condition (3.9) as

$$x\left(\tanh\frac{x}{2}+1\right)=2b, \tag{3.18}$$

where

$$x=\kappa L, \qquad b=\frac{m\beta L}{\hbar^2}. \tag{3.19}$$

Using $1+\tanh x = e^x/\cosh x$, and then rewriting the cosh in terms of exponentials, after a few manipulations this reduces to

$$(x-b)\,e^{x-b}=b\,e^{-b}. \tag{3.20}$$

Comparing this to Eq. (3.17), we can write

$$x-b=W\big(b\,e^{-b}\big), \tag{3.21}$$

or in terms of the original variables,

$$\kappa=\frac{m\beta}{\hbar^2}+\frac{1}{L}W_0\left(\frac{m\beta L}{\hbar^2}\,e^{-m\beta L/\hbar^2}\right). \tag{3.22}$$
(even-parity wave number)

Note that we specifically wrote this solution in terms of the upper branch $W_0(z)$. This is because asymptotically, as $L\longrightarrow\infty$ (or $\beta\longrightarrow\infty$), the argument of $W(z)$ goes to zero, and $W_0(z)$ is the only branch connected continuously to $W_0(0)=0$. Thus, in this limit, $\kappa=m\beta/\hbar^2$, which is consistent with the wave number in the decoupled solution (3.2).

The odd-parity solution follows in a similar way. With the same variable changes, the condition (3.12) is

$$x\left(\coth\frac{x}{2}+1\right)=2b. \tag{3.23}$$

Using $1+\coth x = e^x/\sinh x$, writing out the sinh in terms of exponentials, and then simplifying leads to the alternate condition

$$x-b=W\big(-b\,e^{-b}\big), \tag{3.24}$$

which becomes

$$\kappa=\frac{m\beta}{\hbar^2}+\frac{1}{L}W_0\left(-\frac{m\beta L}{\hbar^2}\,e^{-m\beta L/\hbar^2}\right) \tag{3.25}$$
(odd-parity wave number)

in the original variables. This solution has the same asymptotic behavior of $\kappa\longrightarrow m\beta/\hbar^2$ in the decoupled-well limit $\beta L\longrightarrow\infty$, as it should. However, this solution is a little tricky, in the sense that as a function of $m\beta L/\hbar^2$, the argument of the W function goes from zero to $-1/e$ and back to zero. However, keeping in mind our earlier condition (3.14), the marginal case when the argument $-be^{-b}$ hits $-1/e$ (at $b=1$, or $m\beta L/\hbar^2=1$) corresponds to where the W function changes between branches,[3] and no longer corresponds to a physical solution. Thus, this wave-number solution is only valid subject to condition (3.14).

To summarize the bound-state solutions to the symmetric double-delta well, we have wave numbers

$$\kappa_\pm=\frac{m\beta}{\hbar^2}+\frac{1}{L}W_0\left(\pm\frac{m\beta L}{\hbar^2}\,e^{-m\beta L/\hbar^2}\right), \tag{3.26}$$
(bound-state wave numbers)

[2] This solution was given by T. C. Scott, J. F. Babb, A. Dalgarno, and John D. Morgan, III, "The calculation of exchange forces: General results and specific models," *The Journal of Chemical Physics* **99**, 2841 (1993) (doi: 10.1063/1.465193), who studied the double delta well as a model for a diatomic molecule.

[3] Incidentally, it may be tempting to look at Eq. (3.24) or (3.25), and then look at the defining relation $z=W(ze^z)$, and conclude that we can replace $W(-b\,e^{-b})$ by $-b$, leading to the trivial solution $x=0$ (or $\kappa=0$). For the physical range of b, though it is only the branch $W_{-1}(z)$ where this relation applies; it does not apply to $W_0(z)$. To summarize, $W_{-1}(-b\,e^{-b})=-b$ for $b>1$, but the other branch takes over at the critical point $b=1$, i.e., $W_0(-b\,e^{-b})=-b$ for $b<1$.

where the plus sign refers to the even-parity solution, and the minus sign refers to the odd-parity solution. The corresponding energies $E_\pm = -\hbar^2\kappa_\pm^2/2m$ are then

$$E_\pm = -\frac{\hbar^2}{2m}\left[\frac{m\beta}{\hbar^2} + \frac{1}{L}W_0\left(\pm\frac{m\beta L}{\hbar^2}\,e^{-m\beta L/\hbar^2}\right)\right]^2, \qquad (3.27)$$

(bound-state energies)

Because of the overall minus sign, the even-parity bound state has the lower energy. The odd-parity energy is again only valid provided $\beta L \geq \hbar^2/m$. At the marginal case $\beta L = \hbar^2/m$, the odd-parity energy E_- from Eq. (3.27) becomes $E_- = 0$, meaning it is marginally bound, as we discussed earlier.

Just to finish things off, what remains is to determine the wave-function coefficients $a_{\rm I}$ or $a_{\rm II}$ from the original setup in Eq. (3.4). In the even-parity case, these are determined by Eq. (3.6) and the normalization condition:

$$a_{\rm I} = \frac{\sqrt{2\kappa}\,\cosh(\kappa L/2)}{\sqrt{1+(1+\kappa L)\,e^{-\kappa L}}}, \qquad a_{\rm II} = \frac{a_{\rm I}e^{-\kappa L/2}}{2\cosh(\kappa L/2)} \qquad \text{(even parity)}. \qquad (3.28)$$

In the odd-parity case, these are

$$a_{\rm I} = \frac{\sqrt{2\kappa}\,\sinh(\kappa L/2)}{\sqrt{1-(1+\kappa L)\,e^{-\kappa L}}}, \qquad a_{\rm II} = \frac{a_{\rm I}e^{-\kappa L/2}}{2\sinh(\kappa L/2)} \qquad \text{(odd parity)}, \qquad (3.29)$$

as determined by Eq. (3.10) and the normalization condition.

3.2 Matrix-Diagonalization Model

The results (3.26) and (3.27) above completely characterize the solution to the double-delta potential. However, in terms of the special function $W(z)$, the results are a little opaque. Thus, we'll proceed by constructing an approximate—but more transparent—model for the double-delta problem. First, let's write out the Hamiltonian as

$$H = H_0 + V, \qquad (3.30)$$

where H_0 represents the two delta wells in isolation (i.e., in the limit $L \to \infty$), and V represents the correction required to change the problem into two wells at *finite* distance L.

Since we'll again start by knowing the solutions for a single delta well, it will be most convenient to work in the representation of these ''uncoupled'' states. Calling the uncoupled state in the left-hand well $|\mathrm{L}\rangle$ and the corresponding state in the right-hand well $|\mathrm{R}\rangle$, we can write these states in the position representation using the wave function $\psi_1(x)$ from Eq. (3.2) as

$$\begin{aligned}\psi_{\rm L}(x) &= \langle x|\mathrm{L}\rangle = \psi_1(x+L/2)\\ \psi_{\rm R}(x) &= \langle x|\mathrm{R}\rangle = \psi_1(x-L/2).\end{aligned} \qquad (3.31)$$

Schematically, in terms of the uncoupled states, we can write the uncoupled Hamiltonian H_0 in matrix form as

$$H_0 = \begin{bmatrix} \langle \mathrm{L}|H_0|\mathrm{L}\rangle & \langle \mathrm{L}|H_0|\mathrm{R}\rangle \\ \langle \mathrm{R}|H_0|\mathrm{L}\rangle & \langle \mathrm{R}|H_0|\mathrm{R}\rangle \end{bmatrix} \qquad (3.32)$$

in terms of the four (Dirac-notation) matrix elements. The diagonal elements are given simply by the uncoupled energy E_1 in Eq. (3.3),

$$\langle \mathrm{L}|H_0|\mathrm{L}\rangle = \langle \mathrm{R}|H_0|\mathrm{R}\rangle = -\frac{m\beta^2}{2\hbar^2}, \qquad (3.33)$$

while the off-diagonal elements vanish, because we are working with the eigenstates of H_0:

$$H_0 = -\frac{m\beta^2}{2\hbar^2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \qquad (3.34)$$

To write the interaction potential V in the same basis, the diagonal elements are given just by the overlap integral of the uncoupled states with the *other* potential well. That is, $\langle \mathrm{L}|V|\mathrm{L}\rangle$ is the expectation value of the right-hand potential well with respect to the left-hand state,

$$\begin{aligned}
\langle \mathrm{L}|V|\mathrm{L}\rangle &= -\beta \int dx\, \psi_{\mathrm{L}}^*(x)\, \delta(x - L/2)\, \psi_{\mathrm{L}}(x) \\
&= -\beta \int dx\, \psi_1^*(x + L/2)\, \delta(x - L/2)\, \psi_1(x + L/2) \\
&= -\beta \big|\psi_1(L)\big|^2 \\
&= -\frac{m\beta^2}{\hbar^2}\, e^{-2m\beta L/\hbar^2} \\
&= \langle \mathrm{R}|V|\mathrm{R}\rangle,
\end{aligned} \tag{3.35}$$

with $\psi(x)$ given in Eq. (3.2). By symmetry, the other diagonal element $\langle \mathrm{R}|V|\mathrm{R}\rangle$ has the same value. The off-diagonal elements follow similarly:

$$\begin{aligned}
\langle \mathrm{R}|V|\mathrm{L}\rangle &= -\beta \int dx\, \psi_{\mathrm{R}}^*(x)\, \delta(x - L/2)\, \psi_{\mathrm{L}}(x) \\
&= -\beta \int dx\, \psi_1^*(x - L/2)\, \delta(x - L/2)\, \psi_1(x + L/2) \\
&= -\beta\, \psi_1^*(0)\, \psi_1(L) \\
&= -\frac{m\beta^2}{\hbar^2}\, e^{-m\beta L/\hbar^2} \\
&= \langle \mathrm{L}|V|\mathrm{R}\rangle.
\end{aligned} \tag{3.36}$$

Note that again we include only *one* of the wells in each matrix element, since V represents the action of *assembling* the two wells at finite distance, starting from arbitrarily large separation.

3.2.1 A Correction

Actually, we just let an error slip by: the result (3.35) for $\langle \mathrm{L}|V|\mathrm{L}\rangle = \langle \mathrm{R}|V|\mathrm{R}\rangle$ can't be correct. We can see this in the limit $L \longrightarrow 0$ (both delta wells at the same location), which is equivalent to a single delta well of amplitude 2β. Making the replacement $\beta \longrightarrow 2\beta$ in Eqs. (3.33) leads to

$$\langle \mathrm{L}|H_0|\mathrm{L}\rangle = \langle \mathrm{R}|H_0|\mathrm{R}\rangle = -\frac{2m\beta^2}{\hbar^2}, \tag{3.37}$$

but the contributions from the $L \longrightarrow 0$ limit of two wells gives an energy

$$\begin{aligned}
\langle \mathrm{L}|H_0|\mathrm{L}\rangle + \langle \mathrm{R}|H_0|\mathrm{R}\rangle + \langle \mathrm{L}|V|\mathrm{L}\rangle + \langle \mathrm{R}|V|\mathrm{R}\rangle &= -\frac{m\beta^2}{2\hbar^2} - \frac{m\beta^2}{2\hbar^2} - \frac{m\beta^2}{\hbar^2}\, e^{-2m\beta L/\hbar^2} - \frac{m\beta^2}{\hbar^2}\, e^{-2m\beta L/\hbar^2} \\
&\longrightarrow -\frac{3m\beta^2}{\hbar^2},
\end{aligned} \tag{3.38}$$

which, sadly, is not the same thing. However, we obtain the correct limit here if we replace Eqs. (3.35) by *half* the value we calculated:

$$\langle \mathrm{L}|V|\mathrm{L}\rangle = \langle \mathrm{R}|V|\mathrm{R}\rangle = -\frac{m\beta^2}{2\hbar^2}\, e^{-2m\beta L/\hbar^2}. \tag{3.39}$$

So what's going on here? What we are seeing is a pathology of this delta-well potential. The delta function in the potential induces a kink in the tail of the wave function, of the same form that gives the $e^{-|x|}$ form of the single-well eigenfunction. The energy associated with this kink is, evidently, of the same order as the potential energy associated with occupying the well.

To see this, let's recall the energy (3.3) for a particle bound to a single delta well:

$$E_1 = -\frac{m\beta^2}{2\hbar^2}. \tag{3.40}$$

This of course has kinetic and potential components. The potential energy is easy to calculate as the expectation value of $-\beta\delta(x)$ with respect to the state (3.2),

$$\psi_1(x) = \sqrt{\frac{m\beta}{\hbar^2}}\, e^{-m\beta|x|/\hbar^2}, \tag{3.41}$$

which gives

$$\langle V\rangle = -\beta\frac{m\beta}{\hbar^2} = -\frac{m\beta^2}{\hbar^2}. \tag{3.42}$$

This is twice the total energy, so we can infer the kinetic energy should be $\langle T\rangle = m\beta^2/2\hbar^2$. This is easy to confirm, using the kinetic-energy operator $T = -\hbar^2\partial_x^2/(2m)$. After integrating once by parts, this is

$$\langle T\rangle = \frac{\hbar^2}{2m}\int dx\,|\psi_1'(x)|^2 = \frac{\hbar^2}{2m}\left(\frac{m\beta}{\hbar^2}\right)^2\int dx\,|\psi_1(x)|^2 = \frac{m\beta^2}{2\hbar^2}. \tag{3.43}$$

The thing to notice here is that the kinetic energy is associated with the wave function *outside* the potential well, but let's not forget that there is a *lot* going on kinetic-energy-wise inside the well, because the wave function is kinked, and the kinetic energy is related to the (here, divergent) curvature of the wave function.

In any case, when we set up the calculation of the matrix elements $\langle \mathrm{L}|V|\mathrm{L}\rangle$ and $\langle \mathrm{R}|V|\mathrm{R}\rangle$ in Eqs. (3.35), we are committing some error in neglecting the fact that the opposite well should impose another kink in the wave function. We ignored this kink, in the spirit of treating the interaction as a weak perturbation. Heuristically, we can account for the missing kink by incorporating the same factor of $1/2$ that follows from incorporating the kinetic-energy contribution (3.43) to the total single-well energy (3.40), thus roughly justifying the corrected matrix elements (3.39).

Of course, you could object that we are making the same error in the matrix elements $\langle \mathrm{R}|V|\mathrm{L}\rangle$ and $\langle \mathrm{L}|V|\mathrm{R}\rangle$, and of course, you'd be right. Note that the magnitude of these cross matrix elements is of the order $e^{-m\beta L/\hbar^2}$, while the kinetic-energy correction is of the order $e^{-2m\beta L/\hbar^2}$—in the weakly coupled regime (which is implicit in this matrix model, as we'll come back to below), where this exponential factor is small, the kinetic-energy correction is negligible for the cross matrix elements.

3.2.2 Matrix Model: Solution

Collecting all the matrix elements so far, we can write out the full Hamiltonian (3.30) as

$$H = E_0\begin{bmatrix} 1 & 0\\ 0 & 1\end{bmatrix} + V_0\begin{bmatrix} 1 & 0\\ 0 & 1\end{bmatrix} + \frac{\hbar\Omega}{2}\begin{bmatrix} 0 & 1\\ 1 & 0\end{bmatrix}, \tag{3.44}$$

where we have defined the energies

$$\begin{aligned} E_0 &:= \langle \mathrm{L}|H_0|\mathrm{L}\rangle = \langle \mathrm{R}|H_0|\mathrm{R}\rangle = -\frac{m\beta^2}{2\hbar^2}\\ V_0 &:= \langle \mathrm{L}|V|\mathrm{L}\rangle = \langle \mathrm{R}|V|\mathrm{R}\rangle = -\frac{m\beta^2}{2\hbar^2}\, e^{-2m\beta L/\hbar^2}\\ \frac{\hbar\Omega}{2} &:= \langle \mathrm{L}|V|\mathrm{R}\rangle = \langle \mathrm{R}|V|\mathrm{L}\rangle = -\frac{m\beta^2}{\hbar^2}\, e^{-m\beta L/\hbar^2}. \end{aligned} \tag{3.45}$$

To diagonalize this Hamiltonian, we only need to focus on the last term, which is a matrix of the form

$$\begin{bmatrix} 0 & a\\ a & 0\end{bmatrix}. \tag{3.46}$$

This matrix has (normalized) eigenvectors

$$\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ 1 \end{bmatrix}, \qquad \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -1 \end{bmatrix}, \tag{3.47}$$

with corresponding eigenvalues a and $-a$. (Note that the action of the matrix is just to swap the elements of the two-vector and multiply them both by a.) Thus, the eigenvalues of the Hamiltonian (3.44) are

$$E_\pm = E_0 + V_0 \mp \frac{\hbar|\Omega|}{2}, \tag{3.48}$$
(matrix eigenvalues)

(recalling that $\Omega < 0$) with corresponding eigenvectors

$$\begin{bmatrix} \langle \mathrm{L}|\psi_\pm\rangle \\ \langle \mathrm{R}|\psi_\pm\rangle \end{bmatrix} = \frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ \pm 1 \end{bmatrix}, \tag{3.49}$$
(matrix eigenvectors)

as expressed in the decoupled basis.

Qualitatively speaking, we have obtained the same result as the exact treatment from before: there is one symmetric and one antisymmetric state, with the symmetric state having the lower energy. We don't, however, have anything here about the antisymmetric state only existing for large energies. Because we set up the problem in terms of the uncoupled eigenstates without properly accounting for any *modifications* to the eigenstates due to the interaction potential V, we are effectively making a weak-coupling approximation (large βL).

To be more quantitative in the comparison, we can compare the matrix-diagonalization energies (3.48) to the exact solution (3.27), taking the weak-coupling limit $\beta L \gg \hbar^2/m$ (i.e., small Ω). In this limit, we may use $W(x) \sim x$ for $|x| \ll 1$, with the result

$$E_\pm = -\frac{\hbar^2}{2m}\left[\frac{m\beta}{\hbar^2} \pm \frac{m\beta}{\hbar^2}\, e^{-m\beta L/\hbar^2}\right]^2 = -\frac{m\beta^2}{2\hbar^2} - \frac{m\beta^2}{2\hbar^2}\, e^{-2m\beta L/\hbar^2} \mp \frac{m\beta^2}{\hbar^2}\, e^{-m\beta L/\hbar^2}. \tag{3.50}$$

Comparing the last expression to the energies defined in Eqs. (3.45), we can see that the first term is just E_0, the second term is V_0 (again, justifying the somewhat *ad hoc* factor of $1/2$), and the last term is $\pm\hbar\Omega/2$, in agreement with the energies (3.48). This comparison also reiterates the weak-coupling nature of this particular matrix model of tunneling.

3.2.3 Semiclassical Model

To connect the present tunneling model to our earlier treatment of barrier tunneling in Section 2.6, we can recall that in the semiclassical approximation, the tunneling probability through a barrier was given in Eq. (2.176) by

$$T \approx \exp\left(-\frac{2\sqrt{2m}}{\hbar}\int_{x_1}^{x_2} dx\, \sqrt{V(x) - E}\right). \tag{3.51}$$

To apply this to the double-delta-well problem, we can note that $V(x) = 0$ between the wells, and the uncoupled energy is just E_1 in Eq. (3.40). The integral in the transmission probability is then trivial, and we obtain

$$T \approx \exp\left(-\frac{2\sqrt{2m}}{\hbar}\sqrt{\frac{m\beta^2}{2\hbar^2}}L\right) = e^{-2m\beta L/\hbar^2}. \tag{3.52}$$

This translates into an *amplitude* transmission coefficient of

$$\tau = \sqrt{T} \approx e^{-m\beta L/\hbar^2}, \tag{3.53}$$

keeping in mind the delta wells are equivalent on either side of the barrier (so there is no need to worry about probability currents).

Now, the above transmission coefficients apply to the ''one-off'' case where a wave comes in, hits a barrier once, and either reflects or transmits, never to encounter the barrier again. This is somewhat different than in double-well tunneling, where a particle sits in one potential well, and can have all the time it needs to tunnel through the barrier. Nonetheless, as a simplistic calculation, we can try to adapt it to the current situation by using it to form an estimate for the transition amplitude $\langle \mathrm{R}|V|\mathrm{L}\rangle$. To do this, we need to multiply the transmission amplitude τ by something by some energy to make the units come out right. What energy to use is not completely obvious, but the best candidates are the bound-state energy, the bound-state potential energy, and the bound-state kinetic energy. All of these have a similar order of magnitude, and as it turns out, if we choose the expected potential energy from Eq. (3.42), we obtain

$$\langle \mathrm{R}|V|\mathrm{L}\rangle \sim \tau \langle V\rangle = -\frac{m\beta^2}{\hbar^2}\, e^{-m\beta L/\hbar^2}. \tag{3.54}$$

With this choice, we exactly (and *fortuitously*) reproduce the coupling amplitude from Eqs. (3.36). So in this case, the semiclassical approximation works very well in this tunneling model, at least in the weak-coupling limit (slow tunneling), which is exactly where we expect it to work.

This simple model also shows how the semiclassical amplitude (3.51) may be applied more generally in double-well problems, where the intervening barrier is more complicated. While in such cases it may be harder to guess the correct energy scale for the transition amplitude as in Eqs. (3.54), in any case the semiclassical amplitude (3.51) should correctly characterize the *scaling* of the transition amplitude $\langle \mathrm{R}|V|\mathrm{L}\rangle$ (and thus the tunneling rate Ω) with the height and length scales of the intervening barrier. We can go further, however, if we interpret $\langle \mathrm{R}|V|\mathrm{L}\rangle/\hbar$ as a tunneling *rate*, in which case it should match the tunneling probability T multiplied by the rate at which the particle makes attempts to tunnel through the barrier. If a well can be approximated near the bottom by a harmonic oscillator of frequency ω, then the rate is $\omega/2\pi$, so we should have $\Omega/2 = \langle \mathrm{R}|V|\mathrm{L}\rangle/\hbar = T\omega/2\pi$ with T given by Eq. (3.51), in which case we can write

$$\Omega \approx \frac{\omega}{\pi} \exp\left(-\frac{2\sqrt{2m}}{\hbar}\int_{x_1}^{x_2} dx\, \sqrt{V(x)-E}\right), \tag{3.55}$$

(general semiclassical tunneling rate)

where as before x_1 and x_2 represent the classical turning points of the barrier for the particle's initial energy.

3.3 Tunneling Oscillations

Now we can finally get to the punchline of all this development. In both the matrix model and the ''exact'' double-delta-well model, there is a symmetric/antisymmetric doublet of states that we can write as

$$\begin{aligned} |+\rangle &= \frac{1}{\sqrt{2}}\Big(|\mathrm{L}\rangle + |\mathrm{R}\rangle\Big) \\ |-\rangle &= \frac{1}{\sqrt{2}}\Big(|\mathrm{L}\rangle - |\mathrm{R}\rangle\Big), \end{aligned} \tag{3.56}$$

with $|+\rangle$ of course representing the symmetric superposition and $|-\rangle$ the antisymmetric superposition. We can also write the left/right states in terms of the $|\pm\rangle$ states as

$$\begin{aligned} |\mathrm{L}\rangle &= \frac{1}{\sqrt{2}}\Big(|+\rangle + |-\rangle\Big) \\ |\mathrm{R}\rangle &= \frac{1}{\sqrt{2}}\Big(|+\rangle - |-\rangle\Big), \end{aligned} \tag{3.57}$$

The $|\pm\rangle$ states have energies

$$E_\pm = \mp\frac{\hbar\Omega}{2} \tag{3.58}$$

in the matrix model, with the symmetric state having the lower energy. Note that we are discarding a common-mode energy, which doesn't matter for what we're doing. This energy expression also holds for the

double-delta-well model, if we regard it as a *definition* for Ω in the sense $\hbar\Omega = E_- - E_+$, where the energies are given in Eqs. (3.27).

Now suppose we start with the state at $t = 0$ in the left-hand well:

$$|\psi(0)\rangle = |\mathrm{L}\rangle = \frac{1}{\sqrt{2}}\Big(|+\rangle + |-\rangle\Big). \tag{3.59}$$

The $|\pm\rangle$ states are eigenstates, so it's easy to write out the time-dependence as

$$\begin{aligned} |\psi(t)\rangle &= \frac{1}{\sqrt{2}}\Big(|+\rangle\, e^{-iE_+t/\hbar} + |-\rangle\, e^{-iE_-t/\hbar}\Big) \\ &= \frac{1}{\sqrt{2}}\Big(|+\rangle\, e^{i\Omega t/2} + |-\rangle\, e^{-i\Omega t/2}\Big) \\ &= \frac{e^{i\Omega t/2}}{\sqrt{2}}\Big(|+\rangle + |-\rangle\, e^{-i\Omega t}\Big). \end{aligned} \tag{3.60}$$

In the last expression, we can ignore the overall phase factor, and focus on the $e^{-i\Omega t}$ phase of the $|-\rangle$ state. This is saying that, with angular frequency Ω, that the phase of the $|-\rangle$ component is flipping back and forth between $+$ and $-$. But from Eqs. (3.57), we can see that the *only* difference between $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$ is precisely this sign.

This means that, at angular frequency Ω, the particle is moving back and forth between the two wells. These are **tunneling oscillations**, and more generally, degenerate, coupled states exhibit such oscillations, which are called **Rabi oscillations** (or **Rabi flopping**). The angular frequency Ω is called the **Rabi frequency**.[4]

3.3.1 Recap

Let's summarize all this again, because this is a hugely important and general phenomenon in quantum mechanics. We started with a pair of degenerate levels (the isolated-well states), and then considered a coupling between them (the barrier-tunneling interaction). As a result of the interactions, the states changed into an energy-split, symmetric/antisymmetric doublet. The common phrase for this is that ''the coupling lifts the degeneracy'' of the original states. The resulting energy splitting gives different phase evolution rates for the two states. This in turn gives rise to a time dependence for any superposition of the symmetric/antisymmetric eigenstates, which leads to Rabi oscillations between the original states.

In the language of a general 2×2 Hamiltonian, let's reiterate all the important points.

- A diagonal Hamiltonian proportional to the identity,

$$H = E_0 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \tag{3.61}$$

  means that we have already expressed H in terms of its eigenbasis. There is no possibility for evolution because the energies are the same. (Any phase evolution will be a global phase of the form $e^{-iE_0t/\hbar}$.

- If there are off diagonal elements in the Hamiltonian,

$$H = \begin{bmatrix} E_0 & \hbar\Omega/2 \\ \hbar\Omega/2 & E_0 \end{bmatrix}, \tag{3.62}$$

  then it is no longer expressed in its eigenbasis, and we expect the basis states to evolve in time. This time evolution shows up in the form of Rabi oscillations. The common diagonal energy is still irrelevant (as a global phase rotation). We expect (complete) Rabi oscillations between the two states because the eigenstates turn out to have opposite parity (i.e., even and odd linear combinations of the original

[4] The phenomenon is named after Isador Isaac Rabi, who pioneered the field of nuclear magnetic resonance, where microwaves induce atoms to Rabi-oscillate between nuclear spin states. He was awarded the 1944 Nobel prize for this work.

states). The Rabi oscillations occur at angular frequency Ω, *because* the energy splitting between the eigenstates of H turns out to be $\hbar\Omega$. The oscillations are the manifestation of a time-dependent interference between the opposite-parity eigenstates as the relative phase changes in time at frequency Ω. Of course, expressed in terms of the new eigenstates, H is still diagonal; the difference between this case and that of the previous point is that these eigenvalues are no longer degenerate.

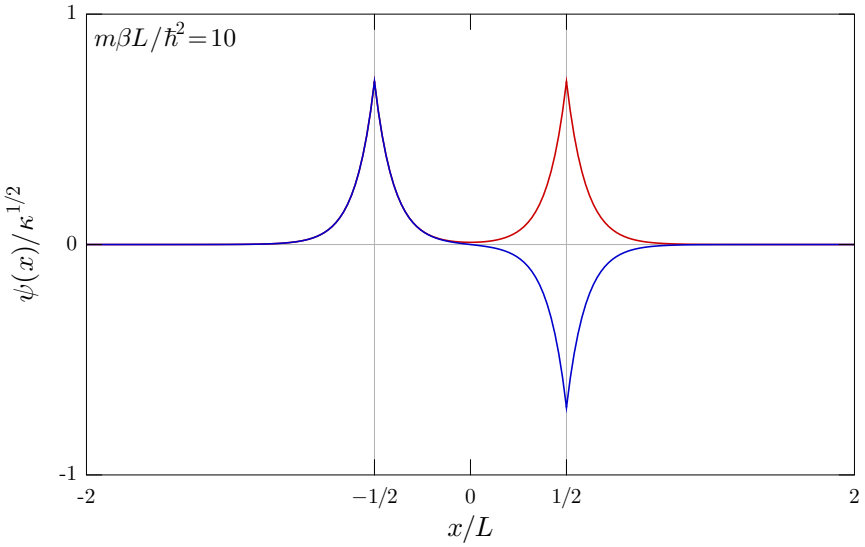
- If the diagonal elements of the Hamiltonian *aren't* the same, then we can no longer ignore them. We will treat this case below in Section 3.5 in terms of an asymmetric double-well potential. The eigenstates will no longer be parity eigenstates, so while Rabi oscillations will still occur, they will be incomplete and occur at a different frequency, because the asymmetry will affect the splitting between the eigenstates.
- If the off-diagonal elements are not real (i.e., Ω is not real), it turns out not to make any difference; Ω in this treatment is replaced by $|\Omega|$. We will prove this later in Chapter 9 when we deal with the evolution of spin-1/2 systems. (See also Problem 3.5.)
- Now test your knowledge. Suppose you have the two-state Hamiltonian

$$H = \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix}, \tag{3.63}$$

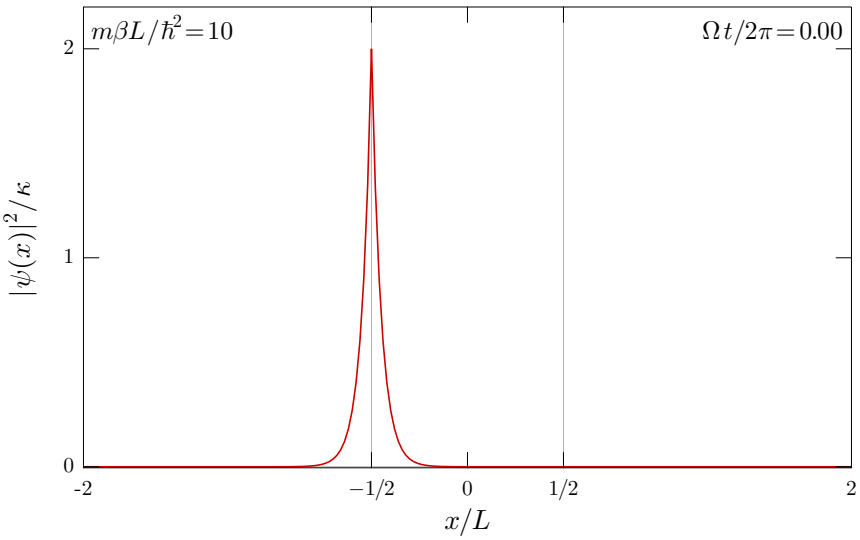
with $E_1 \neq E_2$. Are Rabi oscillations *possible*? If yes, are there *necessarily* Rabi oscillations? If no, what is an extra requirement for Rabi oscillations to occur?

3.3.2 Visualization

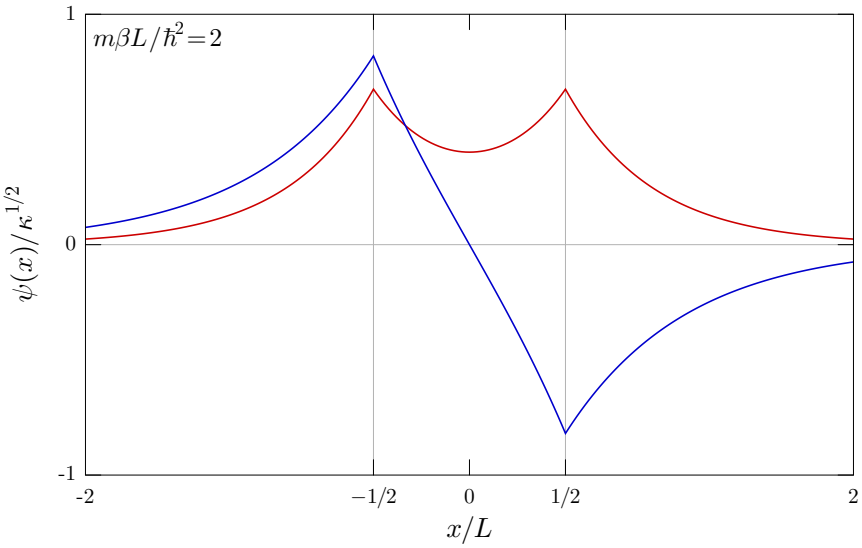
We can return to the eigenstates of the double delta well, mainly characterized by Eqs. (3.26) and (3.27). The dimensionless parameter $m\beta L/\hbar^2$ characterizes the degree of tunnel-coupling between the wells (remember, larger βL means more localization and/or more distant wells, so less coupling). The plot below shows the eigenstates for $m\beta L/\hbar^2 = 10$, corresponding to fairly isolated wells.



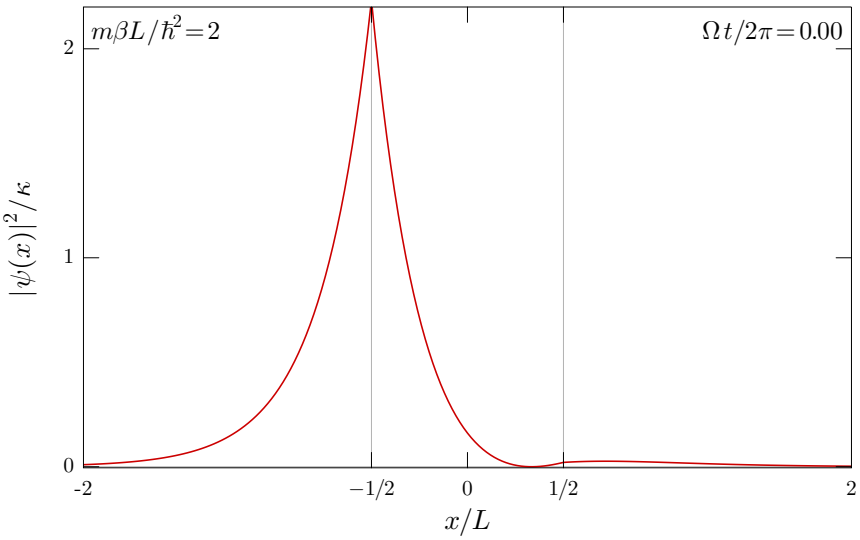
Note that the eigenstates look similar in the vicinity of each well, except of course for the inversion of the state in one well for the antisymmetric state. The movie below shows the time-dependent probability density for the superposition of the form (3.60), showing the tunneling oscillations.



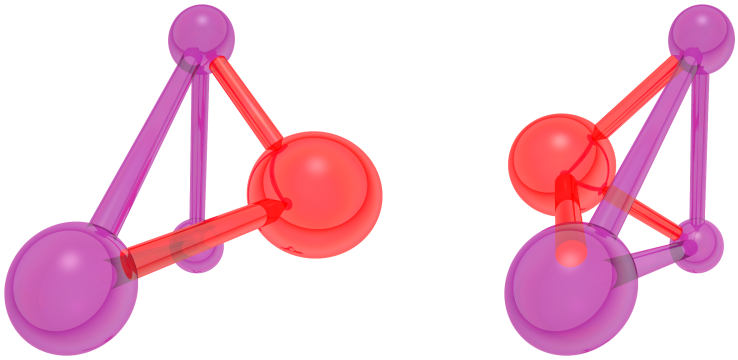
The eigenstates for a more strongly coupled case $m\beta L/\hbar^2 = 2$ are shown below.



Note that due to the stronger tunnel coupling, the eigenstates appear to be somewhat different in each well, as compared to the previous, more weakly coupled case. There is also a more obvious presence of the eigenstates in the region between the wells. The movie below again shows the tunneling oscillations for this case. These oscillations are quite a bit faster than the previous case, although the time scale of the animations is normalized to hide this (“for your viewing pleasure”).



A classic example of tunneling between symmetric double wells is the ammonia (NH_3) molecule. In this case the three hydrogen atoms form an equilateral triangle and thus determine a plane. The nitrogen atom can sit on either side of the plane, and the hydrogen atoms form a potential barrier between these two locations, as shown schematically below.



Because of this tunneling process, NH_3 possesses a doublet, forming a 24.0-GHz microwave doublet, which formed the basis of the first maser.[5]

3.4 Quantum Zeno Effect

So far, we've been talking just about Schrödinger-equation evolution in the double-well potential (or, indeed, in *any* two-state system with degenerate uncoupled levels), in which case the coupling between the states leads to Rabi oscillations. What happens if we throw measurement into the mix? Under the right condition,

[5]Norman F. Ramsey, "History of Atomic Clocks," *Journal of Research of the National Bureau of Standards* **88**, 301 (1983), available at `https://nvlpubs.nist.gov/nistpubs/jres/088/jresv88n5p301_A1b.pdf`.

measurements can stop Rabi oscillations cold in their tracks; this is called the **quantum Zeno effect**.[6,7]

To set up the problem, consider evolution over some time T (which is *not* necessarily the period of the Rabi oscillations), and consider N small time substeps of duration Δt, where

$$\Delta t := \frac{T}{N}, \tag{3.64}$$

where we will want to have $N \gg 1$. After each time step Δt, we will perform a ''which-side'' measurement, which will either return either $|\mathrm{L}\rangle$ or $|\mathrm{R}\rangle$ as a measurement result (this will require a bit of justification, to follow later). Now, suppose we start in the left-hand well,

$$|\psi(0)\rangle = |\mathrm{L}\rangle, \tag{3.65}$$

and in time Δt, this state evolves to

$$|\psi(\Delta t)\rangle \approx \left(1 - \frac{iH\,\Delta t}{\hbar}\right)|\mathrm{L}\rangle, \tag{3.66}$$

where the bracketed factor on the right-hand side is the infinitesimal evolution operator; the error we are making here is $O(\Delta t^2)$. Now the probability amplitude for a measurement to find the particle having made a transition to $|\mathrm{R}\rangle$ is

$$\langle \mathrm{R}|\psi(\Delta t)\rangle \approx -\frac{i\,\Delta t}{\hbar}\langle \mathrm{R}|H|\mathrm{L}\rangle, \tag{3.67}$$

and so the probability of the measurement to collapse into the right-hand well is the square of this:

$$P_{\mathrm{R}}(\Delta t) = |\langle \mathrm{R}|\psi(\Delta t)\rangle|^2 \approx \frac{\Delta t^2}{\hbar^2}|\langle \mathrm{R}|H|\mathrm{L}\rangle|^2. \tag{3.68}$$

We will want to argue that the probability of finding the particle in the right-hand well is zero, and at this point you may be tempted to take the limit $N \longrightarrow \infty$ and thus $\Delta t \longrightarrow 0$. However, this is wrong in the sense of Zeno's original paradox: We haven't yet involved the measurement, so this limit happens for *any* quantum evolution. The thing that is missing is that there are N such steps whose amplitudes (3.67) combine to produce unitary evolution for a general quantum system. The key point here is that we will consider N such short evolutions with a measurement probability (3.68). The probability to *remain* in $|\mathrm{L}\rangle$ is the complementary probability:

$$P_{\mathrm{L}}(\Delta t) = 1 - P_{\mathrm{R}}(\Delta t) \approx 1 - \frac{\Delta t^2}{\hbar^2}|\langle \mathrm{R}|H|\mathrm{L}\rangle|^2. \tag{3.69}$$

Now, assuming we found the particle in $|\mathrm{L}\rangle$ in this measurement, the evolution in the next interval from Δt to $2\Delta t$ is just a replay of what already happened. The probability that the particle stayed in $|\mathrm{L}\rangle$ after every measurement is given by the Nth power of the probability (3.69), and so the probability that the particle was found in $|\mathrm{R}\rangle$ in *any one* of the N time intervals is the complementary probability,

$$P_{\mathrm{R}}(T) \approx N\frac{\Delta t^2}{\hbar^2}|\langle \mathrm{R}|H|\mathrm{L}\rangle|^2, \tag{3.70}$$

[6]The term comes from B. Misra and E. C. G. Sudarshan, ''The Zeno's paradox in quantum theory,'' *Journal of Mathematical Physics* **18**, 756 (1977) (doi: 10.1063/1.523304). Here ''Zeno paradox'' refers to a paradox of an ancient Greek philosopher. What seems to be the most commonly known Zeno paradox goes something like this: Zeno wakes up in bed in the middle of the night, realizing that he *really* needs to go to the bathroom. But to get there, he has to get *halfway* there, and to get *there*, he has to get *halfway to halfway* there, and so on. He keeps going on like this, and concludes that walking through an infinite number of subintervals is just too damn much walking. So he decides to just stay in bed and hold it. The Zeno paradox referred to by Misra and Sudarshan is a different paradox, which is a kind of variation on the first one; it's called the ''arrow paradox.'' Shooting an arrow at an apple at distance L away, you can observe that in *half* the time it takes to get there, it only traveled a distance $L/2$. Continuing in this manner, you get to an arbitrarily small time interval, during which the arrow traveled no distance at all. Since it traveled no distance during each of these infinitely divided intervals, it couldn't have moved anywhere at all, so the apple is safe. It seems that Zeno wouldn't have done well in a modern-day calculus class, in particular in properly handling problems involving double limits. But that's okay, this was a long time ago, before infinitesimals had been sorted out.

[7]For a nice review, see Asher Peres, ''Zeno paradox in quantum theory,'' *American Journal of Physics* **48**, 931 (1980) (doi: 10.1119/1.12204).

after expanding and dropping $O(\Delta t^3)$ terms. From Eq. (3.64), the final probability to tunnel to $|\mathrm{R}\rangle$ is

$$P_{\mathrm{R}}(T) \approx \frac{T^2}{N\hbar^2}|\langle \mathrm{R}|H|\mathrm{L}\rangle|^2, \tag{3.71}$$

and so as the time between measurements goes to zero, we have

$$P_{\mathrm{R}}(T) = \lim_{N\longrightarrow\infty} \frac{T^2}{N\hbar^2}|\langle \mathrm{R}|H|\mathrm{L}\rangle|^2 = 0. \tag{3.72}$$

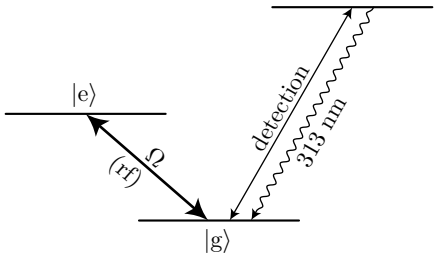
That is, a *continuous* monitoring of a quantum system will *completely* suppress the tunneling (Rabi oscillation).

A couple of important comments are in order. First, notice that we didn't make explicit mention of the Rabi frequency or Rabi oscillations (although of course the Rabi frequency is related to $\langle \mathrm{R}|H|\mathrm{L}\rangle$, and we effectively derived the short-time version of the Rabi oscillation). The key points to the Zeno effect are that we started in a particular state, and that the evolution *out* of that state is *unitary*. This is what led to a second-order-in-Δt probability to (not) tunnel, as in Eq. (3.69).

A second comment is that the measurement, as we posed it, is not completely straightforward to realize, as $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$ are by definition not orthogonal states, if we take them to be the uncoupled, single-well states (they *are* orthogonal if we take them to be linear combinations of the true eigenstates, as in the matrix model). Thus, for example, a simple position measurement that distinguishes $x > 0$ from $x < 0$ doesn't *quite* realize the right measurement. However, given widely separated potential wells, this left-right measurement can come very close to the correct measurement (close enough to produce the right effect, in any case). Also, in other two-state systems, there are more straightforward ways to realize which-state measurements to high fidelity, as we will outline below.

3.4.1 Trapped-Ion Experiment

A particularly elegant and novel experimental demonstration came in the form of a single, trapped Be^+ ion.[8] The relevant energy-level scheme for the atom is shown in the diagram below.



The main two levels are labelled $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$ (for ''ground'' and ''excited'' states). Although the states are not degenerate, a radiofrequency (rf) field tuned with a frequency matching the energy gap divided by $\hbar$ will drive resonant ($\Delta = 0$) Rabi oscillations between the states.

One extra, auxiliary excited state, plus a 313-nm laser tuned to drive $|\mathrm{g}\rangle$ to the auxiliary state, acts as the measurement device. The transition to the auxiliary state and its subsequent spontaneous decay acts as a which-state measurement. An atom in $|\mathrm{g}\rangle$ will get driven to the auxiliary state, and the emitted 313-nm photons can be detected, telling the observer that the atom was, indeed, in $|\mathrm{g}\rangle$. On the other hand, if the atom is in $|\mathrm{e}\rangle$, it does not respond to the 313-nm driving laser, and no photons are scattered. In this case, the absence of scattered photons confirms that the atom is in $|\mathrm{e}\rangle$.

In the experiment, the atom was exposed to an rf pulse that drives $|\mathrm{g}\rangle \longrightarrow |\mathrm{e}\rangle$ with essentially unit probability. Then the rf pulse was interrupted with as many as 64 measurement-laser pulses (effectively instantaneous on the time scale of the rf pulse). The pulse interruptions reduced the total transition probability from $|\mathrm{g}\rangle \longrightarrow |\mathrm{e}\rangle$ by an order of magnitude, from 100% to 10%.

[8] Wayne M. Itano, D. J. Heinzen, J. J. Bollinger, and D. J. Wineland, ''Quantum Zeno effect,'' *Physical Review A* **41**, 2295 (1990) (doi: 10.1103/PhysRevA.41.2295).

3.4.2 Electromagnetic Wave as a Two-State System

To talk about another realization, let's talk about the polarization of an electromagnetic wave, which acts as another realization of a two-state system. A classical electromagnetic plane wave, propagating in the $+z$-direction, can be written

$$\mathbf{E}(z,t) = \hat{\epsilon} E_0^{(+)} e^{i(kz-\omega t)} + \text{c.c.} \tag{3.73}$$

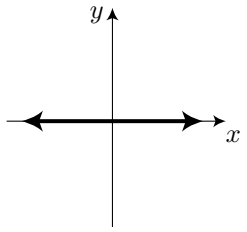
Here, $E_0^{(+)}$ is an amplitude with the dimensions of an electric field (which could be complex-valued), "c.c." means the "complex conjugate" of the first term, and $\hat{\epsilon}$ is a unit **polarization vector** (which could also be complex-valued). Because the electric field is transverse (a consequence of $\nabla \cdot \mathbf{E} = 0$), $\hat{\epsilon}$ must lie in the x-y plane. We can thus write $\hat{\epsilon}$ in the form of a two-vector:

$$\hat{\epsilon} \longrightarrow \begin{bmatrix} \hat{\epsilon} \cdot \hat{x} \\ \hat{\epsilon} \cdot \hat{y} \end{bmatrix}. \tag{3.74}$$

In this two-vector form, in classical optics this unit polarization vector is called a **Jones vector**. To illustrate a few possibilities, let's look at some of the basic Jones vectors:

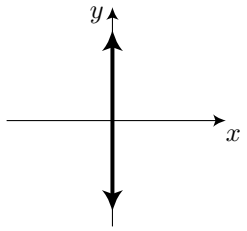
1. **linear polarization** (x-polarization):

$$\begin{bmatrix} 1 \\ 0 \end{bmatrix}$$



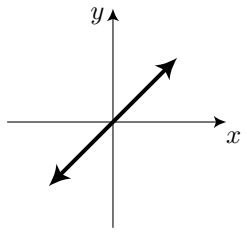
2. **linear polarization** (y-polarization):

$$\begin{bmatrix} 0 \\ 1 \end{bmatrix}$$



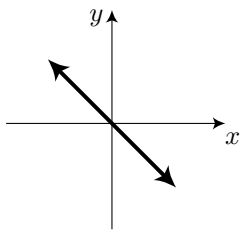
3. **linear polarization** (45°-polarization):

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$



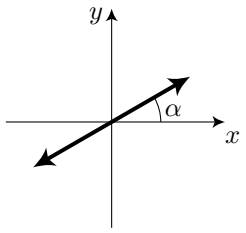
4. **linear polarization** (−45°-polarization):

$$\frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ -1 \end{bmatrix}$$



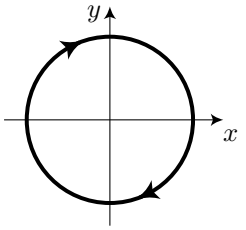
5. **linear polarization** (angle α):

$$\begin{bmatrix} \cos\alpha \\ \sin\alpha \end{bmatrix}$$



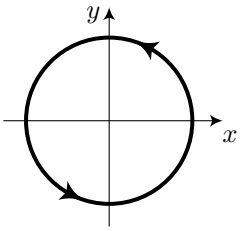
6. **right-circular polarization** (RCP):

$$\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ -i \end{bmatrix}$$



7. **left-circular polarization** (LCP):

$$\frac{1}{\sqrt{2}}\begin{bmatrix} 1 \\ i \end{bmatrix}$$



The sketches here show the trajectory of the (unit) electric-field vector as the wave propagates along $+z$ (i.e., out of the page). Notice first of all that x- and y- polarizations make up the ''normal'' basis in Jones-vector space, while $\pm 45°$ polarizations make up an alternate basis (consisting of even and odd superpositions of the x-y basis vectors). Also, the circular polarizations are similar to the linear polarizations, but with $90°$ phase shifts between the components, which are represented by the complex phase difference between the two components.

What we have here is a classical wave, represented by two states in a way analogous to a quantum two-state system. The Jones vector can be interpreted as a *quantum* object too, since it turns out that the same description applies to a single photon in the same plane-wave state. (Though we haven't defined exactly what we mean by a photon here, nor will we.)

Now having gotten this introduction out of the way, what does this have to do with the Zeno effect? Well, we have a two-state system. A measurement of the state can be accomplished by a polarizer, which is oriented in some direction. For example, the effect of an ideal x-polarizer can be written as the operator

$$P_x := \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}, \tag{3.75}$$

which is just the projection operator for the x-component of the Jones vector. The relative intensity passing through the polarizer (equivalently, the probability for a photon to pass through the polarizer), is just given by the expectation value $\langle P_x \rangle$ as usual, where in dyadic notation

$$\langle P_x \rangle = \hat{\epsilon} \cdot P_x \cdot \hat{\epsilon}. \tag{3.76}$$

Now suppose we consider a stack of $N+1$ ideal polarizers, with the first oriented along the x-direction, and the last oriented along the y-direction. The $N-1$ remaining polarizers are uniformly spread in angle between

these extremes, with angle $\Delta\theta = \pi/2N$ between successive polarizers. Clearly, if $N = 1$ (i.e., two crossed polarizers), nothing gets through, because the first polarizer selects for x, while the second selects for y. But in the limit $N \longrightarrow \infty$, the transmission probability through the entire stack converges to unity (Problem 3.9), as an analogue to the Zeno effect. (Note that the Zeno effect here does not *inhibit* the evolution, but rather the measurements *drag* the polarization state, causing polarization rotation where there was none before.)

3.4.3 Interaction-Free Measurement

In the trapped-ion quantum Zeno experiment of Section 3.4.1, a measurement confirming that the particle is in the ground state $|\mathrm{g}\rangle$ inhibited Rabi oscillations to the excited state $|\mathrm{e}\rangle$, because the detection of scattered photons gave the information required for the Zeno effect to take hold. However, it is worth reiterating that this *also* works when the atom is in $|\mathrm{e}\rangle$—the atom *doesn't* scatter any photons, and the *lack* of photon detections over some time *still* provides the information needed for the Zeno effect to happen (so the atom is inhibited from making a transition to $|\mathrm{g}\rangle$). This **null measurement result**, where the laser field makes a measurement, seemingly without even interacting with the atom, is a simple example of a class of measurements called **interaction-free measurements**.[9]

Interaction-free measurements tend to be closely related to the Zeno effect. As one example, suppose that aliens visited Earth, and in a (square) potential well that they left behind, they may or may not have left behind a bomb. The bomb is of the highly contrived type, which is only detectable by a particular quantum particle, the "schmelectron" (symbol s^-). The problem is that, if a schmelectron interacts with the bomb, the bomb will absorb the schmelectron and detonate, which would be bad news for Earth. (That is, the bomb acts as a perfect absorber for schmelectrons.) So what to do?

The idea is that the aliens (unwittingly) gave you an advantage by leaving the bomb in a potential well. You can take advantage of the transmission resonances of Section 2.6.2.1 for a quantum particle scattering from the potential well. The idea is to send in a delocalized schmelectron at some mean incident momentum (the momentum should be fairly well-defined to mimic the effect of the incident eigenstates that we analyzed), tuned to a transmission resonance. In the case where there is no bomb, the s^- should transmit with unit probability, so the lack of a backscattered s^- will be the indication that a bomb is not present. Since the bomb again acts as an absorber, it masks the effect of the second edge of the potential well. Recall that the transmission resonances of the well depend on a resonant wave circulating and building up inside the potential well. The bomb prevents this from happening, and so the s^- just reflects from the first edge of the well, with probability $R_1 = |r_1|^2$, where r_1 is the reflection amplitude from a single potential step. In this case, a reflected particle is an indication that there is a bomb in the well. But the problem is that, with probability $1 - R$, the s^- will still enter the well and detonate the bomb. Fortunately, in the limit of a deep well, R becomes arbitrarily close to 1, so the probability of setting off the bomb can be made arbitrarily small.[10] But note that this probability can never be made strictly *zero*, because this would turn off the interaction completely, so we would never obtain *any* information about the bomb. Correspondingly, the s^- particle could never transmit through the well. In any case, the effect here comes from the (null) measurement that the bomb makes on the schmelectron, which is a spatial version of the Zeno effect—the measurement prevents the schmelectron from entering the potential well.[11]

[9] For a (biased) discussion of the early papers on null measurement results and interaction-free measurements, see Lev Vaidman, "The Meaning of the Interaction-Free Measurements," *Foundations of Physics* **33** (2003) (doi: 10.1023/A:1023767716236), also available at `https://www.tau.ac.il/~vaidman/lvhp/m87.pdf`.

[10] It should seem strange that this works out in spite of an arbitrarily small interaction. The key point is that the smallness is compensated by the arbitrarily many effective interactions by the wave that *could in principle* circulate in the potential-well resonator. For the first discussion of this, see P. Kwiat, H. Weinfurter, T. Herzog, A. Zeilinger, and M. A. Kasevich, "Interaction-free measurement," *Physical Review Letters* **74**, 4763 (1995) (doi: 10.1103/PhysRevLett.74.4763). The corresponding experimental observation is by Paul Kwiat, Harald Weinfurter, Thomas Herzog, Anton Zeilinger, and Mark Kasevich, "Experimental realization of interaction-free measurements," *Annals of the New York Academy of Sciences* **755**, 383 (1995) (doi: 10.1111/j.1749-6632.1995.tb38981.x). For the more specific proposal in terms of an optical resonator, see Harry Paul and Mladen Pavičić, "Nonclassical interaction-free detection of objects in a monolithic total-internal-reflection resonator," *Journal of the Optical Society of America B* **14**, 1273 (1997) (doi: 10.1364/JOSAB.14.001275). A corresponding experimental demonstration is by T. K. Tsegaye, E. Goobar, A. Karlsson, G. Bjork, M. Y. Loh, and K. H. Lim, "Efficient interaction-free measurements in a high-finesse interferometer," *Physical Review A* **57**, 3987 (1998) (doi: 10.1103/PhysRevA.57.3987).

[11] This version of the Zeno effect also works *without* a potential well. See, for example, Jonathan B. Mackrory, Kurt A. Jacobs,

3.5 Asymmetric Double Wells and Avoided Crossings

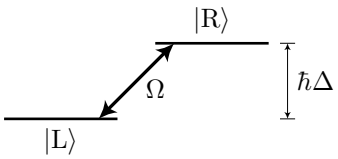
So far, we have only studied tunneling in a *symmetric* double well, but what if we break the symmetry? In the double-delta-potential model, this would correspond to modifying the potential (3.1) to read something like

$$V(x) = -\beta_{\mathrm{R}}\,\delta(x - L/2) - \beta_{\mathrm{L}}\,\delta(x + L/2), \tag{3.77}$$

where in general $\beta_{\mathrm{L}} \neq \beta_{\mathrm{R}}$. This turns out to be a difficult model to solve, so we will stick to modifying the matrix model of Section 3.2, starting with the Hamiltonian

$$H = \begin{bmatrix} -\hbar\Delta/2 & \hbar\Omega/2 \\ \hbar\Omega/2 & \hbar\Delta/2 \end{bmatrix}, \tag{3.78}$$

as a generalization to the previous Hamiltonian (3.44), to which this reduces when $\Delta = 0$ (up to an irrelevant overall energy $E_0 + V_0$). Schematically, this corresponds to the level diagram below, which has two levels $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$, split by energy $\hbar\Delta$ (the diagram shows the case $\Delta > 0$), with a coupling characterized by the Rabi frequency Ω.



This system models, for example, a charged particle in a double-well potential, plus a uniform electric field that induces an extra linear potential, breaking the degeneracy of the wells. (This could also apply to the NH_3 molecule, where a uniform electric field oriented to be orthogonal to the hydrogen plane differentially shifts the energies associated with the two possible locations of the nitrogen atom.)

3.5.1 Solution of Eigenvalues and Eigenvectors

The solution for eigenvalues and eigenvectors is an exercise (see Problem 1.23). The result is that the two energy eigenvalues are

$$E_\pm = \pm\frac{\hbar}{2}\sqrt{\Omega^2 + \Delta^2} = \pm\frac{\hbar\tilde{\Omega}}{2}, \tag{3.79}$$
(asymmetric double-well eigenvalues)

where we have defined the **generalized Rabi frequency**

$$\tilde{\Omega} := \sqrt{\Omega^2 + \Delta^2}. \tag{3.80}$$
(generalized Rabi frequency)

The corresponding eigenvectors are

$$\begin{aligned} |+\rangle &= \sin\theta\,|\mathrm{L}\rangle - \cos\theta\,|\mathrm{R}\rangle \\ |-\rangle &= \cos\theta\,|\mathrm{L}\rangle + \sin\theta\,|\mathrm{R}\rangle, \end{aligned} \tag{3.81}$$
(asymmetric double-well eigenvectors)

where the **Stückelberg angle** θ is defined by

$$\tan 2\theta = \frac{|\Omega|}{\Delta} \qquad \left(0 \leq \theta < \frac{\pi}{2}\right). \tag{3.82}$$

Note that the minus sign in the first of Eqs. (3.81) is a consequence of having $\Omega < 0$, as consistent with our earlier choice. However, note that the notation $|\pm\rangle$ is *not* consistent with our earlier notation, where the $+$ and $-$ labels referred to even and odd eigenstates, respectively. Here, in the asymmetric case we don't have

and Daniel A. Steck, "Reflection of a particle from a quantum measurement," *New Journal of Physics* **12**, 113023 (2010) (doi: 10.1088/1367-2630/12/11/113023) (arXiv: 1009.4968).

any definite parity to fall back on in general, so now the + and − labels refer to higher and lower energies, respectively. (In fact it turns out that these are the *opposite* labels in the case $\Delta = 0$, because remember that the even-parity state should be lower in energy than the corresponding odd-parity state, but here the + state has *higher* energy by definition).

To make sure we understand what's going on, let's look at the eigenvectors in a few specific cases.

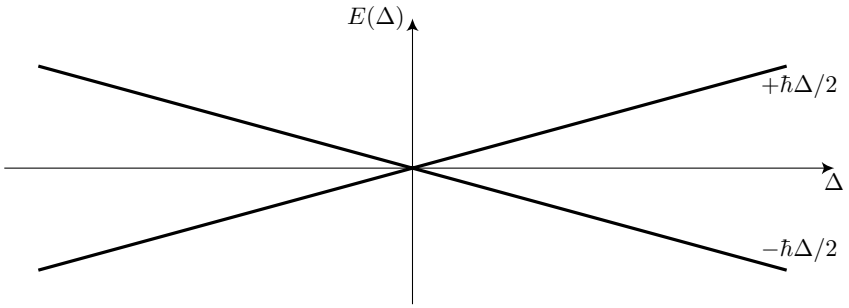
- $\Delta = 0$, the degenerate case. Here $\tan 2\theta \longrightarrow \infty$, so $2\theta = \pi/2$, or $\theta = \pi/4$. Then $\cos\theta = \sin\theta = 1/\sqrt{2}$, so the eigenstates are
$$|+\rangle = \frac{|\mathrm{L}\rangle - |\mathrm{R}\rangle}{\sqrt{2}}, \qquad |-\rangle = \frac{|\mathrm{L}\rangle + |\mathrm{R}\rangle}{\sqrt{2}}, \tag{3.83}$$
which are the eigenstates that we had before (but with opposite labels, as we noted above).

- $\Delta \longrightarrow +\infty$, where the levels are very mismatched. Here $\tan 2\theta \longrightarrow 0^+$, so $\theta = 0$. Then the eigenstates are
$$|+\rangle = -|\mathrm{R}\rangle, \qquad |-\rangle = |\mathrm{L}\rangle. \tag{3.84}$$
These are, of course, the original eigenstates, because when they're very mismatched, there is no hope of tunneling between the wells. The uncoupled state $|\mathrm{R}\rangle$ has the higher energy, as is consistent with our definition of Δ.

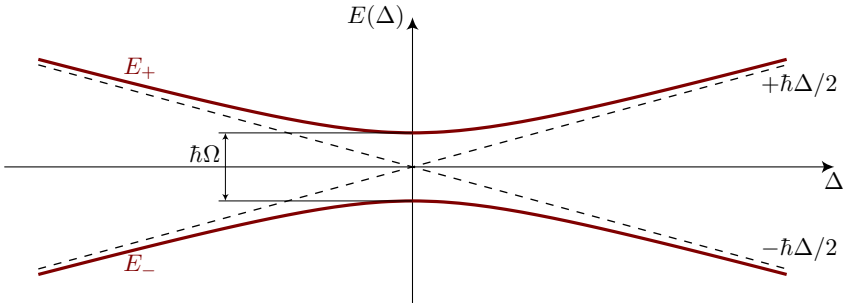
- $\Delta \longrightarrow -\infty$, where the levels are very mismatched, but the other way. Here $\tan 2\theta \longrightarrow 0^-$, which means $\theta = \pi/2$. Then the eigenstates are
$$|+\rangle = |\mathrm{L}\rangle, \qquad |-\rangle = |\mathrm{R}\rangle. \tag{3.85}$$
These are again the original eigenstates, and there is no tunneling. The uncoupled state $|\mathrm{L}\rangle$ has the higher energy this time.

3.5.2 Avoided Level Crossing

Now suppose that we plot the energy levels (3.79). First, in the uncoupled limit $\Omega = 0$, the energies are just the uncoupled levels $\pm\hbar\Delta/2$. As a function of the mismatch Δ these levels cross through each other at $\Delta = 0$, as shown below.



Now when $\Omega \neq 0$, the energies $E_\pm$ from Eqs. (3.79) apply. The interaction Ω is said to "lift the degeneracy" of the states at $\Delta = 0$, and it produces what is called an **avoided level crossing**, as shown below.



The minimum splitting $E_+ - E_-$ is $\hbar\Omega$, and for large $|\Delta|$, asymptotically $E_\pm \sim \pm\hbar|\Delta|$. Overall, the levels $E_\pm$ determine a hyperbola with asymptotes given by the uncoupled energies $\pm\hbar\Delta/2$.

3.5.3 Off-Resonant Rabi Oscillation

Now let's repeat the Rabi-oscillation argument from Section 3.3 to see the difference in the tunneling oscillations in the off-resonant (nondegenerate, $\Delta \neq 0$) case. First, let's write the inverse transformation corresponding to Eqs. (3.81):

$$\begin{aligned} |\mathrm{L}\rangle &= \cos\theta\,|-\rangle + \sin\theta\,|+\rangle \\ |\mathrm{R}\rangle &= \sin\theta\,|-\rangle - \cos\theta\,|+\rangle. \end{aligned} \tag{3.86}$$

Now starting with the initial state

$$|\psi(0)\rangle = |\mathrm{L}\rangle, \tag{3.87}$$

we can use the first of Eqs. (3.86) plus the ordinary time dependence $e^{-iE_\pm t/\hbar}$ of the eigenstates $|\pm\rangle$ to write the general time dependence as

$$|\psi(t)\rangle = \cos\theta\,|-\rangle\, e^{i\tilde{\Omega}t/2} + \sin\theta\,|+\rangle\, e^{-i\tilde{\Omega}t/2}. \tag{3.88}$$

Now using Eqs. (3.86) to transform $|\pm\rangle$ back to the uncoupled states, we have

$$|\psi(t)\rangle = \Big(\cos^2\theta\, e^{i\tilde{\Omega}t/2} + \sin^2\theta\, e^{-i\tilde{\Omega}t/2}\Big)|\mathrm{L}\rangle + \cos\theta\,\sin\theta\,\Big(e^{i\tilde{\Omega}t/2} - e^{-i\tilde{\Omega}t/2}\Big)|\mathrm{R}\rangle. \tag{3.89}$$

Now suppose we compute the probability to find the system in $|\mathrm{R}\rangle$, $P_\mathrm{R}(t) = |\langle\mathrm{R}|\psi(t)\rangle|^2$:

$$P_\mathrm{R}(t) = \cos^2\theta\,\sin^2\theta\,\big|e^{i\tilde{\Omega}t/2} - e^{-i\tilde{\Omega}t/2}\big|^2. \tag{3.90}$$

Simplifying, we can write this as

$$P_\mathrm{R}(t) = 4\cos^2\theta\,\sin^2\theta\,\sin^2(\tilde{\Omega}t/2) = 2\cos^2\theta\,\sin^2\theta\,\big[1-\cos(\tilde{\Omega}t)\big]. \tag{3.91}$$

(generalized Rabi oscillations)

Thus, we see that Rabi oscillations proceed, but now at the generalized Rabi frequency $\tilde{\Omega}$ from Eq. (3.80) instead of Ω. Also, the tunneling is, in general, *incomplete*. Reading off the maximum probability to be in $|\mathrm{R}\rangle$,

$$P_\mathrm{R}(\max) = 4\cos^2\theta\,\sin^2\theta. \tag{3.92}$$

To get a better understanding of this expression, it's time to get rid of the angle θ. Using Eq. (3.82), the maximum probability can be rewritten as (Problem 3.3)

$$P_\mathrm{R}(\max) = \frac{\Omega^2}{\Omega^2+\Delta^2}. \tag{3.93}$$

(maximum tunneling probability)

This is a Lorentzian function in Δ with a full width at half maximum of 2Ω. Putting this factor together with the time dependence gives (Problem 3.2)

$$P_\mathrm{R}(t) = \frac{\Omega^2}{\Omega^2+\Delta^2}\,\sin^2\!\left(\frac{\sqrt{\Omega^2+\Delta^2}\,t}{2}\right). \tag{3.94}$$

(time-dependent tunneling probability)

One thing this means is that the tunneling process is more robust when the coupling rate Ω is large. (In laser physics this is called **power broadening**, where an atomic transition is more tolerant to a laser mismatching the resonance frequency if the intensity is large.) This also says that the *maximum* (in Δ) of the maximum probability occurs when $\Delta = 0$, and we get complete tunneling. For any $\Delta \neq 0$, the tunneling probability is smaller, until it decays away to zero as $|\Delta| \longrightarrow \infty$.

3.6 Exercises

Problem 3.1

In Section 3.3, we studied double-well tunneling by examining the energy splitting, and interpreting the result in terms of tunneling oscillations. The idea is to do the same thing here, but now in more general terms, and in the time domain.

A **qubit** (''quantum bit'') is a generic two-state system. Let's call the states $|0\rangle$ and $|1\rangle$, and let's consider the Hamiltonian

$$(H) = \begin{bmatrix} E_0 & \hbar\Omega/2 \\ \hbar\Omega/2 & E_0 \end{bmatrix}, \tag{3.95}$$

as expressed in the representation of qubit states. For an arbitrary qubit state $|\psi\rangle$, let's work in terms of the qubit representation, using coefficients $c_0 := \langle 0|\psi\rangle$ and $c_1 := \langle 1|\psi\rangle$, or all together,

$$\begin{bmatrix} \langle 0| \\ \langle 1| \end{bmatrix} |\psi\rangle = \begin{bmatrix} c_0 \\ c_1 \end{bmatrix}, \tag{3.96}$$

in the same representation as the Hamiltonian H.

(a) Use the (time-dependent) Schrödinger equation to derive the (coupled) equations of motion

$$\begin{aligned} \dot{c}_0 &= -i\frac{E_0}{\hbar}c_0 - i\frac{\Omega}{2}c_1 \\ \dot{c}_1 &= -i\frac{E_0}{\hbar}c_1 - i\frac{\Omega}{2}c_0. \end{aligned} \tag{3.97}$$

(b) Defining ''slowly varying coefficients''

$$\tilde{c}_0 := c_0 e^{iE_0 t/\hbar}, \qquad \tilde{c}_1 := c_1 e^{iE_0 t/\hbar}, \tag{3.98}$$

derive equations of motion for $\tilde{c}_0$ and $\tilde{c}_1$, and show that they are the same as the equations of motion that follow from a modified (''rotating'') Hamiltonian $\tilde{H}$, which looks like H in Eq. (3.95), but with $E_0 = 0$.

(c) At this point, let's assume we have made the transformation into slowly varying coefficients, so let's use the equations of motion (3.97) with $E_0 = 0$, and let's not bother writing the twiddles anymore. We don't really care about the overall energy, because we now see it only leads to a (common) phase factor $e^{-iE_0 t/\hbar}$. By making the ''rotating-frame'' transformation (3.98), we are essentially cancelling this time dependence in the state amplitudes. You might have heard the exponential factor appearing in Eq. (3.98) called an **integrating factor**.

To proceed with the solution, differentiate and then decouple the equations (3.97), again with $E_0 = 0$, to obtain

$$\begin{aligned} \ddot{c}_0 &= -\left(\frac{\Omega}{2}\right)^2 c_0 \\ \ddot{c}_1 &= -\left(\frac{\Omega}{2}\right)^2 c_1. \end{aligned} \tag{3.99}$$

(d) The solutions to Eqs. (3.99) obviously have the form

$$c_{0,1}(t) = A_{0,1}\sin\left(\frac{1}{2}\Omega t\right) + B_{0,1}\cos\left(\frac{1}{2}\Omega t\right). \tag{3.100}$$

Set $t = 0$ in this solution, in the time derivative of the solution, and in the coupled equations of motion to derive expressions for the coefficients $A_{0,1}$ and $B_{0,1}$ in terms of the initial conditions. You should

find that the solutions may be written

$$\begin{aligned} c_0(t) &= c_0(0)\cos\left(\frac{1}{2}\Omega t\right) - ic_1(0)\sin\left(\frac{1}{2}\Omega t\right) \\ c_1(t) &= c_1(0)\cos\left(\frac{1}{2}\Omega t\right) - ic_0(0)\sin\left(\frac{1}{2}\Omega t\right). \end{aligned} \tag{3.101}$$

(e) Write down the probability $P_0(t) = |c_0(t)|^2$ for finding the qubit in state $|0\rangle$, assuming the initial condition $c_0(t=0) = 1$. Your result should show that the qubit Rabi-oscillates at the Rabi frequency Ω.

Problem 3.2

The idea in this problem is to repeat what you did in Problem 3.1, but for a *nondegenerate* qubit that evolves according to the Hamiltonian

$$(H) = \begin{bmatrix} -\hbar\Delta/2 & \hbar\Omega/2 \\ \hbar\Omega/2 & \hbar\Delta/2 \end{bmatrix}. \tag{3.102}$$

That is, state $|0\rangle$ has energy $-\hbar\Delta/2$, and state $|1\rangle$ has energy $+\hbar\Delta/2$. The states have a net energy difference of $\hbar\Delta$, and this energy can't be removed by a rotating frame transformation like a common-mode energy E_0.

Go through the same procedure as in Problem 3.1: (a) write down the coupled equations of motion for the coefficients, (b) differentiate them to write down decoupled equations, (c) find general solutions in terms of the initial conditions $c_0(0)$ and $c_1(0)$, and (d) find the time-dependent probability $P_0(t) = |c_0(t)|^2$ given $c_0(0) = 1$. You should find that Rabi oscillations occur at the frequency

$$\tilde{\Omega} := \sqrt{\Omega^2 + \Delta^2}, \tag{3.103}$$

i.e., the generalized Rabi frequency. You should also find that the Rabi oscillations are not complete, write down an expression for the maximum probability to be in $|1\rangle$, given that the initial state was $|0\rangle$.

Problem 3.3

In the treatment of tunneling in the asymmetric double well, we ended up with the expression (3.92)

$$P_{\text{R}}(\text{max}) = 4\cos^2\theta\,\sin^2\theta \tag{3.104}$$

for the maximum probability to tunnel to the other well, where again the Stückelberg angle is defined by [Eq. (3.82)]

$$\tan 2\theta = \frac{|\Omega|}{\Delta} \qquad \left(0 \le \theta < \frac{\pi}{2}\right). \tag{3.105}$$

Show from the above equations that $P_{\text{R}}(\text{max})$ reduces to Eq. (3.93),

$$P_{\text{R}}(\text{max}) = \frac{\Omega^2}{\Omega^2 + \Delta^2}. \tag{3.106}$$

Problem 3.4

Consider the Hamiltonian

$$H = \frac{p^2}{2} + \epsilon\cos 2x, \tag{3.107}$$

where ϵ is small compared to the particle's kinetic energy and $x \in [0, 2\pi)$ (with periodic boundary conditions). The Hilbert space for this problem is the pair of momentum eigenstates $|p = \pm\hbar\rangle$ (i.e., $e^{\pm ix}/\sqrt{2\pi}$).

(a) Write down a matrix expression for H in the representation of the two momentum eigenstates.

(b) Argue that Rabi oscillations will occur between the two momentum eigenstates. What is the oscillation frequency?

Note: the Rabi oscillation here is a form of tunneling, because a classical particle can't make a transition between these states (think of a pendulum rotating "over the top," where gravity isn't enough to make the pendulum change the direction of rotation). Since there is quantum tunneling between states not separated by a potential barrier, this is an example of something called **dynamical tunneling**.

Problem 3.5

Quantum schmunneling in the schmymmetric schmouble-shmelta-schmell schmotential is just like quantum tunneling in the symmetric double-delta-well potential, except that the Hamiltonian in the representation of $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$ states reads

$$(H) = \begin{bmatrix} E_0 & \hbar\Omega/2 \\ \hbar\Omega^*/2 & E_0 \end{bmatrix}, \tag{3.108}$$

where Ω is a complex number.

Show that Rabi (Schmabi) oscillations still occur, even when Ω is not a real number. Give an example of an initial state that gives rise to oscillations, and state explicitly the oscillation frequency.

Problem 3.6

Consider a reflection-symmetric double-well potential. We will consider three states $|1\rangle$, $|2\rangle$, and $|3\rangle$; each of these states is localized mainly in the potential wells, and has either even or odd parity with respect to the midpoint of the potential. States $|1\rangle$ and $|2\rangle$ have *opposite* parity, while $|3\rangle$ has the *same* parity as $|2\rangle$. The Hamiltonian in the representation of the three states is

$$(H) = \begin{bmatrix} \epsilon - \delta & 0 & 0 \\ 0 & -\delta & \chi \\ 0 & \chi & +\delta \end{bmatrix}, \tag{3.109}$$

where $\epsilon, \delta, \chi \geq 0$.

(a) What is the tunneling frequency in the limit $|\delta| \gg \chi$?

(b) Sketch the (eigen)energy-level diagram as a function of δ, for fixed ϵ and χ (assume χ is large compared to ϵ). Argue that there is a δ such that tunneling is *suppressed* (i.e., the tunneling frequency goes to zero), and write down an equation that determines this value of δ.[12]

Problem 3.7

In the derivation from class of the quantum Zeno effect, we had the short-time unitary evolution

$$\langle \mathrm{R}|\psi(\Delta t)\rangle = \langle \mathrm{R}|U(\Delta t, 0)|\psi(0)\rangle \approx \langle \mathrm{R}| \left(1 - \frac{i}{\hbar} H\,\Delta t\right) |\mathrm{L}\rangle = -\frac{i}{\hbar}\langle \mathrm{R}|H|\mathrm{L}\rangle\,\Delta t \tag{3.110}$$

in the basis of uncoupled states $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$, with the initial condition $|\psi(0)\rangle = |\mathrm{L}\rangle$.

[12] This effect arises in a driven double-well potential; see F. Grossmann, T. Dittrich, P. Jung, and P. Hänggi, "Coherent destruction of tunneling," *Physical Review Letters* **67**, 516 (1991) (doi: 10.1103/PhysRevLett.67.516).

Suppose we perform the analogous calculation to analyze the same evolution from $|\mathrm{L}\rangle$'s point of view,

$$\langle \mathrm{L}|\psi(\Delta t)\rangle = \langle \mathrm{L}|U(\Delta t, 0)|\psi(0)\rangle \approx \langle \mathrm{L}| \left(1 - \frac{i}{\hbar} H\,\Delta t\right) |\mathrm{L}\rangle = 1, \tag{3.111}$$

under the assumption that $\langle \mathrm{L}|H|\mathrm{L}\rangle = \langle \mathrm{R}|H|\mathrm{R}\rangle = 0$. The squares of these two expressions don't add up to one, which seems like a contradiction. Explain the source of the apparent contradiction and show explicitly how to resolve it.

Problem 3.8

Consider an interaction between two states, characterized by Rabi frequency Ω. The corresponding oscillation period is $T = 2\pi/\Omega$.

Suppose the interaction is turned on for a time $\tau_\pi := \pi/\Omega$. (In the ammonia molecule, the interaction can be pulsed on by turning *off* an electric field for the proscribed time; in the internal states of an atom, the interaction can be pulsed on by turning *on* a resonant radio-frequency or laser field.) Such a pulse, called a **π pulse** (so named because $\Omega\tau_\pi = \pi$), fully transfers a system starting in one state to the other state.

Suppose that *during* the π pulse, N measurements are performed after each time interval $\Delta t = \tau_\pi/N$. Show that for large N, the survival probability for the π pulse may be written

$$P(\tau_\pi) \approx \frac{1}{2}\left[1 + \exp\left(-\frac{\pi^2}{2N}\right)\right], \tag{3.112}$$

with an error of $O(N^{-2})$.

Note that to the same order of accuracy, we could have gone instead with an expression like $1 + \exp(-\pi^2/4N)$. However, the long-time probability here of $1/2$ is a reasonable limit, as it applies to the average over a large ensemble of oscillating two-state systems that are ''restarted'' at random times.

Problem 3.9

Consider a system of N cascaded, ideal polarizers. The polarizers have their transmission axes at angles $\pi/2N, 2\pi/2N, 3\pi/2N, \ldots, \pi/2$ from the x-axis, in the order that an input wave sees them. That is, the last polarizer is oriented along the y-direction. Suppose that an input wave is polarized in the x-direction. Compute the intensity transmission coefficient for the system. Show that the transmission coefficient approaches unity as $N \longrightarrow \infty$. This is a simple realization of the quantum Zeno effect, where each polarizer acts as a ''measurement'' of the polarization state—the polarization is ''dragged'' by the measurements as long as they are sufficiently frequent.

Problem 3.10

A **schmubit** is a schmuantum-mechanical system that undergoes **schmunitary evolution**, which means that, starting in some initial state, the survival probability (the probability for a measurement to reveal that the schmubit is still in the initial state) is

$$P_{\mathrm{surv}}(\Delta t) = 1 - \beta(\Delta t)^\alpha \tag{3.113}$$

for small times Δt. Analyze the survival probability over a long time T, interrupted by N measurements $\Delta t = T/N$ apart in time. What are the conditions on α and β for there to be a Zeno effect?

You should define what you mean by ''Zeno effect,'' and to make things simple, you may assume that once a schmubit is lost from the initial state, that there is no way for it to schmeturn.

Problem 3.11

A simple model for the quantum Zeno effect is a two-state system where the particle in one state is

absorbed. That is, think of double-well tunneling, where the particle ceases to exist once it reaches the other well. Because absorption acts like a measurement (e.g., most photodetectors detect photons by destroying them), this is sufficient to induce a Zeno effect.

To model this problem, consider a qubit (two-state system) with states $|0\rangle$ and $|1\rangle$, with non-Hermitian Hamiltonian

$$(H) = \hbar \begin{bmatrix} 0 & \Omega \\ \Omega & -i\gamma \end{bmatrix}. \tag{3.114}$$

Note that $|1\rangle$ is the absorption state according to this Hamiltonian, with the absorption controlled by parameter γ.

(a) First consider the case $\Omega = 0$, and verify that the Hamiltonian causes absorption of state $|1\rangle$. That is, show that the amplitude of $|1\rangle$ decays in time, according to Schrödinger-equation evolution. What is the rate at which the **probability** for a particle to be found in $|1\rangle$ decays?

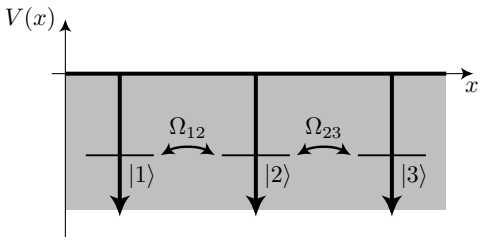
(b) Now returning to the case $\Omega > 0$, derive (coupled) equations of motion for amplitudes c_0 and c_1, where

$$|\psi(t)\rangle = c_0(t)|0\rangle + c_1(t)|1\rangle. \tag{3.115}$$

(c) Show that in the limit $\gamma \gg \Omega$, that $c_1 \approx 0$. Then complete the argument and show that there is a quantum Zeno effect in this limit, given the initial condition $|\psi(t=0)\rangle = |0\rangle$.

Problem 3.12

The sketch below shows a generalization of the double-well tunneling problem to three **identical** potential wells.



The "uncoupled" energy states (i.e., ignoring tunneling) associated with the three isolated wells are $|1\rangle$, $|2\rangle$, and $|3\rangle$. The tunneling coupling between $|1\rangle$ and $|2\rangle$ is represented by Ω_{12}, and the tunneling coupling between $|2\rangle$ and $|3\rangle$ is represented by Ω_{23}. For simplicity, assume $\Omega_{12}, \Omega_{23} > 0$, and ignore any direct tunneling between $|1\rangle$ and $|3\rangle$ (i.e., $\Omega_{13} = 0$).

(a) Write down the Hamiltonian describing a tunneling quantum particle in this potential, expressed in the representation of the uncoupled energy states. Also write down a set of coupled differential equations for the amplitudes c_1, c_2, and c_3 for the quantum state expressed in the same representation.

(b) Suppose that the particle is initially in the $|1\rangle$ state, and consider the time evolution of the particle tunneling to $|2\rangle$. Can the presence of the $|3\rangle$ state plus the unitary coupling Ω_{23} act like a "unitary observer" and produce something analogous to a quantum Zeno effect? That is, can the presence of $|3\rangle$ suppress the tunneling to $|2\rangle$ in some regime? Justify your answer mathematically (and note that your justification is the most important part of your answer here!).

(c) Suppose that the $|3\rangle$ state is modified to include strong absorption at rate γ (i.e., add a term of the form $-\gamma c_3$ to the equation of motion for c_3, in the limit of large γ). Does this change your conclusion from (b)? (Again, justify.)

Problem 3.13

Consider a ''which side of $x = 0$'' measurement that behaves as follows. The two possible outcomes of the measurement are ''I found the particle in the region $x > 0$'' and ''I didn't find it there.'' In the null-result case (''I didn't find it there''), the result is that, just after the measurement, $\psi(x) = 0$ for all $x > 0$ (and the wave function in the region $x < 0$ is appropriately renormalized but otherwise unaffected by the measurement).

Now suppose that that at time $t = 0$, a state $\psi(x)$ is such that $\psi(x) = 0$ for all $x > 0$ (i.e., it is completely contained in the region $x < 0$). Show that the which-side measurement leads to a quantum Zeno effect, in that the particle is excluded from entering the region $x > 0$. (Useless aside: this means physically that a wave packet incident on the boundary $x = 0$ is reflected by the measurement.)

Hint: start by considering the amplitude $\langle x|\psi(\Delta t)\rangle$ at a particular $x > 0$; then use this to argue how the probability of the $x > 0$ measurement scales with Δt.

Chapter 4

Adiabatic Evolution and Geometric Phase

Adiabatic evolution occurs when some parameter of the Hamiltonian changes very slowly. Under the right conditions, under an adiabatic change in the Hamiltonian, there are no transitions between states. We'll start off by illustrating this statement with an example, and then we'll go back and make the statement more precise.

4.1 Adiabatic Passage

As a first example, let's return to the tunneling problem between two potential wells from Chapter 3, and specifically the avoided crossing from Section 3.5. The effect here is so simple in terms of adiabatic evolution, but so interesting, that it's almost magic. The question is: What happens when we dynamically *change* the mismatch Δ between the two wells? If the tunneling problem corresponds to a charged particle tunneling between identical wells, the mismatch can be tuned by changing an applied electric field. Or, in terms of transitions between atomic energy levels due to an applied laser field, it turns out to be equivalent to sweep the frequency of the laser field through the atomic resonance.

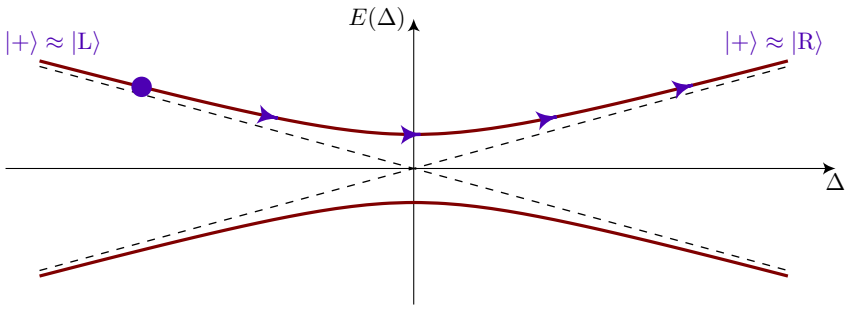
But it turns out that we can do useful things by changing the mismatch. For example, in two-state systems, it is often useful to transfer a system in one state into the other state, with unit probability. In quantum information, this operation applied to a **qubit** (quantum bit, i.e., a generic two-level quantum system) is called a ''`SWAP` gate'' (or ''`QNOT` gate''). In principle, given a Rabi frequency Ω, the oscillation period is $T = 2\pi/\Omega$, so all we have to do is turn on the interaction (say, by shifting the states or the interaction into resonance) for a time $T/2$. However, in practice, this can be a little difficult to do. The Rabi frequency often depends on things like laser intensities, electric fields, etc., which are only easily controlled at the percent level; this can limit the accuracy of a transfer operation.

There is another approach, however, that can get arbitrarily close to a 100% transfer efficiency, provided we are willing to do things *slowly*. We don't even have to do any math to see this, just look at some sketches. The procedure is as follows.

1. Start in the state $|\mathrm{L}\rangle$, and a large mismatch, $\Delta \longrightarrow -\infty$. In this limit, from the discussion above, $|+\rangle \approx |\mathrm{L}\rangle$.

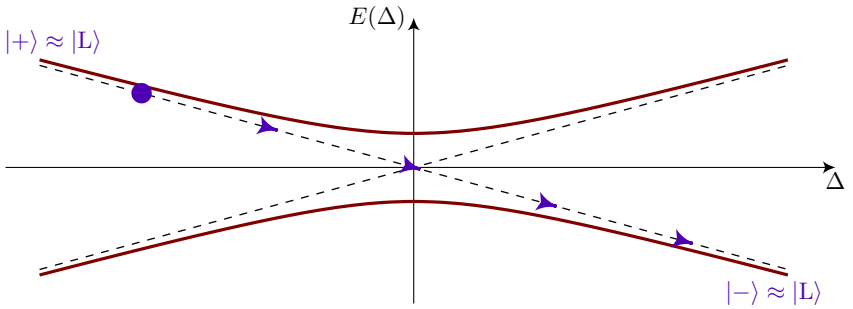
2. Now *slowly* change Δ, increasing to $\Delta \longrightarrow +\infty$. The **adiabatic theorem** (more on this below) says that provided we change Δ sufficiently slowly, the state should ''follow'' the E_+ energy, and stay in the $|+\rangle$ state. (See the diagram below for the path that we are following, marked by blue arrows.)

3. At the end of the day, we are still in state $|+\rangle$, but with $\Delta \longrightarrow +\infty$, where now $|+\rangle \approx |\mathrm{R}\rangle$. Bingo!



So this whole adiabatic process, called **adiabatic transfer** or **adiabatic passage**, led to a transfer from $|\mathrm{L}\rangle$ to $|\mathrm{R}\rangle$, and it is *perfect* to the extent that the process was slow, and we made the initial and final mismatches very large (here, $|\Delta| \gg |\Omega|$ at the beginning and end for the process to work well). Note that this whole process *looks* simple, but it's only simple in the coupled eigenbasis. If we expressed the process in terms of the $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$ states, there would be a whole lot more wiggling going on, especially during the part of the process where $|\Delta|$ is on the order of $|\Omega|$.

What happens if we make a *fast* change instead of a slow change? In this case, the sweep through resonance can happen much more quickly than the time scales over which the coupling Ω acts, and there is no chance to make any tunneling transition. The process is illustrated below, where the state "jumps" the avoided crossing.



This process is called a **diabatic crossing**, and it works out because at the end of the process, when $\Delta \longrightarrow +\infty$, $|-\rangle \approx |\mathrm{L}\rangle$, so although the state jumped a gap, it really stayed in the same state.

These observations are often summarized as in the following statement: In an avoided crossing, *the two states exchange identities*. Thus, staying in the same coupled state while sweeping through the avoided crossing means that we swap uncoupled states. A diabatic crossing means that we switch coupled states, but we stayed in the *same* uncoupled state.

Although we have just given an intuitive treatment of the adiabatic-passage problem, it can also be solved exactly, and the mathematical treatment is called the **Landau–Zener crossing** problem.[1] In this problem the crossing probability can be computed for any rate of change of Δ, provided the rate of change of Δ is constant in time; the solution is not very simple, but the state amplitudes can be computed exactly in terms of parabolic cylinder functions. The result for the probability to cross the energy gap (i.e., the probability that the system is diabatically "lost") is[2]

$$P_{\text{lost}} = \exp\left(-\frac{\pi\Omega^2}{2|\partial_t \Delta|}\right). \qquad (4.1)$$

(Landau–Zener tunnel probability)

[1] L. D. Landau, "Zur Theorie der Energieübertragung. II.," *Physikalische Zeitschrift der Sowjetunion* **2**, 46 (1932); Clarence Zener, "Non-Adiabatic Crossing of Energy Levels," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, **137**, 696 (1932); E. C. G. Stueckelberg, *Helvetica Physica Acta* **5**, 369 (1932). See also Jan R. Rubbmark, Michael M. Kash, Michael G. Littman, and Daniel Kleppner, "Dynamical effects at avoided level crossings: A study of the Landau–Zener effect using Rydberg atoms," *Physical Review A* **23**, 3107 (1981) (doi: 10.1103/PhysRevA.23.3107).

[2] For details, see Daniel A. Steck, *Quantum and Atom Optics*, available online at `http://steck.us/teaching` (2007).

The adiabatic condition (the condition for $P_{\text{lost}} \approx 0$ is then for $|\partial_t \Delta| \ll \Omega^2$; this makes sense, as Ω^2 is dimensionally the only other quantity that we can realistically use as a comparison to $|\partial_t \Delta|$.

4.2 Proof of the Adiabatic Theorem

The adiabatic theorem,[3] which we just used in discussing adiabatic passage, says that if we make sufficiently slow, smooth changes to a Hamiltonian, the eigenstates should never mix: a system in an eigenstate should stay in the same state, even as it smoothly varies. As a plausibility argument, recall from Eq. (3.93) that in the two-state tunneling problem, transitions between two states are largely suppressed if the interaction is small and the energy gap between the states is large, even over long interaction times. Changes to a Hamiltonian induce an effective interaction between states, but *slow* changes induce *weak* interactions. If the spectrum of the Hamiltonian is discrete, there are gaps between all states, and so we might expect that, given sufficiently slow changes, that transitions to other states are suppressed, even though the changes may take place over an arbitrarily long time.

4.2.1 Phase Considerations

An important aspect of the transition between two states is the *relative phase* of the components in each state. After all, if at some instant, a tunneling particle is in an equal superposition of the left- and right-hand wells, how do we know which ''way'' the particle is going? The answer is encoded in this relative phase, which is different depending on which part of the tunneling cycle we're observing. This is easy to see by setting $\Delta = 0$ (and thus $\theta = \pi/4$) in the time-dependent state (3.89), so that the general solution is

$$|\psi(t)\rangle = \cos\left(\frac{\Omega t}{2}\right)|\mathrm{L}\rangle + \sin\left(\frac{\Omega t}{2}\right)|\mathrm{R}\rangle. \tag{4.2}$$

Then, neglecting global phases, the relative phase $|\mathrm{L}\rangle + |\mathrm{R}\rangle$ is associated with $|\mathrm{L}\rangle \longrightarrow |\mathrm{R}\rangle$ transitions, and $|\mathrm{L}\rangle - |\mathrm{R}\rangle$ is associated with $|\mathrm{R}\rangle \longrightarrow |\mathrm{L}\rangle$ transitions. In the off-resonant case, the phase is important too, as it is the differently evolving phases of the two states that ''tell'' the particle to not tunnel very much into the energy-mismatched well. That is, the energy mismatch causes a rapidly rotating relative phase, so the correct phase for complete tunneling is not maintained long enough for the tunneling to actually happen. The point of all of this is just to say that, in the proof of the adiabatic theorem, the relative phases of the states will be *critical*.

4.2.2 Setup of the Proof

Now onto the proof. Suppose we have a parameterized family of Hamiltonians $H(\lambda)$, where the parameter $\lambda \in [0, 1]$, and $H(\lambda)$ is continuous (meaning the eigenvectors and eigenvalues are continuous functions of λ, and in fact we should also assume that the eigenvalues and eigenvectors are differentiable and with bounded derivatives in λ). Also suppose that λ varies with time, such that $\lambda = \lambda(t)$ is continuous and monotocally increasing, with $|d\lambda/dt|$ bounded (i.e., λ doesn't change arbitrarily quickly with time). Time varies in $t \in [0, T]$, and the λ parameter satisfies the boundary conditions $\lambda(0) = 0$ and $\lambda(T) = 1$. We will also assume nondegenerate eigenstates for all λ (and in fact a discrete spectrum). In fact, we can simplify the treatment a bit by assuming a linear time dependence

$$\lambda(t) = \frac{t}{T}, \tag{4.3}$$

without losing generality. This is because, if we want a more general parameterization $\tilde{\lambda}(t)$, we could set $\tilde{H}(\lambda) := H[\tilde{\lambda}[T\lambda(t)]]$, and apply the argument that follows to the reparameterized Hamiltonian $\tilde{H}(\lambda)$.

We want to show that, in the limit $T \longrightarrow \infty$, that an eigenstate at $t = 0$ ($\lambda = 0$) maps to the corresponding eigenstate at $t = T$ ($\lambda = 1$). That is, $|\psi_n(\lambda = 0)\rangle$ maps to the state $|\psi_n(\lambda = 1)\rangle$, which is the state continuously connected to the original state by a continuous change of λ from 0 to 1.

[3] Max Born and Vladimir Fock, ''Beweis des Adiabatensatzes,'' *Zeitschrift für Physik* **51**, 165 (1928) (doi: 10.1007/BF01343193).

4.2.3 Dynamical Phase Evolution

To motivate some of the proof to come, first let's *assume* that the state follows the eigenstate as indicated. Then there is still evolution of the state (because the state evolves with λ), but it should be trivial evolution in the sense of generating a phase factor. Thus, we would expect evolution according to the evolution operator for a time-dependent Hamiltonian [Section 1.8, Eq. (1.184)] as

$$|\psi_n(\lambda_t)\rangle = \exp\left[-\frac{i}{\hbar}\int_0^t dt'\, H(\lambda_{t'})\right]|\psi_n(0)\rangle, \tag{4.4}$$

where we are using the notation $\lambda_t = \lambda(t) = t/T$. Since we assume that the state evolution follows an eigenstate of $H(\lambda_t)$ we can write this as a phase factor in terms of the eigenvalue

$$|\psi_n(\lambda_t)\rangle = \exp\left[-\frac{iT}{\hbar}\int_0^{\lambda_t} d\lambda\, E_n(\lambda)\right]|\psi_n(0)\rangle, \tag{4.5}$$

where we also changed integration variables to λ from t. We expect this phase evolution, and although it is essential as we argued above, we're not especially interested in it, so we will want to try to get rid of it by defining states like

$$|\tilde{\psi}_n(\lambda_t)\rangle = \exp\left[\frac{iT}{\hbar}\int_0^{\lambda_t} d\lambda\, E_n(\lambda)\right]|\psi_n(\lambda_t)\rangle, \tag{4.6}$$

where the phase factor here is designed to cancel the expected phase evolution of $|\psi_n(\lambda_t)\rangle$. We will, however, do this in terms of the eigenstate *amplitudes* rather than the eigenstates themselves.

4.2.4 Time Evolution

Now onto the main proof. First, let's expand a general state in the time-dependent (λ-dependent) eigenstates:

$$|\psi(t)\rangle = \sum_m c_m(t)|\psi_m(\lambda_t)\rangle. \tag{4.7}$$

Notice that the general state is parameterized in time, but the eigenstates are parameterized in terms of λ to match the Hamiltonian. Ultimately this latter parameterization is the more useful one, as it will separate out the effect of a slow perturbation (long T) from the effect of the change in the Hamiltonian, independent of the length of the perturbation (i.e., changing λ from 0 to 1). Putting this state into the Schrödinger equation

$$\partial_t|\psi\rangle = -\frac{i}{\hbar}H|\psi\rangle \tag{4.8}$$

gives

$$\sum_m\left(\dot{c}_m(t)|\psi_m(\lambda_t)\rangle + \frac{c_m(t)}{T}\partial_{\lambda_t}|\psi_m(\lambda_t)\rangle\right) = -\frac{i}{\hbar}\sum_m c_m(t)E_m(\lambda_t)|\psi_m(\lambda_t)\rangle, \tag{4.9}$$

where we changed the derivative by $\partial_t = T^{-1}\partial_\lambda$ (recalling $\lambda_t = t/T$), and we already used the fact that $|\psi_m(\lambda)\rangle$ is an eigenstate of $H(\lambda)$. Now projecting with $\langle\psi_n(\lambda_t)|$, we have

$$\dot{c}_n(t) = -\frac{1}{T}\sum_m c_m(t)\langle\psi_n(\lambda_t)|\partial_{\lambda_t}|\psi_m(\lambda_t)\rangle - \frac{iE_n(\lambda_t)}{\hbar}c_n(t). \tag{4.10}$$

The last term here is the expected, ordinary phase evolution of the eigenstate that we discussed as the prelude to this proof. We can get rid of this term by defining slowly varying amplitudes

$$\tilde{c}_n(t) := c_n(t)\,\exp\left[\frac{i}{\hbar}\int_0^t dt'\, E_n(\lambda_{t'})\right] = c_n(t)\,\exp\left[\frac{iT}{\hbar}\int_0^{\lambda_t} d\lambda\, E_n(\lambda)\right]. \tag{4.11}$$

Differentiating this amplitude gives

$$\dot{\tilde{c}}_n(t) = \left[\dot{c}_n(t) + \frac{i}{\hbar}E_n(\lambda_t)\, c_n(t)\right] \exp\left[\frac{i}{\hbar}\int_0^t dt'\, E_n(\lambda_{t'})\right], \tag{4.12}$$

and using Eq. (4.10), we obtain

$$\dot{\tilde{c}}_n(t) = -\frac{1}{T}\sum_m \tilde{c}_m(t)\, \langle\psi_n(\lambda_t)|\partial_{\lambda_t}|\psi_m(\lambda_t)\rangle \exp\left[-\frac{iT}{\hbar}\int_0^{\lambda_t} d\lambda \left[E_m(\lambda) - E_n(\lambda)\right]\right]. \tag{4.13}$$

Let's hide the mess in the exponent by defining the energy difference and phase by

$$E_{mn}(\lambda) := E_m(\lambda) - E_n(\lambda), \qquad \Phi_{mn}(\lambda) = \frac{T}{\hbar}\int_0^{\lambda_t} d\lambda\, E_{mn}(\lambda), \tag{4.14}$$

so that

$$\dot{\tilde{c}}_n(t) = -\frac{1}{T}\sum_m \tilde{c}_m(t)\, \langle\psi_n(\lambda_t)|\partial_{\lambda_t}|\psi_m(\lambda_t)\rangle\, e^{-i\Phi_{mn}(\lambda)}. \tag{4.15}$$

Formally integrating once with respect to time and then changing to λ_t then gives

$$\tilde{c}_n(t) = \tilde{c}_n(0) - \sum_m \int_0^{\lambda_t} d\lambda\, \tilde{c}_m(\lambda T)\, \langle\psi_n(\lambda)|\partial_\lambda|\psi_m(\lambda)\rangle\, e^{-i\Phi_{mn}(\lambda)}. \tag{4.16}$$

Now, let's work a bit with the matrix element of ∂_{λ_t} in this equation. Starting with the eigenvalue equation

$$H(\lambda)|\psi_m(\lambda)\rangle = E_m(\lambda)|\psi_m(\lambda)\rangle, \tag{4.17}$$

we can compute a derivative as

$$\dot{H}(\lambda)|\psi_m(\lambda)\rangle + H(\lambda)\partial_\lambda|\psi_m(\lambda)\rangle = \dot{E}_m(\lambda)|\psi_m(\lambda)\rangle + E_m(\lambda)\partial_\lambda|\psi_m(\lambda)\rangle, \tag{4.18}$$

and then project with $\langle\psi_n(\lambda)|$:

$$\langle\psi_n(\lambda)|\dot{H}(\lambda)|\psi_m(\lambda)\rangle + E_n(\lambda)\langle\psi_n(\lambda)|\partial_\lambda|\psi_m(\lambda)\rangle = \dot{E}_m(\lambda)\,\delta_{mn} + E_m(\lambda)\langle\psi_n(\lambda)|\partial_\lambda|\psi_m(\lambda)\rangle. \tag{4.19}$$

In the case $m \neq n$, we can solve for the matrix element of ∂_λ to write

$$\langle\psi_n(\lambda)|\partial_\lambda|\psi_m(\lambda)\rangle = \frac{\langle\psi_n(\lambda)|\dot{H}(\lambda)|\psi_m(\lambda)\rangle}{E_m(\lambda) - E_n(\lambda)} =: \frac{\dot{H}_{nm}(\lambda)}{E_{mn}(\lambda)}, \tag{4.20}$$

where, to be explicit, we are employing the usual matrix-element shorthand

$$\dot{H}_{nm}(\lambda) := \langle\psi_n(\lambda)|\dot{H}(\lambda)|\psi_m(\lambda)\rangle. \tag{4.21}$$

Separating out the $m = n$ term in Eq. (4.16) gives

$$\tilde{c}_n(t) = \tilde{c}_n(0) - \int_0^{\lambda_t} d\lambda\, \tilde{c}_n(\lambda T)\, \langle\psi_n(\lambda)|\partial_\lambda|\psi_n(\lambda)\rangle - \sum_{m\neq n}\int_0^{\lambda_t} d\lambda\, \tilde{c}_m(\lambda T)\, \frac{\dot{H}_{nm}(\lambda)}{E_{mn}(\lambda)}\, e^{-i\Phi_{mn}(\lambda)}. \tag{4.22}$$

Now we will argue that the $m \neq n$ terms may be neglected.

4.2.5 Adiabatic Evolution

In Eq. (4.22), we have a phase factor of the form $e^{-i\phi(t)}$; remember that this compares to the constant-frequency phase $e^{-i\omega t}$, except that in the more general case the *instantaneous* frequency is $\omega(t) := \dot{\phi}(t)$, and the phase factor becomes $e^{-i\phi(t)} = \exp[-i\int_0^t \omega(t')\,dt']$. In the case of $\Phi_{mn}(\lambda)$ in Eq. (4.14), we have the instantaneous frequency

$$\dot{\Phi}_{mn}(\lambda) = \frac{T}{\hbar} E_{mn}(\lambda_t). \tag{4.23}$$

Notice that λ_t is the "time" here, not t, a point that is critical to the argument that follows.

Because of the T in the exponential factor, the frequency diverges, and so the phase oscillates arbitrarily quickly with λ_t in the limit $T \longrightarrow \infty$. The brief argument is to note that the rest of the integrand is bounded ($\tilde{c}_m$ is an amplitude, $\dot{H}_{nm}$ is bounded by assumption, and $[\Delta E_{mn}]^{-1}$ is bounded by the assumption of a discrete spectrum) with separated, noncrossing levels. So in the $T \longrightarrow \infty$ limit we can replace the oscillating exponential by its average value, which is just zero. To be a bit more careful, under the integral sign the oscillating phase factor effectively contributes a factor of $\dot{\Phi}_{mn}$. For this to drag the rest of the integrand to zero, we should have

$$\left|\dot{\Phi}_{mn}\right| = \left|\frac{TE_{mn}}{\hbar}\right| \gg \left|\frac{\dot{H}_{nm}(\lambda)}{E_{mn}(\lambda)}\right|. \tag{4.24}$$

Simplifying, this condition becomes

$$T \gg \frac{\hbar\left|\dot{H}_{nm}\right|}{(E_{mn})^2}. \tag{4.25}$$
(adiabaticity condition)

This condition defines more precisely what it means for T to be "sufficiently large" or for the change in the Hamiltonian to be "sufficiently slow." When reading this condition, the system parameters should be read as their worst-case values. That is, the Hamiltonian gradient $\dot{H}_{nm}(\lambda)$ should be the taken to be the maximum value over $\lambda \in [0,1]$, and the energy gap $E_{mn}(\lambda)$ should be taken to be the minimum value.

When the adiabatic condition holds, we can drop the $m \neq n$ terms in Eq. (4.22), and we are left with

$$\tilde{c}_n(t) = \tilde{c}_n(0) - \int_0^{\lambda_t} d\lambda\, \tilde{c}_n(\lambda T)\, \langle \psi_n(\lambda)|\partial_\lambda|\psi_n(\lambda)\rangle. \tag{4.26}$$

The solution to this integral equation is

$$\tilde{c}_n(t) = \tilde{c}_n(0) \exp\left[-\int_0^{\lambda_t} d\lambda\, \langle \psi_n(\lambda)|\partial_\lambda|\psi_n(\lambda)\rangle\right]. \tag{4.27}$$
(final evolution)

What may or may not be obvious is that the remaining exponential factor is just another *phase* factor. This is because ∂_λ is basically a scaled time derivative, and since the Schrödinger equation says $i\hbar\partial_t = H$, then $i\partial_t$ must be Hermitian, in which case ∂_t (hence ∂_λ) is anti-Hermitian, or purely imaginary. Thus, what we have shown is that

$$|\tilde{c}_n(t)|^2 = |\tilde{c}_n(0)|^2, \tag{4.28}$$

and thus

$$|c_n(t)|^2 = |c_n(0)|^2, \tag{4.29}$$

so that there are never any transitions between states. This is what we set out to show.

In the process, though, although we tucked away the expected energy-related phase evolution—the **dynamical phase**—in the transformation (4.11), we still obtained an extra phase factor in Eq. (4.27). This phase only depends on the change in the Hamiltonian, as we can see by setting $t \longrightarrow T$,

$$\tilde{c}_n(T) = \tilde{c}_n(0) \exp\left[-\int_0^{1} d\lambda\, \langle \psi_n(\lambda)|\partial_\lambda|\psi_n(\lambda)\rangle\right], \tag{4.30}$$
(Berry phase)

and in fact it depends on the details of how the Hamiltonian changed along the way. It just doesn't depend at all on how *long* it took. In fact, this phase factor is nontrivial in cases where there is a nontrivial geometry associated with the evolution of the Hamiltonian and eigenstates. Thus, this phase is called a **geometric phase** or a **Berry phase**.[4]

4.3 Second Proof of the Adiabatic Theorem

The above proof is careful and correct, but fairly involved. To highlight some of the more important aspects of the proof, as well as to make use of some techniques that we introduced before in Chapter 1, we'll go through the proof *again*, but using operator techniques. This is a more elegant formulation of the proof, but using more powerful techniques. It sets up the basic idea of how we will approach perturbation theory later on in Chapter 13. However, in order to really see what is happening in this proof, it is useful to compare to the first proof—otherwise, the motivation for some of the steps isn't at all obvious.

To begin, recall that in general we can write the unitary time-evolution operator from $t' = 0$ to t under the action of a general time-dependent Hamiltonian $H(t)$ in the form (1.185)

$$U(t,0) = \mathscr{T} \exp\left[-\frac{i}{\hbar}\int_0^t H(t')\,dt'\right], \tag{4.31}$$

where remember that the chronological operator $\mathscr{T}$ means that the exponential is a time-ordered product of infinitesimal evolution operators. To make the notation more compact, instead of writing $U(t,0)$, we can write instead $U(t)$ or just U, depending on whether or not we want to emphasize the time dependence.

4.3.1 A Change of Representation

Now let's consider a time-dependent unitary transformation $R(t)$, which we will not specify right away. Remember that $R(t)$ induces a change in representation, so that we can write new states

$$|\tilde{\psi}(t)\rangle = R(t)|\psi(t)\rangle \tag{4.32}$$

at each instant in time, subject to initially equivalent representations

$$|\tilde{\psi}(0)\rangle = |\psi(0)\rangle, \qquad R(0) = 1. \tag{4.33}$$

The intent is to use $R(t)$ to carry out the transformation (4.11) to remove the expected dynamical phase from the problem. However, we will end up with this transformation representing *both* the dynamical and geometric phases.

Given a time-dependent unitary transformation, we know from Eq. (1.133) that the Hamiltonian transforms according to

$$\tilde{H} = RHR^\dagger + i\hbar\dot{R}R^\dagger, \tag{4.34}$$

so that the transformed states evolve via

$$i\hbar\partial_t|\tilde{\psi}(t)\rangle = \tilde{H}(t)|\tilde{\psi}(t)\rangle. \tag{4.35}$$

It follows that the evolution operator in the new representation is

$$\begin{aligned}\tilde{U}(t,0) &= \mathscr{T}\exp\left[-\frac{i}{\hbar}\int_0^t \tilde{H}(t')\,dt'\right] \\ &= \mathscr{T}\exp\left[-\frac{i}{\hbar}\int_0^t R(t')H(t')R^\dagger(t')\,dt' + \int_0^t \dot{R}(t')R^\dagger(t')\,dt'\right].\end{aligned} \tag{4.36}$$

[4] Michael Victor Berry, "Quantal phase factors accompanying adiabatic changes," *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **392** 45 (1984) (doi: 10.1098/rspa.1984.0023). The geometric phase is also called the **Pancharatnam phase**, after the prior discovery in optics by S. Pancharatnam, "Generalized Theory of Interference, and Its Applications. Part I. Coherent Pencils," *Proceedings of the Indian Academy of Sciences - Section A* **44** 247 (1956) (doi: 10.1007/BF03046050). Another early example of a geometric phase was also mentioned in the interpretation of molecular vibrational spectra in Hugh Christopher Longuet-Higgins, U. Öpik, Maurice Henry Lecorney Pryce, and R. A. Sack, "Studies of the Jahn-Teller effect. II. The dynamical problem," *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **244**, 1 (1958) (doi: 10.1098/rspa.1958.0022) (see the top of p. 12).

Now it's time to specify $R(t)$: we want to make the new evolution operator *simple*. In particular, we will choose $R(t)$ to be diagonal in the basis of $H(t)$ (at the same time). In particular, then, we can assume $[R(t), H(t)] = 0$, so that

$$\tilde{U}(t,0) = \mathscr{T} \exp\left[-\frac{i}{\hbar}\int_0^t H(t')\,dt' + \int_0^t \dot{R}(t')R^\dagger(t')\,dt'\right] = \mathscr{T}U(t,0)\exp\left[\int_0^t \dot{R}(t')R^\dagger(t')\,dt'\right]. \tag{4.37}$$

Then $R(t)$ is diagonal in the basis of eigenstates $|\psi_n(t)\rangle$ of $H(t)$, so that explicitly,

$$\langle\psi_m(t)|R(t)|\psi_n(t)\rangle = R_{mn}(t) = \delta_{mn}\, e^{-i\varphi_n(t)}, \tag{4.38}$$

for consistency with the requirement that $R(t)$ is unitary. The minus sign of the phase here is designed again to *cancel* the expected dynamical phase. Note that the phases must satisfy the initial condition $\varphi_n(0) = 0$, because $R(0) = 1$.

4.3.2 Evolving the Evolution Operator

Recalling from Eq. (1.179) that the unitary time-evolution operator satisfies the Schrödinger equation,

$$\begin{aligned} i\hbar\partial_t\tilde{U}(t) &= \tilde{H}(t)\,\tilde{U}(t) \\ &= R(t)H(t)R^\dagger(t)\tilde{U}(t) + i\hbar\dot{R}(t)R^\dagger(t)\tilde{U}(t) \\ &= H\tilde{U} + i\hbar\dot{R}R^\dagger\tilde{U}, \end{aligned} \tag{4.39}$$

and then multiplying on the left by $\tilde{U}^\dagger(t)$, we have

$$\tilde{U}^\dagger\dot{\tilde{U}} = -\frac{i}{\hbar}\tilde{U}^\dagger H\tilde{U} + \tilde{U}^\dagger\dot{R}R^\dagger\tilde{U}. \tag{4.40}$$

Computing the expectation value with respect to the initial eigenstate $|\psi_n(0)\rangle$,

$$\langle\psi_n(0)|\tilde{U}^\dagger\dot{\tilde{U}}|\psi_n(0)\rangle = -\frac{i}{\hbar}\langle\psi_n(0)|\tilde{U}^\dagger H\tilde{U}|\psi_n(0)\rangle + \langle\psi_n(0)|\tilde{U}^\dagger\dot{R}R^\dagger\tilde{U}|\psi_n(0)\rangle, \tag{4.41}$$

remembering that all the operators here are explicitly time-dependent. Now we will want to use

$$\tilde{U}(t)|\psi_n(0)\rangle = \tilde{U}(t)|\tilde{\psi}_n(0)\rangle = |\tilde{\psi}_n(t)\rangle, \tag{4.42}$$

but this is only true in the adiabatic limit. Thus it's time to argue that this indeed happens in the adiabatic limit.

4.3.2.1 Adiabaticity

Since we have handled this part of the argument formally in the previous proof, we can be a little less formal here. Consider the evolution from time t to $t + \Delta t$, for some interval Δt:

$$\langle\psi_m(t+\Delta t)|U(t+\Delta t,t)|\psi_n(t)\rangle \approx \langle\psi_m(t+\Delta t)|\exp\left(-\frac{i}{\hbar}H(\lambda_t)\,\Delta t\right)|\psi_n(t)\rangle. \tag{4.43}$$

Here, $\lambda_t = t/T$ as before, where $\Delta\lambda_t$ is small in the limit of large T, and correspondingly $H(\lambda_t)$ is approximately constant over the interval Δt. Then we will use $e^{-iH(\lambda_t)\,\Delta t/\hbar}|\psi_n(t)\rangle = e^{-iE_n\,\Delta t/\hbar}|\psi_n(t)\rangle$, along with $|\psi_m(t+\Delta t)\rangle \approx e^{-iH(\lambda_t)\,\Delta t/\hbar}|\psi_m(t)\rangle = e^{-iE_m(\lambda_t)\,\Delta t/\hbar}|\psi_m(t)\rangle$, which amounts to ignoring the small variation in $|\psi_m(t)\rangle$ over the time interval (due to the small change in λ) other than the normal phase evolution. Thus,

$$\begin{aligned} \langle\psi_m(t+\Delta t)|U(t+\Delta t,t)|\psi_n(t)\rangle &\approx \langle\psi_m(t)|e^{iE_m(\lambda_t)\,\Delta t/\hbar}e^{-iE_n(\lambda_t)\,\Delta t/\hbar}|\psi_n(t)\rangle \\ &= \delta_{mn}\, e^{-iE_{nm}(\lambda_t)\,\Delta t/\hbar} \\ &= \delta_{mn}\, e^{-iE_{nm}(\lambda_t)\,\Delta\lambda\, T/\hbar}, \end{aligned} \tag{4.44}$$

where $E_{nm} := E_n - E_m$. Thus, we have that this matrix element is proportional to δ_{mn} (since $E_{nn} = 0$), and thus the eigenstate at t is mapped to its counterpart at $t + \Delta t$. Any error here, assuming $E_{mn} \neq 0$ for $m \neq n$, oscillates arbitrarily rapidly over each "time" interval $\Delta\lambda$ as $T \longrightarrow \infty$, because the phase factor $e^{-iE_{nm}(\lambda_t)\,\Delta\lambda\,T/\hbar}$ has the effective (dimensionless) frequency $E_{nm}(\lambda_t)\,T/\hbar$ (and should be replaced by its zero average value). Said another way, it is the limit $T \longrightarrow \infty$ that *guarantees* that all the approximations here can work. If T is *not* large, then $U(t + \Delta t, t)$ must be replaced by $\exp[-(i/\hbar)\int_t^{t+\Delta t} dt'\, H(\lambda_{t'})]$, which is not anything simple when acting on $|\psi_n(t)\rangle$.

4.3.3 Adiabatic Phase Evolution

In any case, the only possibility in the small time intervals is that $|\psi_n(t)\rangle$ evolves into $|\psi_n(t + \Delta t)\rangle$, as in Eq. (4.42). Actually, we are missing the possibility of a phase factor; however, we can assume that any such phase has been absorbed into the phase $\varphi_n(t)$.[5] The upshot of this is that we can treat $R(t)$—which is diagonal in the basis $|\psi_n(t)\rangle$—as also diagonal in the basis $\tilde{U}(t)|\psi_n(0)\rangle$, and thus we may write

$$\langle\psi_n(0)|\tilde{U}^\dagger \dot{R} R^\dagger \tilde{U}|\psi_n(0)\rangle = -i\dot{\varphi}_n(t). \tag{4.45}$$

Then putting this into Eq. (4.41) and solving for $\dot{\varphi}_n(t)$, we find

$$\dot{\varphi}_n(t) = -\frac{1}{\hbar}\langle\psi_n(0)|\tilde{U}^\dagger H \tilde{U}|\psi_n(0)\rangle + i\langle\psi_n(0)|\tilde{U}^\dagger \dot{\tilde{U}}|\psi_n(0)\rangle. \tag{4.46}$$

Now using Eq. (4.42), we can transform to the time-dependent states:

$$\dot{\varphi}_n(t) = -\frac{1}{\hbar}\langle\tilde{\psi}_n(t)|H(t)|\tilde{\psi}_n(t)\rangle + i\langle\tilde{\psi}_n(t)|\partial_t|\tilde{\psi}_n(t)\rangle. \tag{4.47}$$

In the first term, the states are still eigenstates of $H(t)$, while in the second we can change variables from t to $\lambda_t = t/T$:

$$\dot{\varphi}_n(t) = -\frac{1}{\hbar}E_n(t) + \frac{i}{T}\langle\tilde{\psi}_n(\lambda_t)|\partial_{\lambda_t}|\tilde{\psi}_n(\lambda_t)\rangle. \tag{4.48}$$

Integrating from 0 to T, the total phase is

$$\varphi_n(T) = -\frac{1}{\hbar}\int_0^T E_n(t')\,dt' + i\int_0^1 \langle\tilde{\psi}_n(\lambda)|\partial_\lambda|\tilde{\psi}_n(\lambda)\rangle\,d\lambda.$$

(dynamical and geometric phases) (4.49)

The first term is the dynamical phase and the second the geometric phase (both terms here are real, as before), matching the phase factors in Eqs. (4.5) and (4.30), respectively.[6] Now, to recap, the state evolves according to

$$\begin{aligned} |\psi_n(t)\rangle &= R^\dagger(t)|\tilde{\psi}_n(t)\rangle \\ &= e^{i\varphi_n(t)}|\tilde{\psi}_n(t)\rangle \\ &= e^{i\varphi_n(t)}\tilde{U}(t)|\tilde{\psi}_n(0)\rangle, \end{aligned} \tag{4.50}$$

where evidently

$$U(t) = e^{i\varphi_n(t)}\tilde{U}(t). \tag{4.51}$$

Note that there is not a single, unique choice of the change $R(t)$ of representation. Any extra phase could be defined into $R(t)$, provided a compensating phase is taken up by $\tilde{U}(t)$. In the proof here, this phase freedom was fixed by ignoring a possible phase in Eqs. (4.42). It turns out that this ambiguity applies not only to

[5] To explain this better: Remember from Eq. (4.32) that we are making a unitary transformation $|\tilde{\psi}\rangle = R|\psi\rangle$. We can write this as $|\tilde{\psi}\rangle = (Re^{i\theta})e^{-i\theta}|\psi\rangle$ for some other phase transformation. Then "absorbing the phase θ into R" means we really made *another* unitary transformation to the state, and compensated by replacing the definition of R by $R_\theta = e^{-i\theta}Re^{i\theta}$.

[6] In comparing the geometric phase here to that of Eq. (4.5), the one here is written in terms of $|\tilde{\psi}_n(\lambda)\rangle$, vs. $|\psi_n(\lambda)\rangle$. These expressions are equivalent because in the previous expression, the phases that are omitted here in $|\tilde{\psi}_n(\lambda)\rangle$ were already removed and put into the coefficients $c_n(t)$.

dynamical phases, but also to geometric phases, leading to a gauge freedom in the geometric phase. This is best illustrated by the example in the next section.

The geometric phase here, being independent of the total time T of the change in the Hamiltonian, also crops up in the case of nonadiabatic evolution.[7] However, the evolution according to Eq. (4.41) is complicated by transitions among the different eigenstates, each one of which may pick up a different phase.

4.4 Aharonov–Bohm Effect

A classic example of the geometric phase is the **Aharonov–Bohm effect**,[8] which is a phase accumulated by a charged quantum particle due to the coupling to the electromagnetic field, even when the particle stays in a region when the electromagnetic fields are **zero**. Here we will derive this phase shift and see that it is, in fact, a geometric phase.

4.4.1 Coupling to the Electromagnetic Field

Consider a particle of charge q coupled to the electromagnetic field. Classically, we may write the Hamiltonian for this particle in canonical coordinates as

$$H = \frac{1}{2m}[\mathbf{p} - q\mathscr{A}(\mathbf{r})]^2 + q\phi(\mathbf{r})$$

(charged particle coupling to the electromagnetic field) (4.52)

in terms of the vector potential $\mathscr{A}(\mathbf{r})$ and the scalar potential $\phi(\mathbf{r})$, recalling that in classical electromagnetic theory, the electric and magnetic fields are given by

$$\mathscr{E} = -\nabla\phi - \partial_t\mathscr{A}, \qquad \mathscr{B} = \nabla \times \mathbf{A}. \tag{4.53}$$

The way to see that this is the right Hamiltonian is to see that Hamilton's equations reduce to (Problem 4.3),

$$m\ddot{\mathbf{r}} = q(\mathscr{E} + \dot{\mathbf{r}} \times \mathscr{B}), \tag{4.54}$$

which is the formula for the classical Lorentz force.

Via canonical quantization, we can interpret the Hamiltonian (4.52) as the proper Hamiltonian for a charged quantum particle coupled to a (classical) background field represented by the potentials $\mathscr{A}$ and ϕ. As we discussed before [see the discussion around Eq. (1.60)], however, there is an ambiguity in the canonical quantization in the coupling to the vector potential $\mathbf{A}$, owing to the various ordering possibilities for the terms $\mathbf{p} \cdot \mathscr{A}(\mathbf{r})$ and $\mathscr{A}(\mathbf{r}) \cdot \mathbf{p}$. As discussed before, the extra assumption to fix the ordering is the **minimal-coupling replacement** $\mathbf{p} \longrightarrow \mathbf{p} - q\mathscr{A}$ in the free-particle Hamiltonian $p^2/2m$, which amounts to a symmetrized (and Hermitian) ordering. The coupling to the scalar potential has the form of an ordinary potential energy.

4.4.2 Transforming Away the Coupling

Including the coupling to the electromagnetic field, the Schrödinger equation now reads

$$i\hbar\dot{\psi} = \frac{1}{2m}[\mathbf{p} - q\mathscr{A}(\mathbf{r})]^2\psi + q\phi(\mathbf{r})\,\psi = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - q\mathscr{A}(\mathbf{r})\right)^2\psi + q\phi(\mathbf{r})\,\psi \tag{4.55}$$

in the position representation. Now consider an arbitrary scalar function $\chi(\mathbf{r})$, and consider a phase transformation of the form

$$\psi \longrightarrow \psi\, e^{-iq\chi(\mathbf{r})/\hbar}. \tag{4.56}$$

[7] C. M. Cheng and P. C. W. Fung, "Analysis of Berry's phase by the evolution operator method," *Journal of Mathematical Physics: Mathematical and General* **22**, 3493 (1989) (doi: 10.1088/0305-4470/22/17/015).

[8] Y. Aharonov and D. Bohm, "Significance of Electromagnetic Potentials in the Quantum Theory," *Physical Review* **115**, 485 (1959) (doi: 10.1103/PhysRev.115.485). This effect was actually discussed earlier by W. Ehrenberg and R. E. Siday, "The Refractive Index in Electron Optics and the Principles of Dynamics," *Proceedings of the Physical Society. Section B* **62**, 8 (1949) (doi: 10.1088/0370-1301/62/1/303).

The gradient of this replacement is

$$\nabla\psi \longrightarrow \left(\nabla\psi - \frac{iq\nabla\chi}{\hbar}\psi\right) e^{-iq\chi(\mathbf{r})/\hbar}. \tag{4.57}$$

If we *also* make the replacement

$$\mathscr{A} \longrightarrow \mathscr{A} - \nabla\chi \tag{4.58}$$

for the vector potential, then the effects of the simultaneous replacement cancel in the Schrödinger equation, so that Eq. (4.55) is invariant under this transformation. Note that the transformation (4.58) for the vector potential has the form of an electromagnetic gauge transformation, although it is usually accompanied by the simultaneous transformation

$$\phi \longrightarrow \phi + \dot{\chi}, \tag{4.59}$$

which leaves the fields $\mathscr{B} = \nabla \times \mathscr{A}$ and $\mathscr{E} = -\nabla\phi - \dot{\mathscr{A}}$ invariant. However, for simplicity here we will consider only a time-independent background field, and thus a time-independent gauge function χ, in which case the scalar gauge transformation (4.59) is trivial.

Now let's assume that in some region of space, $\mathscr{B} = 0$, but still that $\mathscr{A} \neq 0$ in order to obtain a nontrivial result. Also, we will assume that $\phi = 0$ everywhere. Since $\chi(\mathbf{r})$ is an arbitrary function, and because $\mathscr{B} = \nabla \times \mathscr{A}$, we can choose it such that

$$\mathscr{A} = \nabla\chi. \tag{4.60}$$

Then the replacements (4.56) and (4.58) have the form

$$\psi \longrightarrow \psi\, e^{-iq\chi(\mathbf{r})/\hbar}, \qquad \mathscr{A} \longrightarrow \mathscr{A} - \nabla\chi = 0. \tag{4.61}$$

That is, the replacement with this choice of χ transforms the Schrödinger equation (4.55) to the *free-particle* Schrödinger equation.[9] Then if ψ_0 is a solution to the free-particle Schrödinger equation, the inverse transformation gives the solution to the coupled Schrödinger equation (4.55):

$$\psi = \psi_0\, e^{iq\chi(\mathbf{r})/\hbar}. \tag{4.62}$$

Since Eq. (4.60) says that $\mathscr{A}$ is the gradient of a scalar function, we can write the scalar function in terms of a line integral:

$$\chi(\mathbf{r}) = \int_{\mathbf{r}_0}^{\mathbf{r}} \mathscr{A}(\mathbf{r}') \cdot d\mathbf{r}'. \tag{4.63}$$

Then more explicitly, the solution (4.62) is

$$\psi = \psi_0 \exp\left[\frac{iq}{\hbar}\int_{\mathbf{r}_0}^{\mathbf{r}} \mathscr{A}(\mathbf{r}') \cdot d\mathbf{r}'\right]. \tag{4.64}$$

(Aharonov–Bohm phase)

To reiterate the nature of the solution, the phase factor here represents the *extra* phase of the charged particle due to the coupling to $\mathbf{A}$, *beyond* that of the natural (free-particle) evolution.

4.4.3 Interpretation as Geometric Phase

Now returning to the geometric phase from Eq. (4.30) or (4.49), we can write it generically in terms of the integral

$$\varphi_{\text{G}} = i\int_0^1 \langle\psi_n(\lambda)|\partial_\lambda|\psi_n(\lambda)\rangle\, d\lambda. \tag{4.65}$$

[9] Note that here we are basically transforming away an extra additive function from the momentum operator, just as we did in Section 1.7.4.3 when we first considered the momentum operator in the position representation. Actually, the fact that the minimal-coupling Hamiltonian (4.52) still has the form of a squared momentum operator in a $\mathscr{B} = 0$ region is a fairly good justification for the minimal-coupling replacement.

In the case of the Aharonov–Bohm effect, we should consider the transport of a charged particle from $\mathbf{R}_0$ to $\mathbf{R}$ as λ goes from 0 to 1, thinking of λ as a path parameter $\mathbf{R} = \mathbf{R}(\lambda)$.

To evaluate the phase, first let's change variables in the geometric phase (4.65) to write

$$\varphi_{\text{G}} = i \int_{\mathbf{R}_0}^{\mathbf{R}} \langle \psi(\mathbf{R}') | \nabla_{\mathbf{R}'} | \psi(\mathbf{R}') \rangle \cdot d\mathbf{R}', \tag{4.66}$$

since any length ratio that comes from changing variables gives contributions via the derivative ∂_λ and the line element $d\lambda$ that cancel everywhere. Then writing the wave function displaced to $\mathbf{R}$ in the position representation, we have (for an arbitrary position reference $\mathbf{r}_0$)

$$\langle \mathbf{r} | \psi(\mathbf{R}) \rangle = \exp\left[-\frac{iq}{\hbar} \int_{\mathbf{r}_0}^{\mathbf{r}-\mathbf{R}} \mathscr{A}(\mathbf{r}') \cdot \, d\mathbf{r}' \right] \psi_0(\mathbf{r} - \mathbf{R}), \tag{4.67}$$

so that the expectation value corresponds to the integral

$$\langle \psi(\mathbf{R}) | \nabla_{\mathbf{R}} | \psi(\mathbf{R}) \rangle = \int d^3 r \, \psi_0^*(\mathbf{r} - \mathbf{R}) \left(-\frac{iq}{\hbar} \mathscr{A}(\mathbf{R}) \psi_0(\mathbf{r} - \mathbf{R}) + \nabla_{\mathbf{R}} \psi_0(\mathbf{r} - \mathbf{R}) \right). \tag{4.68}$$

The second term is proportional to the center-of-mass velocity of the particle as it is being transported. When it is integrated up to find the phase, the result is the product of the mean velocity times and the total length of the path. In the limit where the particle is transported adiabatically, this term can be neglected.[10] The integral of the first term can be evaluated as a normalization integral, and thus we have

$$\langle \psi(\mathbf{R}) | \nabla_{\mathbf{R}} | \psi(\mathbf{R}) \rangle = -\frac{iq}{\hbar} \mathscr{A}(\mathbf{R}). \tag{4.69}$$

Evaluating the integral in Eq. (4.66), we then have

$$\varphi_{\text{G}} = i \int_{\mathbf{R}_0}^{\mathbf{R}} \langle \psi(\mathbf{R}') | \nabla_{\mathbf{R}'} | \psi(\mathbf{R}') \rangle \cdot d\mathbf{R}' = \frac{q}{\hbar} \int_{\mathbf{R}_0}^{\mathbf{R}} \mathscr{A}(\mathbf{R}') \cdot \, d\mathbf{R}', \tag{4.70}$$

recovering the Aharonov–Bohm phase as a geometric phase.

4.4.4 Gauge Freedom and Physical Results

Now, you have to be a little careful in interpreting the Aharonov–Bohm phase. Suppose we make an electromagnetic gauge transformation of the same form as Eq. (4.58),

$$\mathscr{A} \longrightarrow \mathscr{A}(\mathbf{r}) - \nabla f(\mathbf{r}), \tag{4.71}$$

then from Eq. (4.64) the phase factor transforms as

$$\exp\left[\frac{iq}{\hbar} \int_{\mathbf{r}_0}^{\mathbf{r}} \mathscr{A}(\mathbf{r}') \cdot d\mathbf{r}' \right] \longrightarrow \exp\left[\frac{iq}{\hbar} \int_{\mathbf{r}_0}^{\mathbf{r}} \mathscr{A}(\mathbf{r}') \cdot d\mathbf{r}' \right] \exp\left[-\frac{iq}{\hbar} \Big(f(\mathbf{r}) - f(\mathbf{r}_0) \Big) \right]. \tag{4.72}$$

The last phase factor depends on the gauge transformation, but physical results should be independent of the gauge choice (i.e., gauge invariant). Gauge invariance here only occurs in the case $\mathbf{r} = \mathbf{r}_0$, in which case the path must be *closed*. Thus we can write the gauge-invariant Aharonov–Bohm phase as

$$\varphi_{\text{AB}} = \frac{q}{\hbar} \oint \mathscr{A}(\mathbf{r}') \cdot \, d\mathbf{r}'. \tag{4.73}$$

[10] It is common to argue that this second term in the integral vanishes identically. One argument holds that the integral vanishes due to the normalization of the wave function, but this can be seen to not happen by plugging in a moving wave packet, say of the form $e^{-x^2 - ix}$ (it's true that the *real part* of the integral vanishes via this argument, but we already expect this because ∇ is anti-Hermitian). One way of making this argument more precise is to regard the particle to be confined to a box at position $\mathbf{R}$, and then the box is transported around. In this case, the argument goes, the particle can be assumed to be in an eigenstate of the box. Then since $\nabla_{\mathbf{R}} = -\nabla_{\mathbf{r}}$ when acting on $\psi(\mathbf{r} - \mathbf{R})$, the integral is basically an expectation value of the momentum operator in an eigenstate of the box, and the expected momentum in an energy eigenstate always vanishes. However, this argument obviously misses the "center of mass" velocity of the box, which also imprints a phase on the wave function.

This makes intuitive sense: a phase is only detectable as a *relative* phase, where the transported wave packet must be compared to the original (e.g., by splitting it and comparing after transporting one component of the split wave packet, as in an interferometer; we'll see examples of this later on). Note that although we made this argument in terms of an electromagnetic gauge, this gauge ambiguity is, of course, more generally true for geometric phases.

4.4.5 Solenoid Example

Let's return to the point about the particle traversing a region of zero magnetic field. For a solenoid of very small radius R and oriented in the z direction, the vector potential has the form $\mathscr{A} \sim \hat{\phi}/r$ outside the solenoid, while the exterior magnetic field is $\mathscr{B} = \nabla \times \mathscr{A} = 0$. Now suppose a charged particle is transported in a closed path around the solenoid. In terms of a closed path, we can rewrite the Aharonov–Bohm phase using Stokes' integral theorem as an integral over the area enclosed by the path,

$$\varphi_{\text{AB}} = \frac{q}{\hbar} \oint \mathscr{A} \cdot d\mathbf{s} = \frac{q}{\hbar} \int (\nabla \times \mathscr{A}) \cdot d\mathbf{a} = \frac{q}{\hbar} \Phi_{\mathscr{B}}, \tag{4.74}$$

where $\Phi_{\mathscr{B}}$ is the magnetic-field flux enclosed by the path. For an electron of $q = -e$, this phase is often written as $\varphi_{\text{AB}} = -2\pi\Phi_{\mathscr{B}}/\Phi_0$, where $\Phi_0 = 2\pi\hbar/e = h/e$ is the fundamental unit of magnetic flux.

In this case, we see that the Aharonov–Bohm effect says that the magnetic field can induce a phase shift *without ever touching the particle*. Philosophically, this is an important point. In particular, it shows that the electromagnetic potentials are in some sense more fundamental than the electromagnetic fields, at least as far as quantum mechanics is concerned.

4.5 Topological Phase

There are other examples of geometric phases; a good example is polarized light propagating in an optical fiber, where the output polarization is rotated according to the path of the fiber.

Another, special example is the phase acquired when two indistinguishable particles are exchanged. This is something we will discuss in more detail later, but the idea is that two identical fermions acquire a total phase of π under an exchange, while two identical bosons acquire a total phase of 0 (both of these modulo 2π). This is an intrinsic phase that occurs due to an exchange, independent of the details of the exchange. While it can be interpreted in terms of a geometric phase if the particles are *physically* exchanged, this is a robust phase in the sense that the phase is acquired independent of the paths taken during the exchange (assuming no background potentials or other interactions). This special, intrinsic, path-independent phase is called a **topological phase**.

Topological phases have been of much current interest, because of **anyons**—quasiparticles (collective excitations of quantum many-body systems) in two dimensions that can have exchange phases that are not integer multiples of π. Anyons underlie the **fractional quantum Hall effect**, for example. For another, because of the robust path independence of the phase under exchange operations, anyons are the basis for the proposed **topological quantum computing**, which takes advantage of this robustness for realizing accurate quantum-logic operations (unitary transformations).[11] In a physical realization of such operations, the exchanges must be *physical* exchanges, which in the laboratory may be subject to other possible one-particle geometric and dynamical phases. It is an open question whether these extra phases will compromise the robust nature of topological quantum computing.[12]

[11] A. Yu. Kitaev, "Fault-tolerant quantum computation by anyons," *Annals of Physics* **303**, 2 (2003) (doi: 10.1016/S0003-4916(02)00018-0) (arXiv: quant-ph/9707021); Chetan Nayak, Steven H. Simon, Ady Stern, Michael Freedman, and Sankar Das Sarma, "Non-Abelian anyons and topological quantum computation," *Review Modern Physics* **80**, 1083 (2008) (doi: 10.1103/RevModPhys.80.1083).

[12] S. J. van Enk, "Exchanging identical particles and topological quantum computing," (arXiv: 1810.05208) (2018).

4.6 Exercises

Problem 4.1

From the proof of the adiabatic theorem, the condition (4.25) for adiabaticity to hold is

$$T \gg \frac{\hbar|\dot{H}_{nm}|}{[\overline{\Delta E}_{mn}]^2}. \tag{4.75}$$

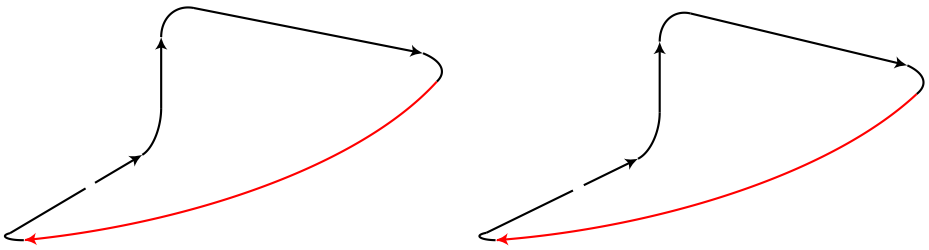
On the other hand, the condition for an adiabatic passage when sweeping through an avoided crossing is [see just after Eq. (4.1)]

$$|\partial_t \Delta| \ll \Omega^2, \tag{4.76}$$

when the splitting parameter Δ is swept at a constant rate through resonance ($\Delta = 0$). Show that these two conditions are equivalent for the adiabatic-passage problem. (Just do a simple comparison; don't sweat things like factors of 2, but come up with relevant estimates for $\dot{H}_{nm}$ and $\overline{\Delta E}_{mn}$.)

Problem 4.2

A fairly simple example of the geometric phase is illustrated by the rotation of light polarization as it travels along a fiber loop. The polarization rotation depends on the geometry of the fiber path. Consider the path below.[13]



The red section is a large-radius loop to close the path; you should think of this in the limit of a large radius, so that the slope of this section is effectively zero.

Suppose the light polarization is vertical, say starting at the gap on the lower straight segment. Trace the polarization orientation as it goes around the fiber, in the limit of a large radius of the long, looping section.

Now as the light propagates through the fiber, think about the propagation vector (tangent vector to the fiber) traces out a curve on a sphere (where the vector points from the sphere's origin). What is the solid angle enclosed by this curve? How does this compare to the angle of polarization rotation?

Problem 4.3

Show that Hamilton's equations for the Hamiltonian (4.52)

$$H = \frac{1}{2m}[\mathbf{p} - q\mathscr{A}(\mathbf{r},t)]^2 + q\phi(\mathbf{r},t) \tag{4.77}$$

reduce to the the Lorentz-force law

$$m\ddot{\mathbf{r}} = q(\mathscr{E} + \dot{\mathbf{r}} \times \mathscr{B}). \tag{4.78}$$

Note that as part of your solution, you should find that $\mathbf{p}_{\text{kinetic}} := m\dot{\mathbf{r}} \neq \mathbf{p}_{\text{canonical}}$. Also, there is one tricky part: when you differentiate the equation of motion for $\mathbf{r}$ to obtain an expression for $\ddot{\mathbf{r}}$, you should interpret the derivative as a *total* time derivative; however, the time derivative in the relation

[13] Why are you seeing double in this figure? See the explanation in the usage chapter, starting on p. 20.

between $\mathscr{A}$ and $\mathscr{E}$ is a *partial* time derivative, so make sure to use the chain rule to convert between these. You will also want to use the general vector identity

$$\nabla(\mathbf{A}\cdot\mathbf{B}) = (\mathbf{A}\cdot\nabla)\mathbf{B} + (\mathbf{B}\cdot\nabla)\mathbf{A} + \mathbf{A}\times(\nabla\times\mathbf{B}) + \mathbf{B}\times(\nabla\times\mathbf{A}) \tag{4.79}$$

for arbitrary vector fields $\mathbf{A}$ and $\mathbf{B}$.

Problem 4.4

We discussed the Aharonov–Bohm effect as an example of a geometric phase, where the gauge-independent phase factor is the line integral of the vector potential $\mathscr{A}(\mathbf{R})$ around a closed path specified by $\mathbf{R}(t)$. It turns out that this is the **general** form of the geometric phase if the adiabatic change has the form of a spatial displacement. To see this, let's start with the geometric phase in the form (4.70),

$$\varphi_n = i\int_{\mathbf{R}_0}^{\mathbf{R}} \langle\psi_n(\mathbf{R}')|\nabla_{\mathbf{R}'}|\psi_n(\mathbf{R}')\rangle\cdot d\mathbf{R}', \tag{4.80}$$

assuming an adiabatic following of the eigenstate $|\psi_n\mathbf{R}\rangle$. Now define an effective vector potential

$$\mathscr{A}_n(\mathbf{R}) := i\langle\psi_n(\mathbf{R})|\nabla_{\mathbf{R}}|\psi_n(\mathbf{R})\rangle. \tag{4.81}$$

Argue that the gauge-invariant form of the geometric phase may be written as the surface integral over an enclosed area of a closed path,

$$\varphi_n = \oint \mathscr{B}_n\cdot d\mathbf{a}, \tag{4.82}$$

in terms of the effective magnetic field

$$\mathscr{B}_n(\mathbf{R}) := \nabla_{\mathbf{R}}\times\mathscr{A}_n(\mathbf{R}). \tag{4.83}$$

Then show that this magnetic field may be written

$$\mathscr{B}_n(\mathbf{R}) = i\sum_{m\neq n}\frac{\langle\psi_n(\mathbf{R})|(\nabla_{\mathbf{R}}H)|\psi_m(\mathbf{R})\rangle\times\langle\psi_m(\mathbf{R})|(\nabla_{\mathbf{R}}H)|\psi_n(\mathbf{R})\rangle}{(E_{mn})^2}, \tag{4.84}$$

in terms of the gradient of the parameterized Hamiltonian $H(\mathbf{R}) = H[\mathbf{R}(t)]$ and the energy gaps $E_{mn} := E_m - E_n$. The sum here runs over all *other* instantaneous eigenstates $|\psi_{m\neq n}(\mathbf{R})\rangle$.

Chapter 5

Harmonic Oscillator

One of the most fundamental and useful quantum problems is the harmonic oscillator, or a quantum particle in a quadratic potential well. A principal reason for this is that *any* smooth potential well is approximately quadratic for small displacements from the minimum, by a simple Taylor expansion of the potential. And, of course, this resulting approximation is *solvable*, in quite a bit of detail. Oddly enough, the harmonic oscillator makes for a perfectly good approximation for small displacements even in potentials where the Taylor-expansion idea doesn't work at all: square wells and the $1/r$ potential are good examples. Why is this? In the energy representation, for example, we will see that the harmonic oscillator has an evenly spaced energy spectrum. We can thus concoct an oscillator that matches a pair of energy levels in an anharmonic system, and this match is useful provided that the *other* states are not important for the problem at hand. But make sure to think through why the harmonic approximation can be valid in pathological potentials in the position representation—the basic idea is that it's important to consider the expansion of $\langle V \rangle$ rather than $V(x)$ itself. Or, more precisely, the harmonic approximation is defined by the response (displacement) of a system to an applied force, and the effective harmonic potential is defined by the expected work done by the force on the particle.

As we will see later in Section 15.2.1, the harmonic oscillator is also useful in defining what we mean by a ''photon,'' because the electromagnetic field turns out to be an ensemble of harmonic oscillators (at least when the field is in vacuum; things can get more complicated in nonlinear or absorbing media). The quantum harmonic oscillator has some features (related to the oscillator's uniformly spaced spectrum) that make it both relatively simple and somewhat peculiar among quantum systems.

5.1 Scaled Units

Before getting into the meat of the problem, we'll define scaled units to work in. The idea is that there may be some parameters in any problem that are redundant if they're viewed in the correct way. The advantage of recognizing this in advance is that we can simplify the problem by eliminating them. There are fewer units to carry around, so we can focus on the most important aspects of the physics without the extra clutter of redundant parameters. Also, this kind of simplification is useful from a cognitive perspective, because there are only so many chunks of information that can fit into your short-term memory, so you want to reduce this to the essential few chunks to reduce memory ''overflow,'' so to speak. On the other hand, there is an opposing philosophy that holds that the extra parameters are valuable as extra, redundant information. Carrying along the extra baggage can be useful in detecting errors at the end of the problem, in the same sense as parity bits on a computer (you can check that the units work out correctly, for example). Since this should not be the first time you've seen this material, and hopefully I can derive the results here without (too many) typos, we'll go with the ''clean'' approach.

To start with, the Hamiltonian for the harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2. \tag{5.1}$$

(harmonic-oscillator Hamiltonian)

Since this is an ordinary particle-in-a-potential Hamiltonian of the form

$$H = \frac{p^2}{2m} + V(x) \tag{5.2}$$

this is equally valid as a classical or quantum object. Quantum mechanically, our fundamental equations are the form of the Hamiltonian, the Schrödinger equation, which amounts to the operator identification

$$i\hbar\frac{\partial}{\partial t} = H, \tag{5.3}$$

as well as the commutator

$$[x, p] = i\hbar. \tag{5.4}$$

Now let's define scaled coordinates, along with rescaled time and energies by

$$\tilde{x} = \frac{x}{x_\mathrm{s}}, \qquad \tilde{p} = \frac{p}{p_\mathrm{s}}, \qquad \tilde{t} = \frac{t}{t_\mathrm{s}}, \qquad \tilde{H} = \frac{H}{E_\mathrm{s}}, \qquad \tilde{V} = \frac{V}{E_\mathrm{s}}, \tag{5.5}$$

where the subscript "s" denotes "scale," where for example the x_s is the length scale, or the unit in which we will measure position. All of the new coordinates (including time and energy) are dimensionless, since the original versions have been divided by a quantity of the same dimensions (and note that the potential energy and Hamiltonian are scaled by the same energy unit E_s). For a general particle in a potential, in the rescaled units

$$\tilde{H} = \left(\frac{p_\mathrm{s}^2}{mE_\mathrm{s}}\right)\frac{\tilde{p}^2}{2} + \tilde{V}(\tilde{x}x_\mathrm{s}), \tag{5.6}$$

where for the harmonic in particular,

$$\tilde{V}(\tilde{x}x_\mathrm{s}) = \left(\frac{m\omega^2 x_\mathrm{s}^2}{E_\mathrm{s}}\right)\frac{\tilde{x}^2}{2}. \tag{5.7}$$

The Schrödinger equation transforms to

$$i\frac{\partial}{\partial\tilde{t}} = \left(\frac{E_\mathrm{s}t_\mathrm{s}}{\hbar}\right)\tilde{H}, \tag{5.8}$$

and the commutation relation transforms to

$$[\tilde{x}, \tilde{p}] = i\Big(\frac{\hbar}{x_\mathrm{s}p_\mathrm{s}}\Big). \tag{5.9}$$

To try to make things simpler, we can set the bracketed fractions to one in Eqs. (5.6)–(5.9), giving the four equations

$$\begin{aligned} p_\mathrm{s}^2 &= mE_\mathrm{s} \\ m\omega^2 x_\mathrm{s}^2 &= E_\mathrm{s} \\ E_\mathrm{s}t_\mathrm{s} &= \hbar \\ x_\mathrm{s}p_\mathrm{s} &= \hbar. \end{aligned} \tag{5.10}$$

Since we have four equations, and four quantities to determine (x_s, p_s, E_s, and t_s), we can exactly determine these quantities without any other freedom. It's important to note two things, however. First, we could have set the bracketed quantities to *other* values besides one, so there is *some* freedom in the choice of units. The other important point is that in some more complicated system, there may be another parameter, for example an independent, temporal period T in a time-modulated harmonic potential. In this case, if we were to try to make the same simplifications, *plus* rescale T to unity or some other constant, we would have more constraints than free scale parameters, and so we would be left over with one more parameter at the end of the rescaling procedure (say, a rescaled version of T, or a rescaled Planck constant). In this particular case, we have four free choices to make (the scales x_s, p_s, E_s, and t_s), but there is one constraint (that $\hbar$ appears

in both the x-p commutator and the Schrödinger equation, and must be scaled consistently); the remaining three degrees of freedom are just enough to eliminate the three parameters in the problem (m, ω, $\hbar$).

To solve Eqs. (5.10), we can start by dividing the first two equations and taking square root to find

$$p_{\rm s} = m\omega x_{\rm s}, \tag{5.11}$$

where in principle there is a possible minus sign from the square root, but it's best to measure all quantities in terms of *positive* units. Now combining this result with the last of Eqs. (5.10), we find the length scale with last one,

$$x_{\rm s} = \sqrt{\frac{\hbar}{m\omega}}, \tag{5.12}$$
(natural length scale, harmonic oscillator)

as well as the momentum scale

$$p_{\rm s} = \sqrt{m\hbar\omega}. \tag{5.13}$$
(momentum scale, harmonic oscillator)

Using $x_{\rm s}$ in the second of Eqs. (5.10) gives the energy scale $E_{\rm s} = m\omega^2 x_{\rm s}^2$, or

$$E_{\rm s} = \hbar\omega. \tag{5.14}$$
(energy scale, harmonic oscillator)

Finally, the time scale is determined by the third of Eqs. (5.10) as $t_{\rm s} = \hbar/E_{\rm s}$, or

$$t_{\rm s} = \frac{1}{\omega}. \tag{5.15}$$
(time scale, harmonic oscillator)

To summarize where we are, we now have the rescaled Hamiltonian

$$H = \frac{p^2}{2} + \frac{x^2}{2}, \tag{5.16}$$
(scaled Hamiltonian)

where from now on, we will drop the twiddles, in the spirit of reducing clutter. We will work consistently in the following in scaled variables, but we will stop to change back to the ''real'' variables when we get to main results (which will be highlighted in the following treatment). Recall that the evolution will be determined by the scaled Schrödinger equation

$$i\frac{\partial}{\partial t} = H, \tag{5.17}$$

and that we will have the simplified commutator

$$[x, p] = i. \tag{5.18}$$

Colloquially, we have defined units in which $m = \hbar = \omega = 1$, and the process of transforming back to the original units is referred to as the process of ''restoring factors'' of m, $\hbar$, and ω. But the safe and conceptually simple approach to handling the dimensionless variables is to regard x as a shorthand for $x/x_{\rm s}$, p for $p/p_{\rm s}$, and so on.

5.2 Creation and Annihilation Operators

Classically, given a quadratic sum $x^2 + y^2$, it is natural to consider its factorization into complex parts as $x^2 + y^2 = (x - iy)(x + iy) = |x + iy|^2$. The Hamiltonian (5.16) is practically *begging* to be factored in the same way. In fact, quantum mechanically, we can write the analogous product

$$(x - ip)(x + ip) = x^2 + ixp - ipx + p^2 = x^2 + p^2 + i[x, p] = x^2 + p^2 - 1, \tag{5.19}$$

where we get an extra bit because of the commutator $[x, p] = i$. Thus, the factored form of the Hamiltonian (5.16) is

$$H = \left(\frac{x - ip}{\sqrt{2}}\right)\left(\frac{x + ip}{\sqrt{2}}\right) + \frac{1}{2}. \tag{5.20}$$

This turns out to be an absurdly useful way to write this Hamiltonian, so much that we will name the factors as

$$a := \frac{x + ip}{\sqrt{2}}, \tag{5.21}$$

and the Hermitian conjugate

$$a^\dagger = \frac{x - ip}{\sqrt{2}}. \tag{5.22}$$

For reasons that will be clear soon, a is called the **annihilation** operator, and in the original units is written

$$a = \frac{1}{\sqrt{2}}\left(\frac{x}{x_\mathrm{s}} + i\frac{p}{p_\mathrm{s}}\right), \tag{5.23}$$

or

$$a = \sqrt{\frac{m\omega}{2\hbar}}\, x + i\frac{p}{\sqrt{2m\hbar\omega}}. \tag{5.24}$$
(annihilation operator)

The operator $a^\dagger$, which has the same form as a except for the sign of the second term, is called the **creation operator**. In terms of these operators, the Hamiltonian (5.20) becomes $H = a^\dagger a + 1/2$, or

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right), \tag{5.25}$$
(Hamiltonian, harmonic oscillator)

since the energy scale $E_\mathrm{s} = \hbar\omega$, which will be very significant in this problem.

The inverse to the transformations (5.21) and (5.22) are

$$x = \frac{a + a^\dagger}{\sqrt{2}}, \qquad p = \frac{a - a^\dagger}{\sqrt{2}\,i} \tag{5.26}$$

Taking these transformations in real units, the position operator is

$$x = \frac{x_\mathrm{s}}{\sqrt{2}}\left(a + a^\dagger\right) = \sqrt{\frac{\hbar}{2m\omega}}\left(a + a^\dagger\right), \tag{5.27}$$
(position operator)

and the momentum operator is

$$p = \frac{p_\mathrm{s}}{\sqrt{2}\,i}\left(a - a^\dagger\right) = \frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}\left(a - a^\dagger\right). \tag{5.28}$$
(momentum operator)

Hopefully, some of the appeal of the dimensionless units is becoming apparent.

5.2.1 Commutation Relations

Since the position and momentum operators are linear combinations of a and $a^\dagger$, these two operators should have their own commutation relation. This is easy to work out as

$$[a, a^\dagger] = \frac{1}{2}[x + ip, x - ip] = -\frac{i}{2}\Big([x, p] - [p, x]\Big) = -i[x, p] = 1, \tag{5.29}$$

or to summarize,

$$[a, a^\dagger] = 1. \tag{5.30}$$
(creation/annihilation commutation)

Note that a and $a^\dagger$ were defined to be intrinsically dimensionless, so nothing changes when we transform out of scaled units.

It's also simple (and important for what will follow) to work out the commutation relation with the Hamiltonian $H = a^\dagger a + 1/2$:

$$[H, a] = [a^\dagger a, a] = a^\dagger [a, a] + [a^\dagger, a]a = -a, \tag{5.31}$$

where we used the product rule for the commutator (see Section 1.6.1), and then $[a, a^\dagger] = 1$. It is also easy to use this result to work out the other commutator

$$[H, a^\dagger] = [a, H]^\dagger = a^\dagger, \tag{5.32}$$

since the Hamiltonian is Hermitian.

5.2.2 Energy Ladder

Now consider an energy eigenvector $|n\rangle$, with energy E_n, which will be the "nth" eigenvector, though we don't yet know what that means. We now want to show that $a|n\rangle$ is *also* an energy eigenket (though possibly unnormalized). Using the commutation relation (5.31),

$$Ha|n\rangle = (aH - a)|n\rangle = (E_n - 1)a|n\rangle. \tag{5.33}$$

Thus, $a|n\rangle$ is an energy eigenvector, but one unit *lower* in energy. Thus, a is also called a **lowering operator** (or **annihilation operator**, since one unit of energy is "annihilated"). Similarly, the commutator (5.32) implies that $a^\dagger|n\rangle$ is an energy eigenvector, but one unit *higher* in energy:

$$Ha^\dagger|n\rangle = (a^\dagger H + a^\dagger)|n\rangle = (E_n + 1)a^\dagger|n\rangle. \tag{5.34}$$

Hence the term **raising operator** for $a^\dagger$ (or **creation operator**, where one quantum of energy is created). Remember that, in both cases, the "unit" of energy is $E_\mathrm{s} = \hbar\omega$. So more than just a convenient scale for measuring energy, energy in the harmonic oscillator is gained or lost in $\hbar\omega$'s.

The Hamiltonian (5.1) is clearly a nonnegative operator, so we can conclude that there should be some minimum eigenenergy, which we will call E_0. It's not necessarily the case that $E_0 = 0$, although zero should be a lower bound for E_0. Now what happens if we hit the corresponding eigenvector $|0\rangle$ with the annihilation operator? Equation (5.33) says

$$Ha|0\rangle = (E_0 - 1)a|0\rangle, \tag{5.35}$$

which means either that we just generated a state with even *lower* energy $E_0 - 1$ (a contradiction), or that

$$a|0\rangle = 0, \tag{5.36}$$

which is by far the more sensible option (and we can see that "annihilation" takes on an extra meaning for this eigenstate). So what is the energy of this state? It's easy to compute this directly using this annihilation property:

$$E_0 = \langle 0|H|0\rangle = \langle 0|(a^\dagger a + 1/2)|0\rangle = \langle 0|a^\dagger a|0\rangle + \frac{1}{2} = \frac{1}{2}. \tag{5.37}$$

This is the well-known **zero-point energy** of the harmonic oscillator, which is a minimum energy *above* the minimum classical energy (which is just zero). The zero-point energy is $\hbar\omega/2$ in unscaled units.

Other eigenenergies are obtained by applying the creation operator repeatedly, which at each application adds one unit of energy, so we may conclude that the eigenenergies are

$$E_n = n + \frac{1}{2}, \tag{5.38}$$

or

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{5.39}$$

(harmonic-oscillator eigenenergies)

in unscaled units.

We constructed the eigenenergies in a ladder starting with the lowest "rung" E_0. (Since a descends the ladder and $a^\dagger$ ascends the ladder, these are also commonly called **ladder operators**.) Is it possible that we missed some eigenstate? The answer is no, as we can see by assuming that we have some energy eigenstate E_ν, where ν is not necessarily an integer. Then operating on the corresponding eigenstate many times with a, descending one unit of energy each time, either we will hit E_0 or we will end up at some energy *below* E_0. The latter is not an option,[1] so we must have hit E_0, in which case we started on the ladder that we already defined.

5.2.3 Ladder Operators in the Energy Representation

We just showed that $a|n\rangle$ is an energy eigenvector, but the problem is that we are not guaranteed that the result is $|n-1\rangle$, because it turns out that $a|n\rangle$ is not normalized. To show this, let's explicitly normalize it by introducing a normalization constant c, where

$$ca|n\rangle = |n-1\rangle. \tag{5.40}$$

Computing the norm of both sides gives

$$|c|^2\langle n|a^\dagger a|n\rangle = 1. \tag{5.41}$$

Now since we had

$$H = a^\dagger a + \frac{1}{2}, \tag{5.42}$$

we can write $a^\dagger a = H - 1/2$, which has the value $E_n - 1/2 = n$ for the state $|n\rangle$. In fact, $a^\dagger a$ is called the **number operator**, as it counts the quantity n (number of energy quanta) for energy eigenstates. Thus, Eq. (5.41) becomes

$$c = \frac{1}{\sqrt{n}}, \tag{5.43}$$

after choosing an arbitrary phase to be $+1$. Thus, after normalization, the action of the annihilation operator is

$$a|n\rangle = \sqrt{n}\,|n-1\rangle. \tag{5.44}$$
(annihilation-operator action)

This normalized equation is sufficient to define the annihilation operator in the energy representation; the appropriate expression is

$$a = \sum_{n=1}^{\infty} \sqrt{n}\,|n-1\rangle\langle n|, \tag{5.45}$$
(annihilation-operator action)

where this can be read as the nth term "detecting" the state $|n\rangle$, and replacing it by the scaled, lowered state $\sqrt{n}|n-1\rangle$.

The creation operator is given by the conjugate of Eq. (5.45),

$$a^\dagger = \sum_{n=1}^{\infty} \sqrt{n}\,|n\rangle\langle n-1| = \sum_{n=0}^{\infty} \sqrt{n+1}\,|n+1\rangle\langle n|, \tag{5.46}$$
(creation-operator action)

where the latter expression is the more customary. This expression in turn implies the action

$$a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle, \tag{5.47}$$
(annihilation-operator action)

as the analogue of Eq. (5.44).

[1] You might think that maybe we can save the fractional energy state in this argument by postulating that $a|\nu\rangle = 0$ whenever $1/2 < \nu < 3/2$. However, all of these states would have the same energy as the ground state, and such a degeneracy is not allowed in one-dimensional potentials like this with (as we will see) normalizable wave functions (Problem 2.10).

5.3 Energy Eigenfunctions in the Position Representation

It's also useful to derive expressions for the energy eigenfunctions—that is, the expressions for the eigenstates in the position representation. The old-school way of doing this is called the **Frobenius method**, which consists of assuming a power series for $\psi(x)$ with undetermined coefficients, cramming it into the Schrödinger equation in the position representation, and solving the resulting equations for the coefficients and the energy eigenvalues. What makes this method work out for the harmonic oscillator is that, set up in the right way, the series will terminate, yielding polynomial solutions (the **Hermite polynomials**). More generally, in the Frobenius method, you have to kind of hope for the best in terms of series convergence, and it's frankly not the most elegant method around. But it's worth knowing that the method exists, as a method of last resort, even though we won't cover it here. We'll proceed with the more elegant operator approach, transforming to the position representation at the last possible moment (recall that we've already found the *eigenvalues* of the Schrödinger equation without resorting to the position representation).

5.3.1 Ground State

For the ground state (state of lowest energy), we can start with $a|0\rangle = 0$ to write

$$(x + ip)|0\rangle = 0, \tag{5.48}$$

and since $p = -i\partial_x$ in the position representation, we can project the equation above with $\langle x|$ into the position representation as

$$(x + \partial_x)\psi_0(x) = 0. \tag{5.49}$$

This is a differential equation for $\psi_0(x) := \langle x|0\rangle$. Rearranging it into the form

$$\frac{\psi_0'}{\psi_0} = -x, \tag{5.50}$$

and recognizing the left-hand side as the derivative of $\log \psi_0(x)$, we can integrate from $x' = 0$ to x to obtain

$$\psi_0(x) = \psi_0(0)\, e^{-x^2/2}. \tag{5.51}$$

The normalization factor $\psi_0(0)$ is determined by normalization; writing the probability density

$$\big|\psi_0(x)\big|^2 = |\psi_0(0)|^2\, e^{-x^2}, \tag{5.52}$$

we can compare to the normalized, centered Gaussian function of rms width σ,

$$G(x;\sigma) = \frac{1}{\sqrt{2\pi}\,\sigma}\, e^{-x^2/2\sigma^2}, \tag{5.53}$$

to conclude $\sigma = 1/\sqrt{2}$ and thus $|\psi_0(0)|^2 = 1/\sqrt{\pi}$. At last, the ground-state wave function is

$$\psi_0(x) = \pi^{-1/4}\, e^{-x^2/2}, \tag{5.54}$$

or in physical units,

$$\psi_0(x) = \frac{1}{\sqrt{\sqrt{\pi}\, x_{\rm s}}}\, e^{-x^2/2x_{\rm s}^2} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}. \tag{5.55}$$

(ground-state wave function)

Note that the expressions are starting to become complicated enough that there isn't much advantage in writing out $x_{\rm s}$ explicitly. Note also that factor of $x_{\rm s}^{-1/2}$ in the prefactor. This comes about because of the normalization (or any other expectation value or matrix element)

$$\langle 0|0\rangle = \int_{-\infty}^{\infty} dx\, \psi_0^*(x)\, \psi_0(x). \tag{5.56}$$

The left-hand side is unit-independent, and thus so must be the right-hand side. Since a rescaling of length changes the integration element dx, there must be a compensating factor in the wave function (another way to say this is that $|\psi_0(x)|^2$ represents a probability density or probability per unit length, so the $x_\mathrm{s}^{-1/2}$ prefactor makes this dimension come out correctly). This is one tricky thing about transforming out of scaled units—you have to be careful to transform out consistently and check the dimensions of the resulting expressions.

Also, as we mentioned above by comparison to the normalized Gaussian state, the ground-state position uncertainty is

$$\sigma_x = \frac{1}{\sqrt{2}}, \tag{5.57}$$

and by symmetry between p and x in scaled units,

$$\sigma_p = \frac{1}{\sqrt{2}} \tag{5.58}$$

as well. Restoring units gives

$$\sigma_x = \frac{x_\mathrm{s}}{\sqrt{2}} = \sqrt{\frac{\hbar}{2m\omega}}, \qquad \sigma_p = \frac{p_\mathrm{s}}{\sqrt{2}} = \sqrt{\frac{m\hbar\omega}{2}}. \tag{5.59}$$

(ground-state uncertainties)

Now note that the product $\sigma_x\sigma_p = \hbar/2$, so the ground state of the harmonic oscillator is a minimum-uncertainty state. That is, it satisfies the uncertainty principle, Eq. (1.43), with the equality.

5.3.2 Excited States

Now for the rest of the states. We can generate other states using the creation operator as in Eq. (5.47):

$$a^\dagger|n-1\rangle = \sqrt{n}\,|n\rangle. \tag{5.60}$$

Applying this to the ground state gives $a^\dagger|0\rangle = |1\rangle$, and then applying it again gives $(a^\dagger)^2|0\rangle = \sqrt{2}|2\rangle$, and then yet again gives $(a^\dagger)^3|0\rangle = \sqrt{6}|3\rangle$. Continuing the pattern n times gives

$$\big(a^\dagger\big)^n|0\rangle = \sqrt{n!}\,|n\rangle. \tag{5.61}$$

Since $a^\dagger = (x-ip)/\sqrt{2}$,

$$|n\rangle = \frac{1}{2^{n/2}\sqrt{n!}}\big(x-ip\big)^n|0\rangle, \tag{5.62}$$

and switching to the position representation,

$$\psi_n(x) = \frac{1}{2^{n/2}\sqrt{n!}}\big(x-\partial_x\big)^n\psi_0(x) = \frac{1}{2^{n/2}\pi^{1/4}\sqrt{n!}}\big(x-\partial_x\big)^n e^{-x^2/2}. \tag{5.63}$$

This is, again, an equation that determines $\psi_n(x)$. Although it is a more complicated one, it only requires computing derivative (i.e., this is not an ODE that needs to be solved). To proceed, as an exercise, you should prove by induction that

$$\big(x-\partial_x\big)^n e^{-x^2/2} = (-1)^n e^{x^2/2}\partial_x^n e^{-x^2}. \tag{5.64}$$

Work this out before proceeding (the proof is at the end of this section).

Now we will define the **Hermite polynomials** by[2]

$$H_n(x) := (-1)^n e^{x^2}\partial_x^n e^{-x^2}. \tag{5.65}$$

(Hermite polynomial)

[2]Note that, obnoxiously, there is an alternate definition of Hermite polynomials that amounts to a rescaling of the coordinate by a factor of $\sqrt{2}$. The definition here is favored by physicists, while the evil doppelgänger is favored by mathematicians (in particular in probability, because the Hermite polynomial arises in the differentiation of the standard-normal distribution, which is of the form $e^{-x^2/2}$).

In terms of these polynomials, Eq. (5.64) becomes

$$\left(x - \partial_x\right)^n e^{-x^2/2} = e^{-x^2/2} H_n(x), \tag{5.66}$$

where the combination $e^{-x^2/2}H_n(x)$ is commonly called a **Hermite–Gaussian function**. Thus, the wave function (5.63) becomes

$$\psi_n(x) = \frac{1}{2^{n/2}\pi^{1/4}\sqrt{n!}}\, e^{-x^2/2} H_n(x) \tag{5.67}$$

in terms of Hermite–Gaussian functions. Restoring units again gives

$$\psi_n(x) = \frac{1}{\sqrt{2^n\sqrt{\pi}\, n!\, x_\mathrm{s}}}\, e^{-x^2/2x_\mathrm{s}^2} H_n\left(\frac{x}{x_\mathrm{s}}\right), \tag{5.68}$$

(harmonic-oscillator energy eigenstates)

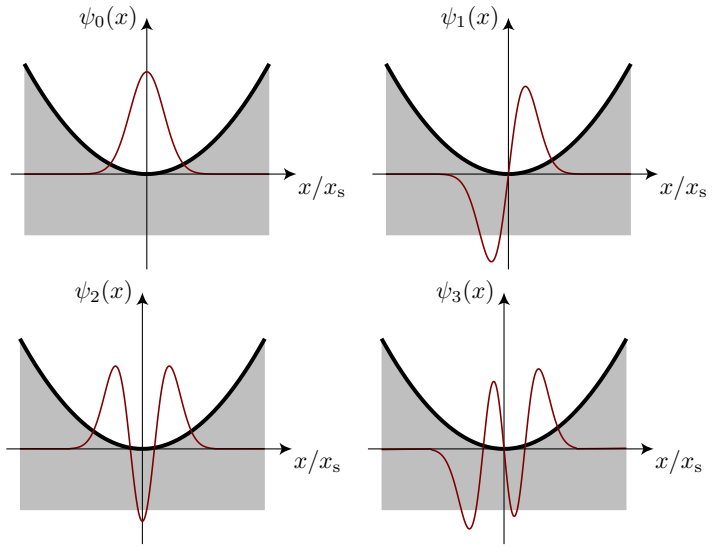
where there doesn't seem to be much advantage at this point in writing out x_s expicitly.

For reference, the first few Hermite polynomials are

$$\begin{aligned} H_0(x) &= 1 \\ H_1(x) &= 2x \\ H_2(x) &= 2(2x^2 - 1) \\ H_3(x) &= 4x(2x^2 - 3). \end{aligned} \tag{5.69}$$

Note that $H_0(x) = 1$ allows Eq. (5.68) to reduce to the Gaussian state for $n = 0$, and that the Hermite polynomials alternate between even and odd parity (as we expect for the eigenstates of the harmonic oscillator, which should have definite parity).

As examples, the lowest four eigenfunctions are plotted below, corresponding to the four Hermite polynomials listed above.



Notice how the wave function increases in width as the energy increases. Note also that the momentum-space wave functions have the same form, again by the symmetry between x and p.

Finally, to return to the proof of Eq. (5.64), which again is

$$\left(x - \partial_x\right)^n e^{-x^2/2} = (-1)^n e^{x^2/2} \partial_x^n e^{-x^2}. \tag{5.70}$$

To prove this by induction, first we prove it for a basis case, here $n = 0$, which is clearly true because both sides reduce to $e^{-x^2/2}$. For the induction step, we *assume* Eq. (5.66) to be true, and then use it to prove the analogous equation where n is replaced by $n + 1$. To start, the left-hand side we want is

$$\big(x - \partial_x\big)^{n+1} e^{-x^2/2} = (-1)^n \big(x - \partial_x\big) e^{x^2/2} \partial_x^n e^{-x^2}. \tag{5.71}$$

The ''new'' derivative operator will act in a chain rule on the right-hand factors, so that

$$\big(x - \partial_x\big)^{n+1} e^{-x^2/2} = (-1)^n \big(x\, e^{x^2/2} - x\, e^{x^2/2} - e^{x^2/2}\partial_x\big) \partial_x^n e^{-x^2}. \tag{5.72}$$

Now canceling terms and simplifying, we have

$$\big(x - \partial_x\big)^{n+1} e^{-x^2/2} = (-1)^{n+1} e^{x^2/2} \partial_x^{n+1} e^{-x^2}. \tag{5.73}$$

This is the incremented form of Eq. (5.66), and so completes the inductive proof.

5.4 Coherent States

An important class of states comes in the form of **coherent states**,[3] which we will define as the eigenstates of the annihilation operator:

$$a|\alpha\rangle = \alpha|\alpha\rangle. \tag{5.74}$$
(coherent state, defining relation)

Using the form (5.45) for the annihilation operator, we can obtain from this

$$\sum_{n=1}^{\infty} \sqrt{n}\, |n-1\rangle\langle n|\alpha\rangle = \alpha|\alpha\rangle, \tag{5.75}$$

and then projecting with $\langle n - 1|$, we obtain the recursion relation

$$\langle n|\alpha\rangle = \frac{\alpha}{\sqrt{n}} \langle n-1|\alpha\rangle. \tag{5.76}$$

Iterating this relation $n - 1$ times, we can obtain the explicit amplitude

$$\langle n|\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}} \langle 0|\alpha\rangle \tag{5.77}$$

in terms of the ground-state amplitude. The value of the ground-state amplitude follows from normalizing the result:

$$\sum_{n=0}^{\infty} |\langle n|\alpha\rangle|^2 = \sum_{n=0}^{\infty} \frac{|\alpha|^{2n}}{n!} |\langle 0|\alpha\rangle|^2 = 1. \tag{5.78}$$

In the second summation the ground-state amplitude is n-independent, and comes out of the sum; the remaining series is the expansion for the exponential function, so that the normalization condition becomes

$$|\langle 0|\alpha\rangle|^2 e^{|\alpha|^2} = 1, \tag{5.79}$$

or

$$\langle 0|\alpha\rangle = e^{-|\alpha|^2/2} \tag{5.80}$$

[3]Introduced in the form of Gaussian wave packets with an oscillating centroid by E. Schrödinger, ''Der stetige Übergang von der Mikro- zur Makromechanik,'' *Naturwissenschaften* **14**, 664 (1926) (doi: 10.1007/BF01507634). As eigenvalues of the annihilation operator, coherent states were written down by John R. Klauder, ''The Action Option and a Feynman Quantization of Spinor Fields in Terms of Ordinary C-Numbers,'' *Annals of Physics* **11**, 123 (1960) (doi: 10.1016/0003-4916(60)90131-7). The term ''coherent state'' was introduced in the context of the electromagnetic field by Roy J. Glauber, ''Coherent and Incoherent States of the Radiation Field,'' *Physical Review* **131**, 2766 (1963) (doi: 10.1103/PhysRev.131.2766).

after fixing the arbitrary phase of $|\alpha\rangle$. Putting this result into Eq. (5.77), we find the general amplitude

$$\langle n|\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}, \tag{5.81}$$

so that we may finally write the coherent state as

$$|\alpha\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}\, |n\rangle, \tag{5.82}$$
(coherent state, energy representation)

as expressed in the energy representation.

5.4.1 Poisson Distribution

One significant consequence of the coherent-state expression (5.82) is that the probability $P(n)$ for an energy measurement to yield $|n\rangle$ as the resulting state is

$$P(n) = |\langle n|\alpha\rangle|^2 = \frac{|\alpha|^{2n}}{n!}\, e^{-|\alpha|^2}. \tag{5.83}$$
(coherent-state Poisson distribution)

This is a common and important probability distribution, known as the **Poisson distribution**. Often, this distribution is written more generally as

$$P(n) = \frac{\lambda^n}{n!}\, e^{-\lambda} \tag{5.84}$$
(general Poisson distribution)

in terms of the parameter $\lambda > 0$. We just showed above that this distribution is normalized. The mean is similarly straightforward,

$$\langle n\rangle = \sum_{n=1}^{\infty} n\, P(n) = \sum_{n=1}^{\infty} \frac{\lambda^n}{(n-1)!}\, e^{-\lambda} = \lambda \sum_{n=0}^{\infty} \frac{\lambda^n}{n!}\, e^{-\lambda} = \lambda, \tag{5.85}$$

and to compute the variance, we can start by computing

$$\langle n(n-1)\rangle = \sum_{n=2}^{\infty} n(n-1)\, P(n) = \sum_{n=2}^{\infty} \frac{\lambda^n}{(n-2)!}\, e^{-\lambda} = \lambda^2 \sum_{n=0}^{\infty} \frac{\lambda^n}{n!}\, e^{-\lambda} = \lambda^2, \tag{5.86}$$

in terms of which we can compute the variance V_n as

$$V_n = \langle n^2\rangle - \langle n\rangle^2 = \langle n(n-1)\rangle + \langle n\rangle - \langle n\rangle^2 = \lambda^2 + \lambda - \lambda^2 = \lambda. \tag{5.87}$$

Summarizing, we computed the mean and variance

$$\langle n\rangle = V_n = \lambda. \tag{5.88}$$
(mean and variance, Poisson distribution)

For the coherent state, we thus have a mean and variance of $|\alpha|^2$. In fact, this is easy to see directly, because if we remember that $n = a^\dagger a$ is the number operator, then $\langle n\rangle = \langle\alpha|a^\dagger a|\alpha\rangle = |\alpha|^2$, and $\langle n^2\rangle = \langle\alpha|a^\dagger a a^\dagger a|\alpha\rangle = |\alpha|^2\langle aa^\dagger\rangle = |\alpha|^2\langle a^\dagger a + 1\rangle = |\alpha|^2(|\alpha|^2 + 1)$.

The interpretation of the Poisson distribution is that it counts the number of random, independent ‘‘arrivals’’ in a certain time interval. For example, it counts the number of cars that arrive at an intersection in some interval of time (in the low-traffic limit where cars are far apart, in order to satisfy the independence criterion). It also counts the number of electrons arriving at a particular point along a wire while a steady (mean) current flows. Because of the randomness in the discrete number of charged particles arriving in any time interval, the current itself is intrinsically noisy. This noise is called **shot noise**.

We will briefly note that a mode of the electromagnetic field acts as a harmonic oscillator in quantum mechanics (where the nth energy eigenstate corresponds to having n **photons**), and we will also see how a coherent state is the ''most classical'' harmonic-oscillator state. It is, for example, a good approximation for the output of a laser (with the technical proviso that the laser must be describable in the low-damping regime); in this case, the laser light intensity is also subject to shot noise. Shot noise is most significant for short detection times or for very weak intensities. Since the Poisson fluctuations scale as the root of the variance (i.e., $\sqrt{\lambda}$), the magnitude of the fluctuations *relative* to the mean is $\sqrt{\lambda}/\lambda = 1/\sqrt{\lambda}$. This is divergently large for small λ, corresponding to small mean photon numbers.

5.4.2 Displacement Operator

The **displacement operator** is defined as

$$D(\alpha) := e^{\alpha a^\dagger - \alpha^* a}, \tag{5.89}$$
(displacement operator)

which provides an alternative definition for the coherent state as

$$|\alpha\rangle := D(\alpha)\,|0\rangle. \tag{5.90}$$
(coherent state, alternate definition)

To see that this is equivalent to our previous definition, first, we need to rewrite the displacement operator as

$$D(\alpha) = e^{-|\alpha|^2/2}\, e^{\alpha a^\dagger}\, e^{-\alpha^* a}. \tag{5.91}$$

This follows from the operator identity

$$e^{A+B} = e^A\, e^B\, e^{-[A,B]/2}, \qquad \text{provided } \big[A,[A,B]\big] = \big[B,[A,B]\big] = 0, \tag{5.92}$$

which holds for operators A and B whose commutator commutes with each operator individually. Because the justification for this identity is fairly involved, we will defer for the moment [until Section 5.4.2.1 below, specifically Eq. (5.109)]. Since $[\alpha a^\dagger, -\alpha^* a] = -|\alpha|^2[a^\dagger, a] = |\alpha|^2$, this identity leads straight to Eq. (5.91).

Now consider the operation

$$e^{-\alpha^* a}|0\rangle = |0\rangle, \tag{5.93}$$

which follows from $a|0\rangle = 0$, so only the zeroth-order term in the series expansion of the exponential will yield any nonzero result.

$$e^{\alpha^* a}|n\rangle = \frac{(\alpha^*)^n}{\sqrt{n!}}|0\rangle + (\text{stuff}), \tag{5.94}$$

which follows from the nth term in the expansion of the exponential lowering $|n\rangle$ n times to $|0\rangle$. There are other terms involving the other states from $|1\rangle$ to $|n\rangle$, which we don't care about, so they are lumped under ''(stuff).'' Now we can form the inner product of these two results by writing

$$\langle n|D(\alpha)|0\rangle = e^{-|\alpha|^2/2}\langle n|e^{\alpha a^\dagger} e^{-\alpha^* a}|0\rangle = e^{-|\alpha|^2/2}\langle 0|\frac{\alpha^n}{\sqrt{n!}}|0\rangle = e^{-|\alpha|^2/2}\frac{\alpha^n}{\sqrt{n!}}. \tag{5.95}$$

This is the same amplitude that we derived in Eq. (5.81) before, thus showing that the alternate definition (5.90) is equivalent to the original definition (5.74) for the coherent state.

5.4.2.1 Exponential-Operator Identities

Now to take a little digression to justify the operator identity (5.92), which is something we will work up to in a few stages. The result we will derive here is broadly useful, as are some of the intermediate results.

First, take operators A and B, where $[A,B]$ commutes with B,

$$\big[B,[A,B]\big] = 0. \tag{5.96}$$

Then we can start by considering

$$\big[A, B^n\big] = [A, B]B^{n-1} + B\big[A, B^{n-1}\big], \tag{5.97}$$

using the product rule for commutators (see Section 1.6.1). We can repeat the process on the second term, and continue iterating the process on the last term, with the result

$$\big[A, B^n\big] = nB^{n-1}[A, B], \qquad ([B, [A, B]] = 0), \tag{5.98}$$
(first operator lemma)

noting that by assumption the B^{n-1} may appear on either side of the commutator. Now let's continue with the assumption (5.96) and consider

$$[A, e^B] = \sum_{n=0}^{\infty} \frac{1}{n!}[A, B^n] = \sum_{n=1}^{\infty} \frac{1}{n!}[A, B^n] = \sum_{n=1}^{\infty} [A, B]\frac{B^{n-1}}{(n-1)!} = [A, B]\, e^B, \tag{5.99}$$

or summarizing,

$$[A, e^B] = [A, B]\, e^B, \qquad ([B, [A, B]] = 0). \tag{5.100}$$
(second operator lemma)

Again, under the same commutation assumption (5.96), let's multiply through by e^{-B} in this last result to obtain

$$e^{-B}\, A\, e^B - A = [A, B], \tag{5.101}$$

where the exponential factors cancelled on the right-hand side in view of Eq. (5.96). Summarizing this result, we have

$$e^{-B} A\, e^B = A + [A, B], \qquad ([B, [A, B]] = 0). \tag{5.102}$$
(third operator lemma)

Now for the main result.[4] Suppose that $[A, B]$ commutes with *both* A and B, and take

$$f(x) = e^{Ax} e^{Bx}, \qquad (x \in \mathbb{R}). \tag{5.103}$$

Then

$$f'(x) = Ae^{Ax} e^{Bx} + e^{Ax} e^{Bx} B, \tag{5.104}$$

being careful with operator orderings. We can then rewrite this derivative as

$$\begin{aligned} f'(x) &= f(x)\big[e^{-Bx} A e^{Bx} + B\big] \\ &= f(x)\big[A + x[A, B] + B\big], \end{aligned} \tag{5.105}$$

after applying Eq. (5.102). The solution of this differential equation can be written

$$f(x) = e^{x(A+B)} e^{(x^2/2)[A,B]}, \tag{5.106}$$

as we can verify by computing

$$f'(x) = (A + B)e^{x(A+B)} e^{(x^2/2)[A,B]} + e^{x(A+B)} e^{(x^2/2)[A,B]} x[A, B] = f(x)\big[(A + B) + x[A, B]\big], \tag{5.107}$$

where we commuted $(A + B)$ through $e^{(x^2/2)[A,B]}$ in the first term by the assumption that $[A, B]$ commutes with both A and B. Finally, writing $f(1)$ from Eqs. (5.103) and (5.106) gives

$$e^A e^B = e^{A+B} e^{[A,B]/2}, \tag{5.108}$$

or

$$e^{A+B} = e^A\, e^B\, e^{-[A,B]/2}, \qquad ([A, [A, B]] = [B, [A, B]] = 0). \tag{5.109}$$
(fourth operator lemma)

as the result we needed to justify Eq. (5.92).

[4] This clever proof appears in Albert Messiah, *Quantum Mechanics* (Wiley, 1958) p. 442 (ISBN: 0486409244), who credits the argument to Glauber. Glauber then refers to Messiah for the argument, completing the circular reference; see K. E. Cahill and R. J. Glauber, "Ordered Expansions in Boson Amplitude Operators," *Physical Review* **177**, 1857 (1969), footnote 8 (doi: 10.1103/PhysRev.177.1857).

5.4.2.2 Interpretation

So now that we've seen that the displacement operator (5.89) changes the ground state $|0\rangle$ into a coherent state, but still none of these objects (besides the ground state) is very intuitively clear. To get a better handle on this, consider the displacement operator for $\alpha \in \mathbb{R}$:

$$D(\alpha) = e^{\alpha(a^\dagger - a)}, \qquad (\alpha \in \mathbb{R}). \tag{5.110}$$

Recalling that in scaled units, $p = (a - a^\dagger)/\sqrt{2}i$, this means $a^\dagger - a = -\sqrt{2}ip$ and so

$$D(\alpha) = e^{-i\sqrt{2}\alpha p}, \qquad (\alpha \in \mathbb{R}). \tag{5.111}$$

To change notation for a moment, we will consider the operator $e^{-ip\chi/\hbar}$ (in unscaled units, where p is the momentum operator and $\chi \in \mathbb{R}$), and show that it displaces a wave function $\psi(x)$ to $\psi(x - \chi)$. To do this, we will write out the displaced state in the position representation as

$$\langle x|e^{-ip\chi/\hbar}|\psi\rangle = \int dp\, \langle x|p\rangle\, \langle p|e^{-ip\chi/\hbar}|\psi\rangle. \tag{5.112}$$

The momentum operator in the exponential now becomes an eigenvalue, and we can use $\langle x|p\rangle = e^{ipx/\hbar}/\sqrt{2\pi\hbar}$ to write

$$e^{-ip\chi/\hbar}\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\, e^{ip(x-\chi)/\hbar}\, \langle p|\psi\rangle. \tag{5.113}$$

Comparing to the usual Fourier-transform expression

$$\psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int dp\, e^{ipx/\hbar}\, \langle p|\psi\rangle, \tag{5.114}$$

we can conclude

$$\langle x|e^{-ip\chi/\hbar}|\psi\rangle = \psi(x - \chi). \tag{5.115}$$

Thus, for $\alpha \in \mathbb{R}$, $D(\alpha)$ shifts a state in position by an amount $\sqrt{2}\alpha$ in scaled position, or $\alpha\sqrt{2\hbar/m\omega}$ in unscaled position. For a coherent state with real α, we can interpret this as a Gaussian state, with uncertainty matching the ground-state uncertainty and shifted to the same center position ($\sqrt{2}\alpha$ or $\alpha\sqrt{2\hbar/m\omega}$, depending on units).

In the case of imaginary α ($i\alpha \in \mathbb{R}$), the displacement operator becomes

$$D(\alpha) = e^{\alpha(a+a^\dagger)} = e^{\sqrt{2}\alpha x} = e^{i\sqrt{2}|\alpha|x}, \qquad (i\alpha \in \mathbb{R}), \tag{5.116}$$

keeping in mind that there is an i buried in α. By an argument similar to the one above, $e^{i\rho x/\hbar}$ ($\rho \in \mathbb{R}$, x an operator) also acts as a *momentum*-shift operator for the momentum-space wave function $\phi(p)$, in the sense

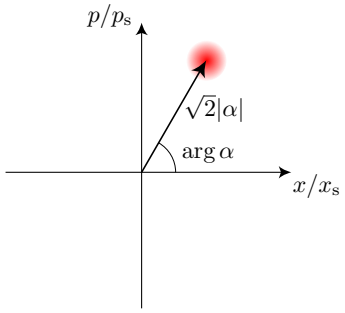
$$\langle p|e^{i\rho x/\hbar}|\psi\rangle = \langle p - \rho|\psi\rangle. \tag{5.117}$$

Briefly, the argument for this is:

$$\langle p|e^{i\rho x/\hbar}|\psi\rangle = \int dx\, \langle p|x\rangle\, \langle x|e^{i\rho x/\hbar}|\psi\rangle = \frac{1}{\sqrt{2\pi\hbar}} \int dx\, e^{-i(p-\rho)x/\hbar} \langle x|\psi\rangle = \phi(p - \rho). \tag{5.118}$$

Thus, in the imaginary case, $D(\alpha)$ shifts the wave function in scaled momentum by $\sqrt{2}\alpha/i$, or $\sqrt{2m\hbar\omega}\alpha/i$ in original momentum units.

Generally speaking, for an arbitrary complex phase, the displacement operator $D(\alpha)$ displaces the state in *some* direction in the scaled x-p plane (i.e., **phase space**) by an amount $\sqrt{2}|\alpha|$, with the complex phase of α giving the displacement direction. That is, $D(\alpha)$ can interpolate between position- and momentum-shift operators via the phase of α. Thus, the coherent state $|\alpha\rangle$ is a shifted version of the ground-harmonic-oscillator state, sitting with a center at a distance $\sqrt{2}|\alpha|$ from the origin. This is shown *schematically* below.



Note that this picture can only be regarded schematically (or classically), because we haven't defined how a quantum state can be represented simultaneously in position and momentum (although such a representation is possible, in terms of something called a **Wigner function**.) Nevertheless, this is a useful picture to have in mind for the coherent state.

(One side note to ponder: We are working with the harmonic oscillator, and yet when we showed the effect of the displacement operator, we used free-particle eigenstates. Is this a sensible/natural thing to do, and why or why not?)

5.4.3 Coherent-State Dynamics

So far, we have only considered the coherent state as a snapshot in time. But what about its time evolution? This is not too difficult to work out. For example, let's start by working out the position and momentum centroids (again, at some snapshot in time). The position centroid is

$$\langle x\rangle = \langle\alpha|x|\alpha\rangle = \frac{\langle\alpha|(a+a^\dagger)|\alpha\rangle}{\sqrt{2}} = \sqrt{2}\,\mathrm{Re}[\alpha], \tag{5.119}$$

after letting a act to the right and $a^\dagger$ to the left. The momentum centroid is similarly

$$\langle p\rangle = \langle\alpha|p|\alpha\rangle = \frac{\langle\alpha|(a-a^\dagger)|\alpha\rangle}{\sqrt{2}\,i} = \sqrt{2}\,\mathrm{Im}[\alpha]. \tag{5.120}$$

These are entirely consistent with our above remarks about the displacement operator.

As for the time evolution of the coherent state, for the state in the form (5.82), we need only include the factor $e^{-in\omega t}$ (in physical units) for the time evolution of $|n\rangle$ to find

$$|\alpha(t)\rangle = \sum_{n=0}^{\infty} \frac{\left(\alpha\, e^{-i\omega t}\right)^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}|n\rangle, \tag{5.121}$$

after lumping in the time-dependence factor with α^n. (Note that this should really be a factor of e^{int} in scaled time, but it's too unnerving to have a phase factor like this, so we'll keep the explicit ω. Also note that we're discarding the common phase factor $e^{i\omega t/2}$ associated with the zero-point energy, which acts here as an ignorable global phase.) Thus, we can implement time dependence in the coherent state simply with the replacement $\alpha \longrightarrow \alpha\, e^{-i\omega t}$. In Eqs. (5.119) and (5.120), these lead to (again, in physical units)

$$\begin{aligned}\langle x(t)\rangle &= \sqrt{2}\,x_s\mathrm{Re}[\alpha\, e^{-i\omega t}] = \sqrt{2}|\alpha|x_s\cos(\omega t - \arg\alpha)\\ \langle p(t)\rangle &= \sqrt{2}\,p_s\mathrm{Im}[\alpha\, e^{-i\omega t}] = -\sqrt{2}|\alpha|p_s\sin(\omega t - \arg\alpha).\end{aligned} \tag{5.122}$$

[Here the argument function is defined such that $z = |z|\exp(\arg z)$ for $z \in \mathbb{C}$, and $\arg z$ should be restricted to some sensible interval such as $[0, 2\pi)$.] Note that these are equivalent to *classical* equations of motion in the harmonic oscillator (in scaled units). The centroid of the coherent state simply follows a classical path (a circle) in scaled phase space, or the corresponding classical ellipse in the original coordinates.

As for the evolution of the variance, we can start by computing

$$\langle x^2 \rangle = \frac{1}{2}\langle \alpha | (a + a^\dagger)^2 | \alpha \rangle = \frac{1}{2}\Big(\alpha^2 + 2|\alpha|^2 + (\alpha^*)^2 + 1\Big) = \frac{(\alpha + \alpha^*)^2}{2} + \frac{1}{2} = \langle x \rangle^2 + \frac{1}{2}. \tag{5.123}$$

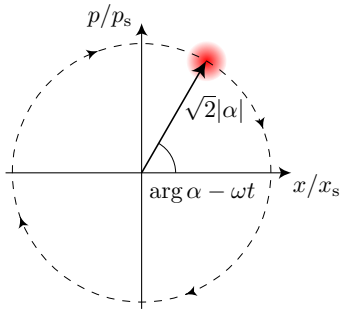
Here, we used

$$(a + a^\dagger)^2 = a^2 + aa^\dagger + a^\dagger a + (a^\dagger)^2 = a^2 + 2a^\dagger a + (a^\dagger)^2 + 1, \tag{5.124}$$

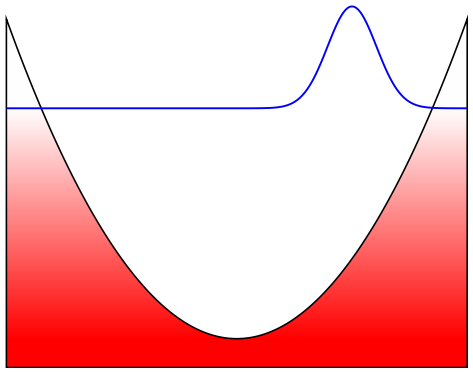
using $[a, a^\dagger] = 1$. The last expression is said to be **normally ordered**, which simply means that all a's appear to the right in each factor, and all $a^\dagger$'s to the left. Now the variance is just

$$V_x = \langle x^2 \rangle - \langle x \rangle^2 = \frac{1}{2}, \tag{5.125}$$

again keeping in mind that this result is in scaled units. The analogous result $V_p = 1/2$ follows from a similar argument. Of course, these match the variances of $|0\rangle$, which is a special case of a coherent state with $\alpha = 0$. Since these variances are independent of α, the variances themselves are constants of the motion. Thus the coherent state remains a minimum-uncertainty Gaussian state (it turns out that being of minimum uncertainty is sufficient to establish a wave function as Gaussian), whose shape (in scaled coordinates) is time-independent. Its centroid follows the expected classical trajectory in phase space, rotating about the origin with (angular) frequency ω (in unscaled time), as shown schematically below.



The evolution of a coherent state is illustrated in the animation below. The plotted curve is $\mathrm{Re}[\psi(x,t)]$, in order to show some phase information (the probability density $|\psi(x,t)|^2$ is more mundane, because it is just a Gaussian of fixed profile, moving around). Note that the phase variation is greatest when the speed of the wave packet is largest.



5.4.4 Interpretation as Eigenstate of the Annihilation Operator

It is something of a curious thing that the coherent state $|\alpha\rangle$ is an eigenstate of the annihilation operator a. Equally curious is that the creation operator $a^\dagger$ has *no* nontrivial eigenstate (i.e., no eigenstate other than the null vector, which is by the way *not* the same as $|0\rangle$). What do these statements mean?

The mathematical treatment that underlies the interpretation of these statements is beyond the scope of what we'd like to cover here, so we'll have to stick only to general statements.[5] Briefly, the application of the annihilation operator lowers the energy of the harmonic oscillator by something like $\hbar\omega$ (or rather this statement applies to the part of the quantum state that is *not* in $|0\rangle$; the ground-state component is annihilated completely, potentially leading to an unnormalized state). It is thus a useful operator to model energy damping in the quantum harmonic oscillator.

In a damped oscillator, energy should be removed from both the mean and variance in both position and momentum (the kinetic energy is proportional to $\langle p^2\rangle = V_p + \langle p\rangle^2$, and the potential energy is proportional to $\langle x^2\rangle = V_x + \langle x\rangle^2$). In terms of the variance energy, the damping seeks to minimize $V_p + V_x$, subject to the constraint $V_x V_p \geq 1/4$, which yields $V_x = V_p = 1/2$—precisely what we expect for a coherent state or the oscillator's ground state. The centroid motion will be damped too, but note that centroid motion can be excited independently of the variance energy, for example by a driving potential of the form $x\sin(\omega_{\text{drive}}t)$. (A drive that excites variance energy must have a form more like x^2 rather than x.) In fact, the steady state of a damped, driven quantum harmonic oscillator is a coherent state.

The creation operator, on the other hand, tends to *raise* the energy of the oscillator by something like $\hbar\omega$. This is a *gain* process, and is different from a damping process in that a quantum amplification of energy necessarily entails the injection of quantum noise. This effectively increases both the position and momentum variances in such a way that the quantum state can no longer be simply represented by a state vector (rather, it should be represented by a density operator, which we haven't discussed so far). This is an intuitive way to think of why the creation operator doesn't have an eigenvector in the same sense as the annihilation operator.

5.5 Classical Limit

Now we are at a good point to consider how the quantum harmonic oscillator matches up with its classical counterpart. The harmonic oscillator (along with special cases like the free particle or a particle under constant acceleration) is quite special among quantum systems in that it is relatively easy to see how the **Correspondence Principle**—the idea that quantum mechanics should reproduce classical mechanics in some sensible limit—works out.

The classical harmonic oscillator has trajectories of the general form

$$\begin{aligned} x(t) &= x_0\cos\omega t \\ p(t) &= -p_0\sin\omega t, \end{aligned} \tag{5.126}$$

where for consistency in the sense $p = m\dot{x}$, we must have $p_0 = m\omega x_0$. **We expect classical behavior to emerge from quantum mechanics when the action scale of the dynamics is large compared to the Planck scale**. For this problem, this means we expect classical behavior provided

$$x_0 p_0 \gg \hbar. \tag{5.127}$$
(classicality condition)

Using $p_0 = m\omega x_0$, this condition becomes

$$x_0 \gg \sqrt{\frac{\hbar}{m\omega}} = x_{\text{s}}. \tag{5.128}$$

That is, we expect classical behavior if the motion occurs over distances large compared to the natural quantum length scale x_{s} for the harmonic oscillator. Alternately, again using $p_0 = m\omega x_0$ in Eq. (5.127) and multiplying by ω gives

$$m\omega^2 x_0^2 \gg \hbar\omega. \tag{5.129}$$

The left-hand side is twice the energy of the classical oscillator, so we can write the condition as

$$E \gg \hbar\omega. \tag{5.130}$$

[5] For more details, see Daniel A. Steck, *Quantum and Atom Optics*, available online at `http://steck.us/teaching` (2007).

Again, we can interpret this as an expectation of classical behavior when the oscillator energy is large compared to the natural quantum energy scale $E_s = \hbar\omega$. We can express this condition also as the presence of many energy quanta $\langle n\rangle = \langle a^\dagger a\rangle \gg 1$.

5.5.1 Coherent State

Now from the discussion of coherent-state dynamics in Section 5.4.3, it is straightforward to see the correspondence principle in action in both position and momentum. In position, we already have classical motion for the centroid $\langle x\rangle$, with amplitude $x_0 = \sqrt{2}|\alpha|$. There is also an uncertainty in the position, given by

$$\sigma_x = \sqrt{V_x} = \frac{1}{\sqrt{2}}, \tag{5.131}$$

in scaled units. Note that this uncertainty is *fixed*, not depending on the amplitude. However, the relevant way to think about the uncertainty is *relative* to the oscillation amplitude. For example, if a classical pendulum swings over a 1-m amplitude, we're not so concerned if the relative uncertainty is 10^{-10}, because this uncertainty would be on the atomic scale. Computing the relative uncertainty, we find

$$\frac{\sigma_x}{x_0} = \frac{1}{2|\alpha|}, \tag{5.132}$$

which becomes arbitrarily small in the classical limit of large $|\alpha|$ (large $\langle n\rangle$). To check consistency, note that for a classical, macroscopic oscillator, with an energy of the order of 1 J and a period of 1 s, the quantum energy scale is of the order of 10^{-33} J, so $\langle n\rangle \sim 10^{33}$ and $|\alpha| \sim 10^{16}$. The fractional position uncertainty is on the order of 10^{-16}, which is quite ignorable. A similar argument goes through for the momentum coordinate.

From the discussion of the Poisson distribution in Section 5.4.1, we again know that the mean and variance in the energy quanta are

$$\langle n\rangle = V_n = |\alpha|^2, \tag{5.133}$$

where these quantities should be much larger than unity in the classical limit. Again, we should consider the relative uncertainty in the energy quanta:

$$\frac{\sigma_n}{\langle n\rangle} = \frac{\sqrt{V_n}}{\langle n\rangle} = \frac{|\alpha|}{|\alpha|^2} = \frac{1}{|\alpha|}, \tag{5.134}$$

which becomes vanishingly small in the classical limit. This means that the oscillator energy (in the coherent state) becomes well-defined in the classical limit. Similarly the discreteness in energy (where $\delta E_n = \hbar\omega$ is the discrete step between energy states), in a relative sense,

$$\frac{\delta E_n}{E_n} = \frac{\hbar\omega}{\hbar\omega(n + 1/2)} \approx \frac{1}{|\alpha|^2}, \tag{5.135}$$

also becomes negligibly small in the classical limit, as it should.

There are a couple of important caveats here. Mainly, we started with a very easy state to see the emergence of a classical limit—the Gaussian wave packet remains localized, and the center already follows a classical trajectory. This is not generally the case, as for more general quantum systems the wave packet will spread, in some cases very quickly so. In such systems it is much more difficult to explain how classical behavior arises (it is already beyond the capabilities of the formalism that we have developed so far). The related comment is that, if we start a harmonic oscillator in a nonclassical state (say, a superposition of two coherent states), the behavior will never be classical unless we invoke some other process to destroy the superposition. Again, this is beyond the tools that we have at hand at the moment, though we will return to these issues later.

5.5.2 Number State

Having said that, considering the energy eigenstates, which are fairly nonclassical states, we can also see how they can match up to the classical distribution in the classical limit. To obtain the analogous classical

distribution, we can start with a typical classical trajectory (as usual, in scaled units):

$$x(t) = x_0 \cos t. \tag{5.136}$$

At $t = 0$, all the energy in the oscillator is in the potential energy $V(x) = x^2/2$. Thus, $E = x_0^2/2$, or

$$x_0 = \sqrt{2E} = \sqrt{2n+1} \tag{5.137}$$

comparing to the energy of the nth energy eigenstate in scaled units. In a time-averaged sense, the probability of finding the oscillator in an interval $[x, x+dx)$ by looking at a random time is

$$P(x)\,dx = \frac{2dt}{T} = \frac{dt}{\pi}, \tag{5.138}$$

where $2dt$ is the amount of time spent in this interval (the 2 accounts for occupying the same interval, traveling in either direction), and $T = 2\pi$ is the period in scaled units. Then changing variables with $dt = |dx/dt|^{-1}dx$ (and noting that dx/dt is well-defined, but will go to zero, leading to a divergence)

$$P(x)\,dx = \frac{dx}{\pi|x_0 \sin t|}. \tag{5.139}$$

Then with $\sin(\cos^{-1} x) = \sqrt{1-x^2}$ for the first half of the oscillation cycle, and $t = \cos^{-1}(x/x_0)$,

$$P(x)\,dx = \frac{dx}{\pi\left|x_0\sqrt{1-(x/x_0)^2}\right|} = \frac{dx}{\pi\sqrt{x_0^2-x^2}} = \frac{dx}{\pi\sqrt{2E-x^2}} = \frac{dx}{\pi\sqrt{2n+1-x^2}}. \tag{5.140}$$

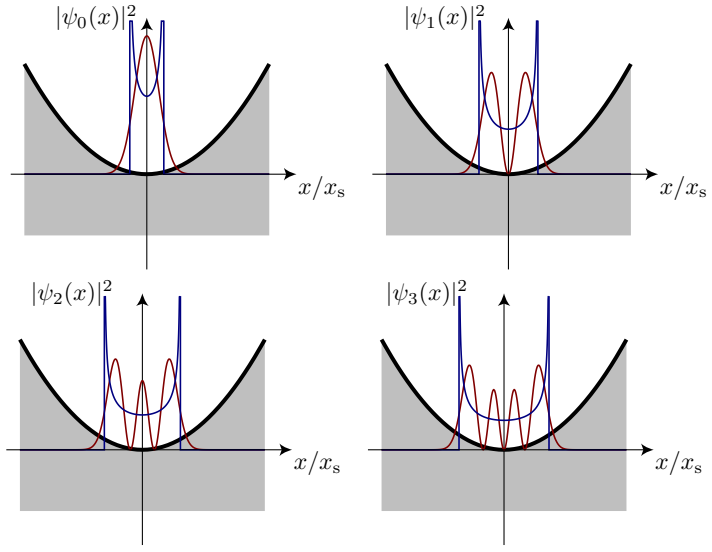
Thus, the time-averaged *classical* probability density is

$$P(x) = \frac{1}{\pi\sqrt{2E-x^2}} = \frac{1}{\pi\sqrt{2n+1-x^2}}, \qquad (x^2 < 2n+1).$$

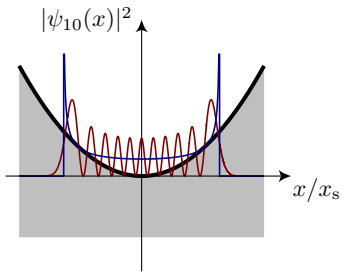
(classical occupation density, scaled units) (5.141)

In physical units, the energy term $2E$ here (or the $2n+1$) is essentially just multiplied by $x_s^2/E_s = 1/m\omega^2$ in this expression.

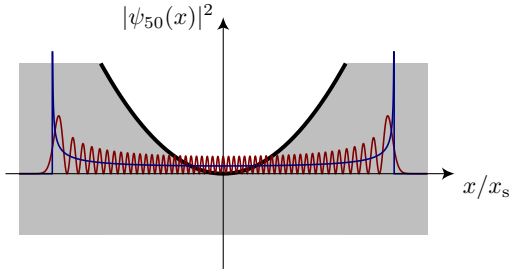
To compare the classical and quantum distributions, the diagrams below compare the densities $|\psi_n(x)|^2$ for the first few energy eigenstates, with the corresponding classical distribution. The lowest eigenvalues don't look very classical, but for the $n = 2$ and 3 cases, the classical shape is beginning to emerge.



For a higher energy state, like $n = 10$, the classical shape emerges even more.



For an even higher energy state, like $n = 50$, the classical shape emerges yet more.



The quantum eigenfunctions reflect the overall classical structure, with a couple of modifications. The eigenfunctions "leak" a bit into the energetically forbidden region, so there are some exponentially damped tails that extend beyond the classical distribution. Also, the quantum distributions have interference fringes, because in a time-independent sense the wave function has components going in either direction, which produce interference fringes. This is in the same sense that for the free particle, $\psi(x) \propto e^{ipx/\hbar}$ has a well-defined momentum and a structureless probability density, while $\psi(x) \propto e^{ipx/\hbar} + e^{-ipx/\hbar}$ is a superposition of two momenta, and the probability has interference fringes of the form $\cos^2(px/\hbar)$. Also, note that the fringes are most closely spaced near $x = 0$, where the momentum should be largest, and the fringes are taller and more widely spaced at the edges, when the momentum is smaller (and even zero at the turning points).

5.5.2.1 Generating Function of the Hermite Polynomials

Although the convergence is readily apparent graphically, we can also show this directly by considering the asymptotic behavior of the Hermite–Gauss function. To begin, let's start with the displacement-operator definition of the coherent state, as in Eq. (5.90) in the position representation:

$$\langle x|D(\alpha)|0\rangle = \langle x|\alpha\rangle. \tag{5.142}$$

If we take $\alpha \in \mathbb{R}$, then from Eqs. (5.111) and (5.115), the displacement operator is a position-shift operator, shifting the wave function by $\sqrt{2}\alpha$, as in Eq. (5.115). Then on the left-hand side, we can write down the shifted, ground-state wave function from Eq. (5.54), while on the right-hand side we can use the coherent state (5.82) in the energy representation,

$$|\alpha\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}|n\rangle, \tag{5.143}$$

to obtain

$$e^{-(x-\sqrt{2}\alpha)^2/2} = \sum_{n=0}^{\infty} \frac{\alpha^n e^{-\alpha^2/2}}{2^{n/2}n!}\, e^{-x^2/2} H_n(x), \tag{5.144}$$

where we used the wave functions [from Eq. (5.67)]

$$\psi_n(x) = \frac{1}{2^{n/2}\pi^{1/4}\sqrt{n!}}\, e^{-x^2/2} H_n(x) \tag{5.145}$$

for $\langle x|n\rangle$. Collecting all exponential factors on the left,

$$e^{\sqrt{2}\alpha x-\alpha^2/2}=\sum_{n=0}^{\infty}\frac{\alpha^n}{2^{n/2}n!}\,H_n(x), \tag{5.146}$$

and then changing variables by setting $z=\alpha/\sqrt{2}$, we find

$$e^{2zx-z^2}=\sum_{n=0}^{\infty}\frac{z^n}{n!}\,H_n(x). \tag{5.147}$$

(generating function, Hermite polynomials)

The exponential function on the left hand side is the generating function for the Hermite polynomials, in the sense that differentiating n times with respect to z and then setting $z=0$ gives $H_n(x)$. Since α was real, z is as well, although at this point we will want to think about extending z to the complex plane.

Now to obtain an expression for the Hermite polynomials in terms of the generating function, we can start with the Cauchy integral formula (generalized to the kth derivative),

$$f^{(k)}(a)=\frac{k!}{2\pi i}\oint_\gamma\frac{f(z)}{(z-a)^{k+1}}\,dz \tag{5.148}$$

where the path γ of integration passes around $z=a$ counterclockwise. Applying this to the case where the $f(z)$ is the generating function (5.147), we find

$$H_n(x)=\frac{n!}{2\pi i}\oint_\gamma z^{-(n+1)}e^{2zx-z^2}\,dz=\frac{n!}{2\pi i}\oint_\gamma e^{2zx-z^2-(n+1)\log z}\,dz. \tag{5.149}$$

At this point, we haven't yet defined the contour γ, and there isn't a simple contour that we can define that will make the integral go through in closed form.

5.5.2.2 Method of Steepest Descent: Saddle-Point Approximation

To continue, we will need to introduce the **method of steepest descent**.[6] The integral we need to solve has the generic form

$$I(x)=\int_\gamma e^{f(x,z)}\,dz. \tag{5.150}$$

Schematically, the procedure we will outline works well when the integrand behaves something like $e^{xf(z)}$, where $f(z)$ falls to $-\infty$ at the integration endpoints; then as x becomes large, the integrand is only significant in some concentrated region. Namely, at a **saddle point** z_0 where $\partial_z f=0$, we can write

$$\begin{aligned}f(x,z)&\approx f_0+\frac{1}{2}(f_0'')(z-z_0)^2\\&=f_0+\frac{1}{2}\big|f_0''\big|\,|z-z_0|^2e^{i(\varphi+2\zeta)}\\&=f_0+\frac{1}{2}\big|f_0''\big|\,|z-z_0|^2\big[\cos(\varphi+2\zeta)+i\sin(\varphi+2\zeta)\big],\end{aligned} \tag{5.151}$$

where f_0 is shorthand for $f(x,z_0)$, f_0'' is shorthand for $\partial_z^2 f(x,z)|_{z=z_0}$, and the phase angles are defined by $f_0''=|f_0''|e^{i\varphi}$ and $(z-z_0)=|z-z_0|e^{i\zeta}$. Note that we are assuming analyticity of $e^{f(x,z)}$ in a region around z_0, so the stationary point z_0 cannot correspond to any extremum, hence a saddle point. The steepest *decrease* of the exponential integrand occurs when $\cos(\varphi+2\zeta)=-1$, or $\varphi+2\zeta=\pm\pi$, or $\zeta=\pm\pi/2-\varphi/2$. These correspond to two directions (180° apart) in the complex plane. Briefly, the idea behind the method of

[6] George B. Arfken, Hans J. Weber, and Frank E. Harris, *Mathematical Methods for Physicists*, 7th ed. (Academic Press, 2013), Section 12.7, p. 585 (ISBN: 9780123846549); R. Courant and D. Hilbert, *Methods of Mathematical Physics*, vol. I, 1st English ed. (Springer, 1937), Section VII.6.3, p. 526 (ISBN: 047017952X).

steepest descent is that when the integration contour passes through the saddle point along this direction, and when $|f_0''|$ is large, the dominant contribution to the integral comes from a narrow region around the saddle point. Then we can make the approximation of replacing the integration contour γ by a straight-line contour through z_0 in the direction $\zeta = \pm\pi/2 - \varphi/2$, with the result

$$I(x) \approx e^{f_0+i\zeta} \int_{-\infty}^{\infty} dz\, e^{-|f_0''|z^2/2} = e^{f_0+i\zeta}\sqrt{\frac{2\pi}{|f_0''|}}. \quad \text{(saddle-point approximation)} \tag{5.152}$$

This last expression is the **saddle-point approximation** to the integral $I(x)$. Note that the phase factor $e^{i\zeta}$ amounts to $\pm i$, depending on the direction of the integration path, since ζ was already fixed modulo π by the steepest-descent condition (and thus it cancels the phase φ from f_0'').

5.5.2.3 Large-n Asymptotics of the Hermite Polynomials

To apply the saddle-point approximation to the Hermite-polynomial integral (5.149), we will first need the saddle points, which are determined by

$$\partial_z\big[2zx - z^2 - (n+1)\log z\big] = 0. \tag{5.153}$$

Carrying out the derivative, this condition becomes

$$2(x - z) - \frac{(n+1)}{z} = 0. \tag{5.154}$$

Solving this condition amounts to finding the roots of a quadratic polynomial; the two solutions are

$$z_\pm := \frac{x}{2} \pm \frac{1}{2}\sqrt{x^2 - 2(n+1)}. \tag{5.155}$$

The character of the square root will change depending on the relative magnitudes of x^2 and $2(n+1)$. In the case $x^2 < 2(n+1)$, where we expect the oscillator to reside, the saddle points are

$$z_\pm = \frac{x}{2} \pm \frac{i}{2}\sqrt{2(n+1) - x^2}. \tag{5.156}$$

The saddle points then define the contour γ in the integral (5.149): the contour should be deformed to pass through *both* saddle points, while still passing counterclockwise around $z = 0$. This means that the contour should pass through z_+ from right to left, and z_- from left to right, with the exact angles of passage are determined by the directions of steepest descent. That the descent should be sufficiently steep (i.e., that the saddle-point approximation will be good) is guaranteed by the z^{-n} factor in the integral (5.149) in the asymptotic regime of large n. This will be most obvious when we compute the second derivative f_0'', as we will do below in Eq. (5.159).

Now assembling the pieces we will need, we will start with the second derivative f_0'', evaluated at the two saddle points:

$$\partial_z^2\big[2zx - z^2 - (n+1)\log z\big]_{z=z_\pm} = -2 + \frac{4(n+1)}{x \pm \sqrt{x^2 - 2(n+1)}}. \tag{5.157}$$

Again, for $x^2 < 2(n+1)$ we should be careful with the square root:

$$\begin{aligned}
\partial_z^2\big[2zx - z^2 - (n+1)\log z\big]_{z=z_\pm} &= -2 + \frac{4(n+1)}{\big[x \pm i\sqrt{2(n+1) - x^2}\big]^2} \\
&= -2 + \frac{4(n+1)\big[x \mp i\sqrt{2(n+1) - x^2}\big]^2}{4(n+1)^2} \\
&= 2\frac{x^2 - 2(n+1) \mp ix\sqrt{2(n+1) - x^2}}{(n+1)}.
\end{aligned} \tag{5.158}$$

The modulus of this expression is

$$\begin{aligned}\left|\partial_z^2\left[2zx-z^2-(n+1)\log z\right]_{z=z_\pm}\right| &= 2\frac{\sqrt{\left(x^2-2(n+1)\right)^2+\left(x\sqrt{2(n+1)-x^2}\right)^2}}{(n+1)}\\ &= 2\frac{\sqrt{4(n+1)^2-2x^2(n+1)}}{(n+1)}\\ &= 4\sqrt{1-\frac{x^2}{2(n+1)}},\end{aligned} \tag{5.159}$$

while the phase is

$$\varphi = \tan^{-1}\frac{\pm x}{\sqrt{2(n+1)-x^2}} = \sin^{-1}\frac{\pm x}{\sqrt{2(n+1)}} = \pm\sin^{-1}\frac{x}{\sqrt{2(n+1)}}. \tag{5.160}$$

Again, in Eq. (5.159) in the limit of large n, this second derivative can never become small justifying the saddle-point approximation to come (while the second derivative and thus the length scale over which it varies is bounded, it is large in the sense that for large n, the saddle points move far away from the origin, so the saddle-point variation of the integrand becomes rapid on the scale of the contour). Additionally, we will need f_0,

$$\begin{aligned}\left[e^{2zx-z^2-(n+1)\log z}\right]_{z=z_\pm} &= \frac{2^{n+1}}{\left[x\pm\sqrt{x^2-2(n+1)}\right]^{n+1}}\,e^{[n+1+x^2\pm x\sqrt{x^2-2(n+1)}]/2}\\ &= \frac{2^{n+1}}{\left[x\pm i\sqrt{2(n+1)-x^2}\right]^{n+1}}\,e^{[n+1+x^2\pm ix\sqrt{2(n+1)-x^2}]/2}\\ &= \frac{(\pm 2)^{n+1}}{\left[\sqrt{2(n+1)}\right]^{n+1}}\,e^{-i(n+1)\cos^{-1}[\pm x/\sqrt{2(n+1)}]}\,e^{[n+1+x^2\pm ix\sqrt{2(n+1)-x^2}]/2}\\ &= \frac{(\pm 1)^{n+1}2^{(n+1)/2}}{(n+1)^{(n+1)/2}}\,e^{-i(n+1)\cos^{-1}[\pm x/\sqrt{2(n+1)}]}\,e^{[n+1+x^2\pm ix\sqrt{2(n+1)-x^2}]/2},\end{aligned} \tag{5.161}$$

again in the case $x^2 < 2(n+1)$. To make this expression a little easier to handle, we will work in the limit $2(n+1) \gg x^2$, where we can make use of the expansion $\cos^{-1} x = \pi/2 - x + O(x^3)$ to write the asymptotic expression

$$\begin{aligned}\left[e^{2zx-z^2-(n+1)\log z}\right]_{z=z_\pm} &\sim \frac{(\pm 1)^{n+1}2^{(n+1)/2}}{(n+1)^{(n+1)/2}}\,e^{-i(n+1)\pi/2}\,e^{\pm ix\sqrt{(n+1)/2}}\,e^{[n+1+x^2\pm ix\sqrt{2(n+1)-x^2}]/2}\\ &\sim \frac{2^{(n+1)/2}}{(n+1)^{(n+1)/2}}\,e^{\mp i(n+1)\pi/2}\,e^{\pm ix\sqrt{2(n+1)}}\,e^{(n+1+x^2)/2}.\end{aligned} \tag{5.162}$$

Going back to the integral (5.149), we can employ the saddle-point approximation (5.152) to find

$$H_n(x) = \frac{n!}{2\pi i}\frac{2^{(n+1)/2}}{(n+1)^{(n+1)/2}}\frac{\sqrt{2\pi}\,e^{(n+1+x^2)/2}}{2[1-x^2/2(n+1)]^{1/4}}\left[e^{i(n+1)\pi/2}\,e^{-ix\sqrt{2(n+1)}}-e^{-i(n+1)\pi/2}\,e^{ix\sqrt{2(n+1)}}\right]. \tag{5.163}$$

Note that we have summed over the contributions from both saddle points. The signs of each term are determined by the direction of the contour through each point, as we discussed before, relative to the steepest-descent angles φ from Eq. (5.160), which indicate that the ''normal'' passage direction is asymptotically left

to right. The upshot is that the z_+ contribution picks up a minus sign, while the z_- contribution doesn't. Simplifying Eq. (5.163), we find the large-n asymptotic expression[7]

$$H_n(x) \sim \frac{2^{n/2} n!}{\sqrt{\pi}(n+1)^{(n+1)/2}} \frac{e^{(n+1)/2+x^2/2}}{[1-x^2/2(n+1)]^{1/4}} \sin\left(\frac{(n+1)\pi}{2} - x\sqrt{2(n+1)}\right), \qquad x^2 < 2(n+1).$$

(Hermite polynomial, large-n asymptotic form) (5.164)

This expression will now allow us to investigate the large-n behavior of the harmonic-oscillator eigenfunctions.

5.5.2.4 Convergence of the Asymptotic Number State

The energy-eigenstate wave function (5.67) implies the probability density

$$\left|\psi_n(x)\right|^2 = \frac{1}{2^n \sqrt{\pi}\, n!}\, e^{-x^2} H_n^2(x). \tag{5.165}$$

Putting in the asymptotic expression (5.164), we find

$$\left|\psi_n(x)\right|^2 \sim \frac{1}{2\sqrt{\pi}} \frac{n!}{\pi(n+1)^{n+1}} \frac{e^{n+1}}{\sqrt{1-x^2/2(n+1)}} \tag{5.166}$$

where we have replaced the rapidly oscillating $\sin^2$ function by its average value $1/2$. With the large-n Stirling approximation

$$n! \sim \sqrt{2\pi n}\, n^n e^{-n}, \tag{5.167}$$

the asymptotic quantum distribution (5.166) becomes

$$\left|\psi_n(x)\right|^2 \sim \frac{e\, n^{n+1/2}}{(n+1)^{n+1/2}} \frac{1}{\pi\sqrt{2(n+1)-x^2}}. \tag{5.168}$$

Finally using

$$\lim_{n\to\infty} \left(\frac{n+1}{n}\right)^{n+1/2} = \lim_{n\to\infty} \left(1+\frac{1}{n}\right)^n = e, \tag{5.169}$$

we have the asymptotic quantum density

$$\left|\psi_n(x)\right|^2 \sim \frac{1}{\pi\sqrt{2(n+1)-x^2}}.$$

(quantum occupation density, asymptotic) (5.170)

Note that we have only considered the region $x^2 < 2(n+1)$; however, we can infer that the density becomes vanishingly small outside this region, because this density is normalized on the region $x^2 < 2(n+1)$.

We should compare this to the classical occupation density (5.141),

$$P(x) = \frac{1}{\pi\sqrt{2n+1-x^2}}. \tag{5.171}$$

What we found for the quantum density (5.170) doesn't *quite* match this—it's just a bit wider at any given n, and strictly speaking, the difference in width is n-independent. In fact, the quantum asymptotic distribution doesn't even quite have the right variance—it is $n+1$, when it should be $n+1/2$—which is a symptom of having not correctly handled the region $x \sim 2(n+1)$. However, recall that the proper way to compare is to rescale the dynamical motion to some *fixed* scale, and examine the convergence in the classical limit. In

[7] This expression was derived using the saddle-point method ("*la méthod du col*") by M. Plancherel and W. Rotach, "Sur les valeurs asymptotiques des polynomes d'Hermite," *Commentarii mathematici Helvetici* **1**, 227 (1929), Eq. (8) `http://eudml.org/doc/138522`.

the present case, we should rescale to the expected position excursion $\sqrt{2n+1}$ of the classical oscillator, by defining the rescaled classical density

$$\sqrt{2n+1}\,P\big(\sqrt{2n+1}\,x\big) = \frac{1}{\pi\sqrt{1-x^2}}, \tag{5.172}$$

and the rescaled classical density

$$\sqrt{2n+1}\,\big|\psi_n\big(\sqrt{2n+1}\,x\big)\big|^2 \sim \frac{1}{\pi\sqrt{(n+1)/(n+1/2)-x^2}}. \tag{5.173}$$

Both of these densities are then defined over $|x|<1$. The ratio in the large-n limit is

$$\lim_{n\to\infty}\frac{\big|\psi_n\big(\sqrt{2n+1}\,x\big)\big|^2}{P\big(\sqrt{2n+1}\,x\big)} = \lim_{n\to\infty}\frac{\sqrt{(n+1)/(n+1/2)-x^2}}{\sqrt{1-x^2}} = 1, \tag{5.174}$$

so that in this rescaled sense, the quantum distribution converges to the classical distribution. In this rescaled form, note that it is not a concern that we assumed $x^2 \ll 2(n+1)$, because as n increases, the range of the scaled x coordinate over which the asymptotic distribution is valid approaches the entire interval $(-1,1)$.

5.5.3 Classical Evolution of the Quantum Harmonic Oscillator

The connection between the classical and quantum harmonic oscillators is even deeper than we have suggested by the classical-limit analyses above. The quantum harmonic oscillator is in some sense classical *even at all scales of evolution*, not just for large oscillations or energies.

To see this, recall that the classical equations of motion are Hamilton's equations, which in this case are

$$\begin{aligned}\dot{x} &= \frac{p}{m}\\ \dot{p} &= -m\omega^2 x.\end{aligned} \tag{5.175}$$

Now the idea is to consider the *classical* equations of motion for expectation values, but of course we first have to define what this means. A classical phase-space density $\rho_{\text{L}}(x,p)$, called a **Liouville density**, defines the state of a classical ensemble of harmonic oscillators. The expectation value of a phase-space function $f(x,p)$ is simply the average with respect to this density:

$$\big\langle f(x,p)\big\rangle = \int dx \int dp\, f(x,p)\,\rho_{\text{L}}(x,p). \tag{5.176}$$

There is, however, some subtlety in interpreting this expression. A natural and conventional way to think of this expression is in terms of an evolving density $\rho_{\text{L}}(x,p)$ (which, being a phase-space function, evolves according to the Poisson bracket, as in Section 0.4.3), where the x and p are merely dummy integration variables. However, we would like to make use of the equations of motion (5.175), in which case a different interpretation of the expectation value is appropriate. In this picture, the expectation value depends on time through the time dependence of the coordinates $x(t)$ and $p(t)$ in the integral. However, to properly account for the time dependence in this picture, the density ρ_{L} should *not* depend on time. All the time dependence should enter through $f(x(t),p(t))$—which is equivalent to the evolution of $f(x,p)$ via the Poisson bracket—and the integration of the expectation value is taken with respect to the *initial* coordinates (x_0,p_0). The reason is that the density associated with the small neighborhood around an evolving phase-space point, parameterized by $x(t)$ and $p(t)$, is an invariant, as a consequence of Liouville's theorem (that areas in phase space don't change under Hamiltonian flow). Thus, if both f and ρ_{L} depend on the same time-dependent coordinates $x(t)$ and $p(t)$, the time dependences would cancel out, leaving a *time-independent* expectation value. Another way to see that the density ρ_{L} should be regarded as time-independent is to consider the density corresponding to a single particle, which would be a delta function at (x_0,p_0). As this point evolves in time, the *only* point in phase space at which the density is nonzero is at $(x(t),p(t))$. Thus, the time-dependent expectation value can be regarded as an average of a time-dependent phase-space function with

respect to the *initial* phase-space distribution, something analogous to the Heisenberg picture in quantum mechanics.

To compute the equations of motion for the mean coordinates, we can simply take the expectation values of Eqs. (5.175).

$$\begin{aligned} \frac{d}{dt}\langle x\rangle &= \frac{\langle p\rangle}{m} \\ \frac{d}{dt}\langle p\rangle &= -m\omega^2\langle x\rangle\,. \end{aligned} \tag{5.177}$$

This is calculation is simple because the equations are linear in the coordinates, and the upshot of the above discussion of time dependence is that the time derivative commutes with the expectation value.

To compute equations of motion for the variances, we need to differentiate the quadratic quantities

$$\begin{aligned} \frac{d}{dt}\langle x^2\rangle &= 2\langle x\dot{x}\rangle = \frac{2\langle xp\rangle}{m} \\ \frac{d}{dt}\langle p^2\rangle &= 2\langle p\dot{p}\rangle = -2m\omega^2\langle xp\rangle \\ \frac{d}{dt}\langle xp\rangle &= \langle \dot{x}p + x\dot{p}\rangle = \frac{\langle p^2\rangle}{m} - m\omega^2\langle x^2\rangle\,. \end{aligned} \tag{5.178}$$

For the position variance, we can then for example write

$$\frac{dV_x}{dt} = \frac{d}{dt}\langle x^2\rangle - \frac{d}{dt}\langle x\rangle^2 = \frac{2\langle xp\rangle}{m} - \frac{2\langle x\rangle\langle p\rangle}{m} = \frac{2C_{xp}}{m}, \tag{5.179}$$

where the classical covariance is

$$C_{xp} := \langle xp\rangle - \langle x\rangle\langle p\rangle\,. \tag{5.180}$$

We can carry out similar computations for the other variances, and to summarize the results,

$$\begin{aligned} \dot{V}_x &= \frac{2C_{xp}}{m} \\ \dot{V}_p &= -2m\omega^2 C_{xp} \\ \dot{C}_{xp} &= \frac{V_p}{m} - m\omega^2 V_x. \end{aligned} \tag{5.181}$$

The equations of motion (5.177) and (5.181) are *exactly the same as their quantum counterparts*, provided that C_{xp} is interpreted in terms of the proper (symmetrized) ordering (Problem 5.3).

From the classical equations of motion (5.175), we know that classical evolution is just a (scaled) rotation of the entire phase space, since the solutions have the form $x(t) = x_0\cos\omega t$ and $p(t) = -m\omega x_0\sin\omega t$. Thus, although we have not formally defined how to represent a quantum state in phase space (instead of either the position or momentum representation separately), we can intuitively think of time evolution as a rotation in phase space, at least for Gaussian states. We can go even further than this, though, because it turns out that (and it isn't too hard to believe that) *any* state, quantum or classical, can be represented as a linear combination of Gaussian states. (Classically, for example, this is just a Gaussian deconvolution of the Liouville density.) In this sense, the equations of motion are essentially equivalent between quantum and classical mechanics. This dynamical equivalence can be shown more formally and elegantly through the **Wigner function**, which is one possible phase-space representation of the quantum state. The equation of motion for the Wigner function involves another bracket, called the **Moyal bracket**; for the harmonic oscillator, and *only* for the harmonic oscillator, the Moyal bracket reduces to the classical Poisson bracket, which turns out to generate the motion of the Liouville density.[8]

[8] For more details, see Daniel A. Steck, *Quantum and Atom Optics*, available online at `http://steck.us/teaching` (2007).

5.6 Exercises

Problem 5.1

Consider the two-dimensional anisotropic harmonic oscillator

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{1}{2}m\left(\omega_x^2 x^2 + \omega_y^2 y^2\right). \tag{5.182}$$

Note that we have one more parameter here than we did for the one-dimensional case, so it won't be possible to scale all of them away. Derive a set of scaled units for this system where effectively $m = \hbar = \omega_x = 1$, and ω_y is replaced by a dimensionless parameter $\tilde{\omega}_y$ (give the scaled Hamiltonian as well as the units for every dimensionless physical quantity such as length, energy, etc.).

Problem 5.2

For the harmonic oscillator, compute $\langle x\rangle$, $\langle p\rangle$, V_x, V_p, the uncertainty product $\sigma_x\sigma_p = \sqrt{V_x V_p}$, the symmetrized covariance $C_{xp} := \langle [x,p]_+\rangle/2 - \langle x\rangle\langle p\rangle$, the mean kinetic energy $\langle T\rangle$, and the mean potential energy $\langle V\rangle$ in the $|n\rangle$ energy eigenstate. You can work in scaled units, but restore factors of m, ω, and $\hbar$ in your final answers. Note that among your results, you should find that the only minimum-uncertainty eigenstate is $|0\rangle$, and that $\langle T\rangle = \langle V\rangle = \langle H\rangle/2$.

Problem 5.3

For the harmonic oscillator in an arbitrary initial state, derive the (closed, coupled) equations of motion for the five expectation values $\langle x\rangle$, $\langle p\rangle$, V_x, V_p, and C_{xp}. If you work in scaled variables, make sure to restore scaling factors at the end of the derivation. You might make use of the relations $[f(x), p] = i\hbar f'(x)$ and $[x, g(p)] = i\hbar g'(p)$, and maybe also a commutator product rule.

Problem 5.4

In Problem 2.3, you showed that the solution to the free-particle problem, starting with a minimum-uncertainty Gaussian wave packet, has the time-dependent uncertainty

$$\sigma_x(t) = \sigma\sqrt{1 + \frac{\hbar^2 t^2}{4m^2\sigma^4}}. \tag{5.183}$$

Adapt the harmonic-oscillator moment equations (5.181), the equations of motion for for $\langle x\rangle$, $\langle p\rangle$, V_x, V_p, and C_{xp}, to this case and solve them to show that they reproduce this result.

Problem 5.5

Use the moment equations (5.181) to show that the generalized uncertainty function $V_x V_p - C_{xp}^2$ is a constant of the motion for the harmonic oscillator.

Problem 5.6

(a) Consider a harmonic oscillator of mass m and frequency ω. Derive an explicit solution for the symmetrized covariance $C_{xp}(t)$ in terms of initial conditions $V_x(0)$, $V_p(0)$, and $C_{xp}(0)$.

(b) Suppose that the oscillator is in a minimum-uncertainty state at $t = 0$, in the sense $V_x(0)V_p(0) = \hbar^2/4$, and suppose also that the oscillator is *not* in the ground state. What is the first time $t > 0$ when the oscillator is again in a minimum-uncertainty state? Give a (mathematical) argument to support your answer.

Problem 5.7

For an arbitrary initial state of the harmonic oscillator,

$$|\psi(0)\rangle = \sum_{n=0}^{\infty} c_n |n\rangle, \tag{5.184}$$

compute the time-dependent expectation values $\langle a(t)\rangle$ and $\langle a^\dagger(t)\rangle$. Work in the Schrödinger picture so the time-dependence comes from the state $|\psi(t)\rangle$. Show that the time dependences appear respectively as factors of $e^{-i\omega t}$ and $e^{i\omega t}$.

Problem 5.8

Show that $a^\dagger$ has no nontrivial eigenvectors (i.e., no eigenvectors other than the null vector), where $a^\dagger$ is the creation operator of the harmonic oscillator. *Hint*: try working out what an eigenvector would look like in the energy representation.

Problem 5.9

(a) By considering the action $a|n\rangle$ of the lowering-operator on an eigenstate of the harmonic oscillator in the position representation, derive the recursion relation

$$H_n'(x) = 2nH_{n-1}(x) \tag{5.185}$$

for the Hermite polynomials.

(b) Similarly consider $x|n\rangle$ to derive the recursion

$$H_{n+1}(x) = 2xH_n(x) - 2nH_{n-1}(x). \tag{5.186}$$

Problem 5.10

Take the limits:

(a)

$$L(x) = \lim_{a\to 0^+} \frac{1}{a} H_2(x/a)\, e^{-x^2/2a^2}. \tag{5.187}$$

(b)

$$M(x) = \lim_{a\to 0^+} \left[\frac{1}{a^3} H_2(x/a)\, e^{-x^2/2a^2} - \frac{2}{a^3}\, e^{-x^2/2a^2}\right]. \tag{5.188}$$

Problem 5.11

Consider the nth energy eigenstate $|n\rangle$ of the harmonic oscillator, and let Π denote the parity operator, which induces the operation $x \longrightarrow -x$.

(a) Show that Π anticommutes with the creation operator $a^\dagger$: $[\Pi, a^\dagger]_+ := \Pi a^\dagger + a^\dagger \Pi = 0$.

(b) Use your result from (a) along with the assumption that $|0\rangle$ has even $(+1)$ parity $(\Pi|0\rangle = |0\rangle)$ to show that the parity of $|n\rangle$ is $(-1)^n$.

Problem 5.12

(a) Show that

$$\int d^2\alpha\, |\alpha\rangle\langle\alpha| = \pi, \tag{5.189}$$

which is called the **overcompleteness** property of the coherent states. Here, the integration measure $d^2\alpha = dx\,dy$ (where $\alpha = x + iy$) indicates a two-dimensional integration over all (complex) values of α.

Hint: try working in the energy representation.

(b) Now consider the following operator, with a weighted sum over coherent-state projectors:

$$\int d^2\alpha\, |\alpha\rangle\langle\alpha|\, e^{-|\alpha|^2}. \tag{5.190}$$

Derive an expression for this operator in the energy representation (evaluating the integral).

Problem 5.13

Recall that a coherent state can be defined by $|\alpha\rangle = D(\alpha)|0\rangle$, where $|0\rangle$ is the harmonic-oscillator ground state, and in the case of purely imaginary α,

$$D(\alpha) = e^{i\sqrt{2}|\alpha|x}, \qquad (i\alpha \in \mathbb{R}). \tag{5.191}$$

Also remember that the coherent state has the expansion

$$|\alpha\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}\, |n\rangle \tag{5.192}$$

in the energy basis.

Use the above coherent-state expressions to derive an expression for the nth moment $\langle 0|x^n|0\rangle$ of the harmonic-oscillator ground state.[9] You should **not** be setting up any integrals in this problem; work entirely in Dirac notation.

Problem 5.14

Recall the exponential operator identity

$$e^{A+B} = e^A\, e^B\, e^{-[A,B]/2}, \qquad ([A,[A,B]] = [B,[A,B]] = 0), \tag{5.193}$$

which we can rewrite in the form

$$e^A\, e^B = e^B\, e^A\, e^{[A,B]}. \tag{5.194}$$

One useful application of this identity is to derive the commutator[10]

$$[x^m, p^\ell] = -\sum_{k=1}^{\min\{\ell,m\}} \binom{m}{k}\binom{\ell}{k} k!(-i\hbar)^k x^{m-k} p^{\ell-k}. \tag{5.195}$$

Prove this result by setting $A = \lambda p$ and $B = \mu x$, with $\lambda, \mu \in \mathbb{R}$. Then take appropriate derivatives with respect to λ and μ, setting both parameters to zero afterwards.

Problem 5.15

A classic and simple example of the saddle-point approximation is the derivation of Stirling's approximation for $n!$. To set this up, recall the integral representation for the gamma function,

$$\Gamma(x) = \int_0^\infty dt\, t^{x-1}\, e^{-t}, \tag{5.196}$$

[9] Incidentally, in an experiment this means that if you can displace an arbitrary state in momentum and measure the overlap with the undisplaced state, in principle you can infer all the moments and thus the position probability density. With similar measurements with displacements in other directions of phase space (i.e., other phases of α), you can reconstruct the entire quantum state.

[10] This commutator dates back to M. Born und P. Jordan, "Zur Quantenmechanik," *Zeitschrift für Physik 34*, 858 (1925) (doi: 10.1007/BF01328531), in particular the footnote on p. 873.

and since $n! = \Gamma(n+1)$, we have

$$n! = \int_0^\infty dt\, t^n\, e^{-t} = \int_0^\infty dt\, e^{-t+n\log t}. \tag{5.197}$$

(a) The idea is to approximate the integrand by a Gaussian factor, which is valid because the integrand becomes sharply peaked as n becomes large. To do this, write the integrand as $e^{f(t)}$, and expand $f(t)$ to second order in t about the maximum to write

$$n! \approx e^{-n+n\log n} \int_0^\infty dt\, e^{-(t-n)^2/2n}. \tag{5.198}$$

(b) To finish the integration, since the integrand is sharply peaked far away from $t = 0$, we can extend the lower integration limit so that

$$n! \approx e^{-n+n\log n} \int_{-\infty}^\infty dt\, e^{-(t-n)^2/2n}. \tag{5.199}$$

Now carry out the integral to find Stirling's approximation,

$$n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n. \tag{5.200}$$

Problem 5.16

Work out the asymptotic behavior of the function

$$I(x) := \int_0^\infty dt\, e^{xt-e^t} \tag{5.201}$$

in the limit of large x.

Chapter 6

Semiclassical Mechanics

6.1 Ehrenfest Equations

Recall that an operator A, in the Heisenberg picture where operators effect the time evolution, obeys the equation of motion [Eq. (1.195)]

$$\frac{dA}{dt} = -\frac{i}{\hbar}[A, H], \tag{6.1}$$

assuming a time-independent Hamiltonian and no explicit time dependence of the operator A (in the Schrödinger picture). Taking the expectation value of this equation leads to the equation of motion

$$\frac{d\langle A\rangle}{dt} = -\frac{i}{\hbar}\langle[A, H]\rangle \tag{6.2}$$
(expectation value equation of motion)

for the expectation value $\langle A\rangle$ (see also Problem 1.5).

Now let's specialize to the Hamiltonian for a particle in a potential:

$$H(\mathbf{p}, \mathbf{r}) = \frac{p^2}{2m} + V(\mathbf{r}). \tag{6.3}$$

Using Eq. (6.2), it is straightforward to compute equations of motion for the position and momentum centroids. Using the commutator $[\mathbf{r}, p^2] = 2i\hbar\mathbf{p}$, which is an instance of the more general commutator $[\mathbf{r}, f(\mathbf{p})] = i\hbar\nabla_{\mathbf{p}} f(\mathbf{p})$ for a scalar function f, gives the equation of motion

$$\frac{d}{dt}\langle\mathbf{r}\rangle = \frac{\langle\mathbf{p}\rangle}{m}. \tag{6.4}$$
(Ehrenfest equation for $\langle\mathbf{r}\rangle$)

Similarly, the commutator $[f(\mathbf{r}), \mathbf{p}] = i\hbar\nabla_{\mathbf{r}} f(\mathbf{r})$ leads to the equation

$$\frac{d}{dt}\langle\mathbf{p}\rangle = -\langle\nabla V(\mathbf{r})\rangle = \langle\mathbf{F}(\mathbf{r})\rangle\,, \tag{6.5}$$
(Ehrenfest equation for $\langle\mathbf{p}\rangle$)

where the force function $\mathbf{F}$ is given as in classical mechanics by $\mathbf{F}(\mathbf{r}) := -\nabla V(\mathbf{r})$. Together, Eqs. (6.4) and (6.5) are called the **Ehrenfest equations**.[1]

The basic lesson of the Ehrenfest equations is that quantum mechanically, the centroids obey equations of motion that are *almost* classical trajectory equations. Equation (6.4) is truly classical; however, in general,

$$\langle\mathbf{F}(\mathbf{r})\rangle \neq \mathbf{F}(\langle\mathbf{r}\rangle), \tag{6.6}$$

and thus the second Ehrenfest equation is not manifestly classical. What it instead says is that the momentum centroid responds to the classical force, but *averaged over the spatial extent of the quantum wave packet.*

[1] P. Ehrenfest, "Bemerkung über die angenäherte Gültigkeit der klassischen Mechanik innerhalb der Quantenmechanik," *Zeitschrift für Physik* **45**, 455 (1927) (doi: 10.1007/BF0132920).

6.1.1 Localized State

There are two situations where the Ehrenfest equations reduce to proper classical form. The first is for a localized wave packet. For example, in a position eigenstate, we would have

$$\langle \mathbf{F}(\mathbf{r}) \rangle = \mathbf{F}(\langle \mathbf{r} \rangle) \tag{6.7}$$

exactly, because the expectation value only ''sees'' the force function at one point. This is not a physically reasonable state, but if the spatial extent of the wave packet is small on the scales over which $V(\mathbf{r})$ varies, then the approximation

$$\langle \mathbf{F}(\mathbf{r}) \rangle \approx \mathbf{F}(\langle \mathbf{r} \rangle) \tag{6.8}$$

may hold to a high degree of accuracy.

This observation is often presented as proof that classical mechanics emerges as a limit of quantum mechanics for macroscopic systems, because for such systems the quantum uncertainties is small compared to relevant length an momentum scales of the evolution of the system. This argument indeed has a grain of truth to it, but it is not so simple, because there exist classical systems (*chaotic systems*) where a small spatial uncertainty (in an ensemble of initial conditions) becomes magnified exponentially with time. The problem then is that once the uncertainty has expanded sufficiently, the Ehrenfest equations become nonclassical. Then the predictions of quantum mechanics and classical mechanics will no longer agree.[2]

Said another way, the time scale for an initial, small position uncertainty to grow exponentially to an extent that causes the Ehrenfest equations to become nonclassical should scale *logarithmically* in the initial width. More precisely, this should be expressed in terms of the action scale S of the system: the time at which quantum and classical mechanics should diverge should scale as $\log(S/\hbar)$. (Often, this is written $\log(1/\hbar)$, which is a funny statement given that $\hbar$ is a constant; however it is understood to mean $\hbar$ normalized to the action of the system.) Now suppose that we have a manifestly quantum-mechanical system, where $S \sim \hbar$, which diverges from classical (chaotic) mechanics in some short time, say $1\,\mu$s. A version of the same system scaled up to the macroscopic world, on the other hand, should have a much larger action scale, something more like $S/\hbar \sim 10^{34}$ (think of some chaotic pendulum that you can hold in your hand). However, because of the logarithmic scaling, we would then expect a divergence time of about $30\,\mu$s. However, quantum effects in macroscopic objects on such time scales is not usually observed. This suggests that this explanation is incomplete—something else is required for quantum and classical mechanics to agree in such a scenario (indeed, something to keep the wave packet localized enough to make Ehrenfests's equation classical).[3]

6.1.2 Harmonic Oscillator

The second case in which the Ehrenfest equations reduce to classical form is for the harmonic oscillator (and it's other siblings in the quadratic-potential family, the free particle and the linear-potential problem). In this case $\mathbf{F}(\mathbf{r})$ is at most linear in $\mathbf{r}$, and so

$$\langle \mathbf{F}(\mathbf{r}) \rangle = \mathbf{F}(\langle \mathbf{r} \rangle) \tag{6.9}$$

follows from the linearity of $\mathbf{F}(\mathbf{r})$. This means that the centroid of the wave packet of a harmonic oscillator *always* follows a classical trajectory. We already saw this for coherent states and in the analysis of the moment equations for the harmonic oscillator, but this is true always, for any initial wave function, full stop. In this sense the harmonic oscillator is quite unique among quantum-mechanical systems; for any potential with beyond-quadratic components, we expect the evolution to be eventually nonclassical. More on this in a bit.

[2]For a good illustration of the spreading an nonclassical behavior in classically chaotic systems, see Fig. 2 in Salman Habib, Kosuke Shizume, and Wojciech Hubert Zurek, ''Decoherence, Chaos, and the Correspondence Principle,'' *Physical Review Letters* **80**, 4361 (1998) (doi: 10.1103/PhysRevLett.80.4361). That figure also illustrates a return to classical behavior at the level of a phase-space distribution when the quantum system is coupled to a high-temperature reservoir (the model for this is treated in Chapter 17).

[3]In fact, a *continuous* measurement of the particle's position does exactly this. See Tanmoy Bhattacharya, Salman Habib, and Kurt Jacobs, ''Continuous Quantum Measurement and the Emergence of Classical Chaos,'' *Physical Review Letters* **85**, 4852 (2000) (doi: 10.1103/PhysRevLett.85.4852).

6.1.3 Variance Analysis

Beyond just analyzing the centroids, we can obtain some more insight by examining the variances (second moments). The derivation is more or less the same as for the harmonic-oscillator results (5.181), so we will skip the derivation and just quote the generalized results (and only in one dimension, to avoid having to deal with a tensor covariance):

$$\begin{aligned}\dot{V}_x &= \frac{2C_{xp}}{m}\\ \dot{V}_p &= -\big\langle pV'(x) + V'(x)p\big\rangle + 2\langle p\rangle\langle V'(x)\rangle\\ \dot{C}_{xp} &= \frac{V_p}{m} - \big\langle xV'(x)\big\rangle + \langle x\rangle\langle V'(x)\rangle\,.\end{aligned} \tag{6.10}$$

Again, the harmonic oscillator is special because $\nabla V(\mathbf{r})$ is linear in $\mathbf{r}$. In every appearance of the potential in these equations, a linear $\nabla V(\mathbf{r})$ leads to the appearance of at most a second moment. That is, *it is only for the harmonic oscillator that the equations of motion for the means and variances are closed.* For any potential with beyond-quadratic components, the variances couple to third-and-higher moments.

Another somewhat odd feature is that the quantum-mechanical variance equations do not involve $\hbar$; the same is of course true of the Ehrenfest equations for the centroids. In which case it doesn't even *look* like we're doing quantum mechanics, because the main quantum parameter hasn't made an appearance. So where does $\hbar$ (and thus quantum behavior) come into the evolution?

The answer here is somewhat subtle, and we can only give a rough explanation (a proper justification involves a more phase-space-adapted development of quantum mechanics, which is beyond the scope of what we want to do here. But the main idea is that in the equation of motion for V_p, the first expectation value will involve products of the form $\langle xp^n\rangle$ and $\langle p^n x\rangle$ for $n > 1$. There are many possible orderings of these terms, and it turns out that only moments involving a specific, symmetric ordering (called **Weyl ordering**) is comparable to the classical moments. In the $n = 1$ case (i.e., the moments that appear for the harmonic oscillator), the products are already Weyl ordered, so we don't have to worry about this. However, these products are *not* properly ordered for $n > 1$. The reordering of these products generates extra ''quantum'' terms involving $\hbar$. Importantly, however, this only occurs at the third and higher moments, which is another way to see why the harmonic oscillator is apparently immune to quantum dynamical effects.[4]

6.1.4 Gaussian "Semiclassical" Approximation

An often-used approximation to quantum mechanics is start by pretend that the centroid of the quantum wave packet follows a classical trajectory, because this is easier to calculate than the full evolution of the quantum wave packet. This is justified by the Ehrenfest equations in the regime where we expect the wave packet to be reasonably localized (e.g., if the action scale of the system is relatively larger, or this could be used as an rough, uncontrolled approximation in the quantum regime). For example, this could be used for the evolution of an electron in a highly excited atom.

However, this is clearly a classical approach at this stage. In attempt to put a little quantum mechanics back into the method, one can keep some small uncertainty to the wave packet (i.e., ''keep the quantum fluctuations to lowest order). This involves defining the position-fluctuation operator (simplifying to one dimension to keep the notation compact)

$$\delta x := x - \langle x\rangle\,, \tag{6.11}$$

where x is the usual position operator. The idea is to then perform a expansion in this operator to second order, e.g.,

$$V'(x) \approx V'(\langle x\rangle) + \delta x\, V''(\langle x\rangle) + \frac{(\delta x)^2}{2}\, V'''(\langle x\rangle). \tag{6.12}$$

In computing moment equations, we would then discard any moments beyond second order overall [e.g., discarding $\big\langle p\,(\delta x)^2\big\rangle$]. Since this approach effectively assumes a small effect of quantum uncertainties, this is often used as one of a family of **semiclassical approximations** to quantum mechanics.

[4] For a more detailed analysis and everything you could possibly want to know about quantum and classical moments, see Salman Habib, ''Gaussian Dynamics is Classical Dynamics'' (arXiv: quant-ph/0406011).

Doing this, the Ehrenfest equations (6.4) and (6.5) become

$$\begin{aligned}\frac{d}{dt}\langle x\rangle &= \frac{\langle p\rangle}{m}\\ \frac{d}{dt}\langle p\rangle &= -V'(\langle x\rangle) - \frac{V_x}{2}V'''(\langle x\rangle),\end{aligned} \tag{6.13}$$

where we used $\langle \delta x^2\rangle = V_x$. Note that the momentum centroid now responds to an **effective potential** at the centroid,

$$V_{\text{eff}}(\langle x\rangle) := V(\langle x\rangle) + \frac{V_x}{2}V''(\langle x\rangle), \tag{6.14}$$

due to the averaging over the wave packet. The variance equations (6.10) similarly become

$$\begin{aligned}\dot{V}_x &= \frac{2C_{xp}}{m}\\ \dot{V}_p &= -2V''(\langle x\rangle)C_{xp}\\ \dot{C}_{xp} &= \frac{V_p}{m} - V''(\langle x\rangle)V_x.\end{aligned} \tag{6.15}$$

Note that these have the form of the harmonic-oscillator equations (5.181), where now $V''(\langle x\rangle)$ takes the place of the harmonic-oscillator parameter combination $m\omega^2$.

We can now make some straightforward but important observations here. The mean and variance equations again close, and have the form of the harmonic oscillator (though there could be some effective time variation of oscillator parameter ω^2). Thus, this lowest-order expansion in the fluctuations amounts to an approximation where the wave packet is always assumed to be Gaussian. Hence this approximation is also called a **Gaussian approximation**. Again, $\hbar$ never appears in these equations and can't enter via high-order moments, so the evolution here is manifestly *classical*—the evolution is the same as if a *classical* ensemble, constrained to be Gaussian, evolves according to classical dynamics.[5]

6.2 Standard Quantum Limit

Now we can turn to a slightly different question, but still based on quantum uncertainty: When does a macroscopic object (or any object, for that matter) behave quantum mechanically? We will look at this specifically in terms of a quantum measurement—when is the measurement sensitive to quantum uncertainty?

As a model for this, suppose we make a measurement of the position of an object, and that the duration of the measurement is τ (physically, a measurement would involve some sensing apparatus, such as a laser interferometer in a gravitational-wave detector, and so the measurement must be integrated over some averaging time). As a crude model for this measurement,[6] consider two instantaneous measurements, with results x_1 and x_2, of position occurring respectively at $t = 0$ and $t = \tau$. Suppose that we call the respective uncertainties in the measurements Δx_1 and Δx_2. Now the measurement at $t = 0$ causes a disturbance to the system, because it causes the position of the object to become localized. This in turn disturbs the momentum, causing a *minimum* increase in the momentum uncertainty of

$$\Delta p = \frac{\hbar}{2\Delta x_1}, \tag{6.16}$$

to be consistent with the uncertainty principle. As this is a crude argument, we will use this as an estimate of the actual momentum uncertainty after the measurement. After time τ, assuming free-particle evolution,

[5] Salman Habib, *op. cit.*

[6] Vladimir B. Braginsky and Farid Ya. Khalili, *Quantum Measurement*, Kip S. Thorne, Ed. (Cambridge, 1992) (ISBN: 052141928X); Carlton M. Caves, Kip S. Thorne, Ronald W. P. Drever t Vernon D. Sandberg, and Mark Zimmermann, "On the measurement of a weak classical force coupled to a quantum-mechanical oscillator. I. Issues of principle," *Reviews of Modern Physics* **52**, 341 (1980) (doi: 10.1103/RevModPhys.52.341).

this momentum uncertainty will lead to an additional uncertainty

$$\Delta x_{\text{B}} = \frac{\tau}{m}\Delta p = \frac{\hbar\tau}{2m\Delta x_1}. \tag{6.17}$$

This uncertainty represents the **quantum backaction**, or disturbance, due to the first measurement. Now if the final measurement result is taken to be the average

$$x = \frac{x_1 + x_2}{2}, \tag{6.18}$$

the resulting uncertainty is

$$\Delta x = \frac{1}{2}\sqrt{\Delta x_1^2 + \Delta x_2^2 + \Delta x_{\text{B}}^2}, \tag{6.19}$$

where we add the component errors in quadrature under the assumption that they are independent, and scale the result by $1/2$ because of the same factor in the average x. If we assume the same apparatus performed both measurements, we can set $\Delta x_2 = \Delta x_1$, so that

$$\Delta x = \frac{1}{2}\sqrt{2\Delta x_1^2 + \left(\frac{\hbar\tau}{2m\Delta x_1}\right)^2}. \tag{6.20}$$

Now let's find the minimum achievable uncertainty Δx—Δx_1 obviously can't be huge, but it also can't be too small, otherwise the backaction component of the error becomes large. We are essentially minimizing the function $2x^2 + A/x^2$, which occurs at $x^2 = \sqrt{A/2}$, where $2x^2 = A/x^2 = \sqrt{2A}$, so the contributions from the backaction is equal to the contribution from the measurements. Thus, the minimum error is

$$\Delta x = \sqrt{\frac{\hbar\tau}{2\sqrt{2}m}}. \tag{6.21}$$

Different assumptions lead to different factors of two; for example, if we discard the contribution from Δx_2 (making the second measurement arbitrarily accurately, if we don't care about the backaction after $t = \tau$), and simply summing the errors in quadrature without the factor of $1/2$ leads to $\Delta x = \sqrt{\hbar\tau/m}$. These factors don't matter much in a crude estimate, so let's call the result

$$\Delta x = \sqrt{\frac{\hbar\tau}{m}}. \tag{6.22}$$
(standard quantum limit)

This result is called the **standard quantum limit** for a position measurement over time τ. To put in some numbers for context, around 2009 the LIGO gravitational wave detector used test masses (mirrors) with[7] $m \sim 11\,\text{kg}$ and a measurement time $\tau \sim 1\,\text{ms}$ (corresponding to the time light takes to traverse one arm of the interferometer, including multiple passes in an optical resonator). With these parameters, $\Delta x \sim 3\times10^{-14}\,\text{m}$. More recently, in 2023,[8] LIGO surpassed the standard quantum limit (with a mass $m \sim 40\,\text{kg}$).

In an optical-interferometer based gravitational-wave sensor like LIGO, an alternate interpretation that leads to the same standard quantum limit focuses more on the light.[9] The optimum sensitivity of the optical measurement balances the effect of radiation pressure (where intrinsic fluctuations in the number of photons leads to a stochastic force on the test mass) and shot noise (detection noise due to fluctuations in the number of photons arriving at the detector). Balancing these two effects optimally leads to essentially the same standard quantum limit. However, it also suggests a way to circumvent the standard quantum limit: by using special states of light (**squeezed states**, which are Gaussian states of the harmonic oscillator

[7] B. P. Abbott *et al.*, "LIGO: the Laser Interferometer Gravitational-Wave Observatory," *Reports on Progress in Physics* **72**, 076901 (2009), Table 1 (doi: 10.1088/0034-4885/72/7/076901).

[8] D. Ganapathy *et al.*, "Broadband Quantum Enhancement of the LIGO Detectors with Frequency-Dependent Squeezing," Physical Review X **13**, 041021 (2023) (doi: 10.1103/PhysRevX.13.041021).

[9] For a good overview, see M. T. Jaekel and S. Reynaud "Quantum Limits in Interferometric Measurements," *Europhysics Letters* **13**, 301 (1990) (doi: 10.1209/0295-5075/13/4/003).

with time-dependent variances differing from those of the coherent states), the different error contributions end up being correlated (remember, we assumed *uncorrelated* errors), and thus the quantum measurement limit can be effectively reduced.

The standard quantum limit can be translated into other measurements as well. For example, a force acting over time τ causes a displacement $\Delta x \sim (F/m)\tau^2/2$; using Eq. (6.22) leads to a standard quantum limit

$$\Delta F = \sqrt{\frac{\hbar m}{\tau^3}}, \tag{6.23}$$

after dropping an overall factor of 2. The same two position measurements can also be used to infer a momentum via

$$p = \frac{m(x_2 - x_1)}{\tau}. \tag{6.24}$$

This again leads to a momentum uncertainty

$$\Delta p = \sqrt{\frac{m\hbar}{\tau}}, \tag{6.25}$$

up to factors of 2.

6.3 WKB Approximation

The last semiclassical method we will consider here is the **WKB approximation** (where "WKB" stands for "Wentzel, Kramers, Brillouin, and sometimes Jeffreys and maybe others"[10]), which is a useful method in generating approximate eigenfunctions and eigenenergies in general, one-dimensional potentials.[11] Because there are some nice connections to classical mechanics along the way, we will spend some time setting up and justifying the approximation before getting on with some calculations.

6.3.1 Semiclassical Approximation

We will start as usual with the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right)\psi. \tag{6.26}$$

Although the idea will be to construct approximate eigenstates, for the moment we will include time dependence to motivate the approximations. We will now transform the Schrödinger equation by using a polar decomposition of the wave function,

$$\psi(\mathbf{r}, t) = R\, e^{iS/\hbar}, \tag{6.27}$$

in terms of real scalar fields $R(\mathbf{r}, t)$ and $S(\mathbf{r}, t)$. To proceed, we will need the derivatives (in one dimension for compactness of notation)

$$\begin{aligned}
\dot\psi &= \left(\dot R + \frac{iR\dot S}{\hbar}\right) e^{iS/\hbar} \\
\psi' &= \left(R' + \frac{iRS'}{\hbar}\right) e^{iS/\hbar} \\
\psi'' &= \left(R'' - \frac{R(S')^2}{\hbar^2} + \frac{iRS''}{\hbar} + \frac{i2RS'}{\hbar}\right) e^{iS/\hbar}.
\end{aligned} \tag{6.28}$$

[10] For an overview of "history and semantics," see R. B. Dingle, *Asymptotic Expansions: Their Derivation and Interpretation* (Academic Press, 1973), pp. 316-9 (available at `https://michaelberryphysics.wordpress.com/rb-dingles-book-on-asymptotics/`).

[11] For a discussion of the generalization to multiple dimensions (with some mention of methods for classically nonintegrable systems), with a nice historical overview of "old quantum theory," see Joseph B. Keller, "Semiclassical Mechanics," *SIAM Review* **27**, 485 (1985) (JSTOR: 2031056).

Then we can put this form of ψ into the Schrödinger equation, drop the overall common factor of $e^{iS/\hbar}$, and separate the result into real and imaginary parts. The imaginary part leads to the relation

$$\dot{R} = -\frac{2R'S' + RS''}{2m} \tag{6.29}$$

which we can write in three dimensions as

$$\frac{\partial R}{\partial t} = -\frac{2\nabla R \cdot \nabla S + R\nabla^2 S}{2m}.$$

(first Schrödinger-equivalent equation) (6.30)

The real part of the Schrödinger equation leads to

$$\dot{S} + \frac{(S')^2}{2m} + V - \frac{\hbar^2}{2m}\frac{R''}{R} = 0. \tag{6.31}$$

The last term is a function of position and time via the wave function, and has the form of an effective time-dependent potential. It is also the only place in which $\hbar$ appears. Thus, we will define an effective ''quantum potential'' via,

$$V_{\mathrm{Q}}(\mathbf{r}) := -\frac{\hbar^2}{2m}\frac{\nabla^2 R}{R}, \tag{6.32}$$

and write Eq. (6.31) in three-dimensional form as

$$\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} + V(\mathbf{r}) + V_{\mathrm{Q}}(\mathbf{r}) = 0.$$

(second Schrödinger-equivalent equation) (6.33)

This equation has a particularly significant form. If we set $V_{\mathrm{Q}} = 0$, we obtain

$$\frac{\partial S}{\partial t} + \frac{(\nabla S)^2}{2m} + V(\mathbf{r}) = 0, \tag{6.34}$$

which is the **Hamilton–Jacobi equation** of classical mechanics for a particle in a potential $V(\mathbf{r})$. The Hamilton–Jacobi equation is derived in Section 0.4.5; see Eq. (0.90) in particular. To briefly recap, the significance of the Hamilton–Jacobi equation is that it determines a generating function $S(\mathbf{r}, t)$, which induces a canonical transformation to coordinates (''action–angle variables'') in which the dynamical evolution is trivial. Thus finding a solution to the Hamilton–Jacobi equation is essentially equivalent to finding an analytic solution to the corresponding Hamiltonian classical system. However, the Hamilton–Jacobi equation is not solvable in general (owing to the nonlinearity in ∇S), which means that classical Hamiltonian systems are not in general solvable (owing to the existence of classical chaos).

So while we started with the Schrödinger equation, which is very different from Newton's equations, we began to see some closer similarity to classical mechanics in terms of moments and the Ehrenfest equations. Now we can see another, very different connection to classical mechanics, with the difference encapsulated in the quantum potential V_{Q}. In fact, the WKB approximation will amount to ignoring V_{Q}, justifying the ''semiclassical'' nature of the approximation.

6.3.2 Hydrodynamic Interpretation

Through some additional transformations, we can see yet another connection between classical and quantum mechanics, where the Schrödinger equation will reduce to the classical equations for an incompressible fluid, plus a quantum correction.[12] First we can define a density via

$$\rho := R^2, \tag{6.35}$$

[12] See, e.g., A. Askar and J. H. Weiner, ''Wave Packet Dynamics on Two-Dimensional Quadratic Potential Surfaces,'' *American Journal of Physics* **39**, 1230 (1971) (doi: 10.1119/1.1976611). This formulation dates back to E. Madelung, ''Quantentheorie in hydrodynamischer Form,'' *Zeitschrift für Physik* **40**, 322 (1926) (doi: 10.1007/BF01400372); and Louis de Broglie ''La mécanique ondulatoire et la structure atomique de la matière et du rayonnement,'' *Journal de Physique et Le Radium* **8** 225 (1927) (doi: 10.1051/jphysrad:0192700805022500).

which corresponds to the usual probability density $|\psi|^2$. Then we can define a velocity field by the phase gradient

$$\mathbf{v} := \frac{\nabla S}{m}. \tag{6.36}$$

Now multiplying Eq. (6.30) by $2R$, we obtain

$$2R\frac{\partial R}{\partial t} + \frac{R^2\nabla^2 S}{m} + \frac{2R\nabla R\cdot\nabla S}{m} = 0. \tag{6.37}$$

Then we can identify $\partial_t\rho = \partial_t R^2 = 2R\partial_t R$ for the first term, $\rho\nabla\cdot\mathbf{v}$ for the second term, and $\mathbf{v}\cdot\nabla\rho$ for the third term, we obtain

$$\frac{\partial\rho}{\partial t} + \rho\nabla\cdot\mathbf{v} + \mathbf{v}\cdot\nabla\rho = 0. \tag{6.38}$$

Combining the two spatial-derivative term gives

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{v}) = 0. \tag{6.39}$$
(continuity equation)

This is just the continuity equation, where $\rho\mathbf{v}$ is a flux current (i.e., the probability current density).

Now computing the gradient of Eq. (6.33) gives

$$\frac{\partial\nabla S}{\partial t} + \frac{\nabla(\nabla S)^2}{2m} = -\nabla\Big[V(\mathbf{r}) + V_{\rm Q}(\mathbf{r})\Big]. \tag{6.40}$$

In the firs term, $\nabla S = m\mathbf{v}$; while in the second term, $\nabla(\nabla S)^2/2m = (\nabla S)\cdot\nabla(\nabla S)/m = m\mathbf{v}\cdot\nabla\mathbf{v}$. Thus, we have

$$m\frac{\partial\mathbf{v}}{\partial t} + m\mathbf{v}\cdot\nabla\mathbf{v} = -\nabla\Big[V(\mathbf{r}) + V_{\rm Q}(\mathbf{r})\Big]. \tag{6.41}$$

The first two terms combine into a total time derivative, with the result

$$m\frac{d\mathbf{v}}{dt} = -\nabla\Big[V(\mathbf{r}) + V_{\rm Q}(\mathbf{r})\Big]. \tag{6.42}$$
("Newton" equation)

This is Newton's equation for a particle subject to a force from the potential V, plus an effective quantum force due to $V_{\rm Q}$.

The equations (6.39) and (6.42) together give a formulation in terms of an ensemble of particles, distributed according to the density ρ. The particles evolve according to Eq. (6.42), and are coupled via the quantum potential, which we can write as

$$V_{\rm Q}(\mathbf{r}) := -\frac{\hbar^2}{2m}\frac{\nabla^2\sqrt{\rho}}{\sqrt{\rho}}. \tag{6.43}$$

This formulation of the Schrödinger equation is also the basis for the de Broglie–Bohm formation of quantum mechanics.[13]

6.3.3 Approximation for Propagating Waves

Now to proceed with the WKB approximation proper, we want to specialize to energy eigenstates in one dimension. To this end we can make the replacements

$$S(x,t) \longrightarrow S(x) - Et, \qquad R(x,t) \longrightarrow R(x). \tag{6.44}$$

The effect on the form of the wave function is that the time dependence appears as a phase factor,

$$\psi = R\,e^{iS/\hbar} \longrightarrow \psi = R\,e^{iS/\hbar}e^{-iEt/\hbar}, \tag{6.45}$$

[13] See, e.g., Peter Holland, *The Quantum Theory of Motion: An Account of the de Broglie-Bohm Causal Interpretation of Quantum Mechanics* (Cambridge, 1995) (ISBN: 0521485436).

as appropriate for an energy eigenstate. In the usual way, we can drop this phase factor, and the Schrödinger equation (6.26) becomes

$$-\frac{\hbar^2}{2m}\psi'' + \big[V(\mathbf{r}) - E\big]\psi = 0. \tag{6.46}$$

Under the same replacements, Eq. (6.30) becomes

$$2R'S' + RS'' = 0, \tag{6.47}$$

and we can then write this more simply as

$$(R^2 S')' = 0. \tag{6.48}$$

This means that $R^2 S'$ is constant; more conveniently, we can write

$$R = \frac{\eta}{\sqrt{S'}}, \tag{6.49}$$

where η is a normalization constant.

Similarly, Eq. (6.33) becomes

$$\frac{(S')^2}{2m} + V - E = \frac{\hbar^2}{2m}\frac{R''}{R}, \tag{6.50}$$

where we have written out the quantum potential explicitly. The WKB approximation is to neglect this quantum term compared to the others. To justify this approximation, consider a plane wave,

$$\psi \sim e^{ipx/\hbar}. \tag{6.51}$$

This solution corresponds to $S(x) = px$ and a constant $R(x)$, such that $R'' = 0$—the quantum potential vanishes identically for a plane wave. Since $S' = p$, Eq. (6.50) amounts to the expression $p = \pm\sqrt{2m(E-V)}$ for the (constant) momentum. The WKB approximation is thus justified when the wave function is "almost" a plane wave. That is, $V(x)$ should vary slowly on the scale of the wiggles of $e^{iS/\hbar}$, which either implies a slowly varying potential or a large momentum (and thus fast wiggles). In either case, ψ should look *locally* like a plane wave, but possible with a slowly varying wavelength and amplitude.

Now forging ahead with the WKB approximation, we will replace Eq. (6.50) by

$$\frac{(S')^2}{2m} + V - E = 0. \tag{6.52}$$

Solving for S', we can define this as the local momentum (no longer constant, in general):

$$S' = \pm\sqrt{2m(E-V)} =: \pm p(x). \tag{6.53}$$

Then we can integrate to find the action (phase function),

$$S(x) = \pm\int^x p(x')\,dx', \tag{6.54}$$

which is the classical reduced action from Eq. (0.31). With Eqs. (6.45) and (6.49), the wave function in the WKB approximation reads

$$\psi(x) \approx \frac{\eta}{\sqrt{p(x)}}\exp\left[\pm\frac{i}{\hbar}\int^x p(x')\,dx'\right] \quad \text{(WKB wave function, } E > V(x)\text{)} \tag{6.55}$$

for the propagating-wave case of $E > V(x)$. (Note that we have omitted the lower integration limit, preferring to defer this to the setup of more specific problems.) There are two possibilities here, of a wave going to the right or to the left. The general solution is of course a superposition of these two cases. Note, however, that the two possibilities correspond to *pure* motion in either direction—the two cases are not coupled, at least in the region where $E > V(x)$. Thus, the WKB approximation involves ignoring quantum reflection from the smoothly varying potential. Reflections are, evidently, one of the functions of the quantum potential that we have discarded.

6.3.4 Classically Forbidden Region and Tunneling

If the wave function is in the classically forbidden region, $E < V(x)$, the solution (6.55) still applies, but the momentum function (6.53) is modified to

$$p(x) = i\sqrt{2m|V(x) - E|} \tag{6.56}$$

because of the sign change, and then Eq. (6.55) is modified to read

$$\psi(x) \approx \frac{\eta}{\sqrt{|p(x)|}} \exp\left[\pm\frac{1}{\hbar}\int |p(x)|\, dx\right], \quad \text{(WKB wave function, } E < V(x)\text{)} \tag{6.57}$$

corresponding to damped, rather than propagating, solutions, as expected based on our past work with potential wells.

This solution is useful for approximating the tails of eigenstates in potential wells, but is also useful in estimating barrier tunneling. If we have a particle incident on a barrier of arbitrary shape but slow spatial variation (generally implying a wide barrier), we can estimate the transmitting amplitude by

$$|\tau| := \left|\frac{\psi_{\text{out}}}{\psi_{\text{in}}}\right| \sim \exp\left[-\frac{1}{\hbar}\int_{x_1}^{x_2} |p(x)|\, dx\right], \tag{6.58}$$

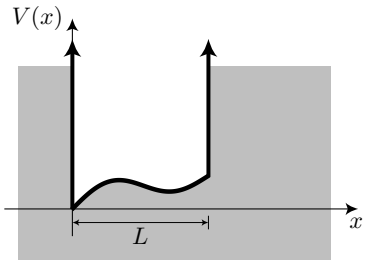
where x_1 and x_2 are the two points where $E = V(x)$, and the prefactors of the exponential have cancelled, being equal at the entry and exit points. We are only keeping the exponentially decaying solution, and not the growing solution, in order to obtain a sensible result. The transmission probability is then

$$T = |\tau|^2 \sim \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2} |p(x)|\, dx\right]. \tag{6.59}$$

This is exactly the result we obtained before in the semiclassical analysis of tunneling of Section 2.6.3. There, we took the barrier of arbitrary shape, approximated it by a stack of square barriers, and applied the tunneling probabilities for the individual square barriers, ignoring multiple reflections among the layers. Discarding those multiple reflections is equivalent to the WKB approximation, which also neglects quantum reflections. (However, see Problem 6.6 for a better estimate of the transmission probability.)

6.3.5 Bound States with Hard Walls

Now let's look in more detail at how to apply the WKB approximation to finding eigenstates. The simplest case is a potential well that has hard walls, but some arbitrary (slowly varying) profile in between, as shown below.



The analysis of this problem is much like the infinite square well of Section 2.3. In general the solution will be a superposition of the two possibilities represented by Eq. (6.55). However, because there should be an equal superposition between left- and right-going waves, it is more convenient to change from exponential to sinusoidal functions:

$$\psi(x) \approx \frac{A}{\sqrt{p(x)}} \sin\left[\frac{1}{\hbar}\int_0^x p(x')\, dx'\right] + \frac{B}{\sqrt{p(x)}} \cos\left[\frac{1}{\hbar}\int_0^x p(x')\, dx'\right]. \tag{6.60}$$

Requiring $\psi(0) = 0$ implies $B = 0$; requiring $\psi(L) = 0$ implies

$$\sin\left[\frac{1}{\hbar}\int_0^L p(x)\,dx\right] = 0, \tag{6.61}$$

which has solutions

$$\int_0^L p(x)\,dx = n\pi\hbar \qquad (n \in \mathbb{Z}^+). \tag{6.62}$$

At this point, any such problem can be solved by using Eq. (6.53) to write $p(x)$ in terms of $V(x)$, and then we have an integral equation that determines the allowed values of E.

There is a nice interpretation of Eq. (6.62), if you recognize that $p(x)$ represents the classical trajectory in phase space, say as the particle moves to the right from 0 to L. In this case, the integral is the area under this curve. On the way back from $x = L$ to $x = 0$, $p(x)$ has the same shape, but with a negative sign, and so the *total* area A enclosed by the classical path is twice the value of the integral. That is,

$$A = n(2\pi\hbar) = nh, \tag{6.63}$$

so that the area enclosed by the classical path must be an integer multiple of the Planck constant h. More generically, this condition may be written

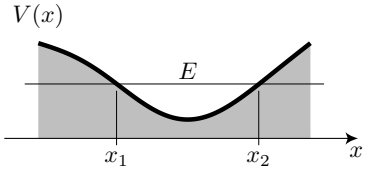
$$\oint p(x)\,dx = nh, \tag{6.64}$$

(Bohr–Sommerfeld quantization condition)

where the path is taken to be a classical phase-space trajectory at constant energy. This condition is called the **Bohr–Sommerfeld quantization condition**, and reflects how quantum mechanics was more closely adapted to classical mechanics in the early days of quantum theory.

6.3.6 Patching Solutions

The hard-wall potential well above is straightforward, because the vanishing of the wave function at the walls implies a simple, inverted reflection of the traveling-wave components of the wave function—just like the standard infinite-square-well problem. But what happens if we have a ‘‘soft’’ potential well, as illustrated below?



The points x_1 and x_2, satisfying $V(x_{1,2}) = E$, are the classical turning points, where a classical particle would reverse direction. The problem here is that $p(x_{1,2}) = 0$, and thus the WKB wave function (6.55) blows up at the turning points. So although we can apply the WKB approximation inside the potential well and in the two classically forbidden regions, there are gaps in the wave function at $x_{1,2}$ where the WKB wave function doesn't make sense.

To handle this, the idea is to ‘‘patch’’ the WKB wave functions together via an extension of what we have done so far. Suppose that in the vicinity of a turning point x_0 we use a linear approximation to the potential:

$$\begin{aligned} V(x) &\approx V(x_0) + V'(x_0)(x - x_0) \\ &= E + V'(x_0)(x - x_0). \end{aligned} \tag{6.65}$$

Then the time-independent Schrödinger equation (6.46) becomes

$$-\frac{\hbar^2}{2m}\psi'' + V'(x_0)(x - x_0)\psi = 0. \tag{6.66}$$

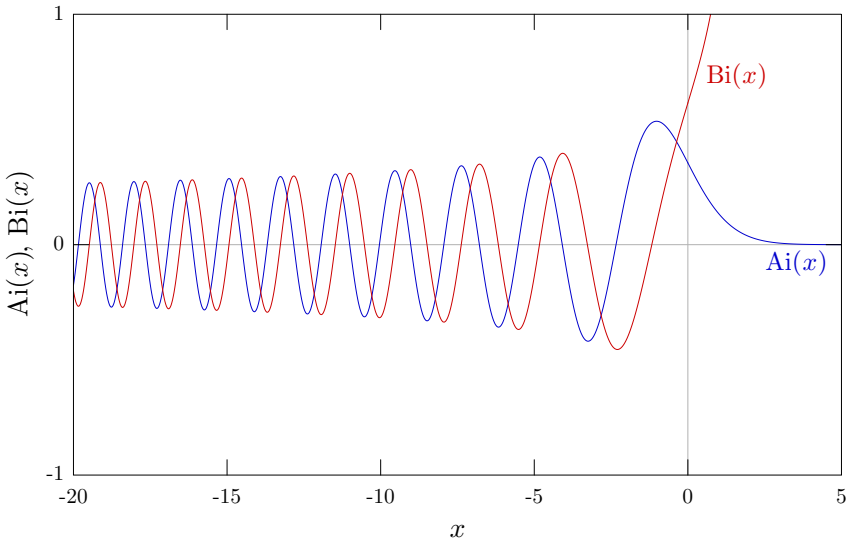
The second term here, in terms of units, scales as x, while the first term effectively has dimensions x^{-2} (ignoring dimensions of ψ itself, since we won't bother to scale it). Thus, we will define the scaled coordinate

$$z := \sqrt[3]{\frac{2mV'(x_2)}{\hbar^2}}\,(x - x_2), \tag{6.67}$$

where we will have to specialize now to the right-hand turning point to fix the sign of $V'(x_2) > 0$ (we will deal with the solution at x_1 separately). In terms of z, Eq. (6.66) becomes

$$\psi''(z) = z\psi, \tag{6.68}$$

which has the form of Airy's differential equation. The solutions are the **Airy functions Ai**(z) and **Bi**(z). These functions are plotted below. Recalling that the turning point is at $z = 0$, for $z > 0$ **Ai**(z) acts like an exponentially damped wave, and **Bi**(z) acts like an exponentially diverging wave; for $z < 0$ the two functions are oscillating with a relative phase of $\pi/2$.



6.3.6.1 Aymptotics of the Airy Functions

For the purposes of calculation, we will need the asymptotic behavior of the Airy functions. For large $z > 0$,

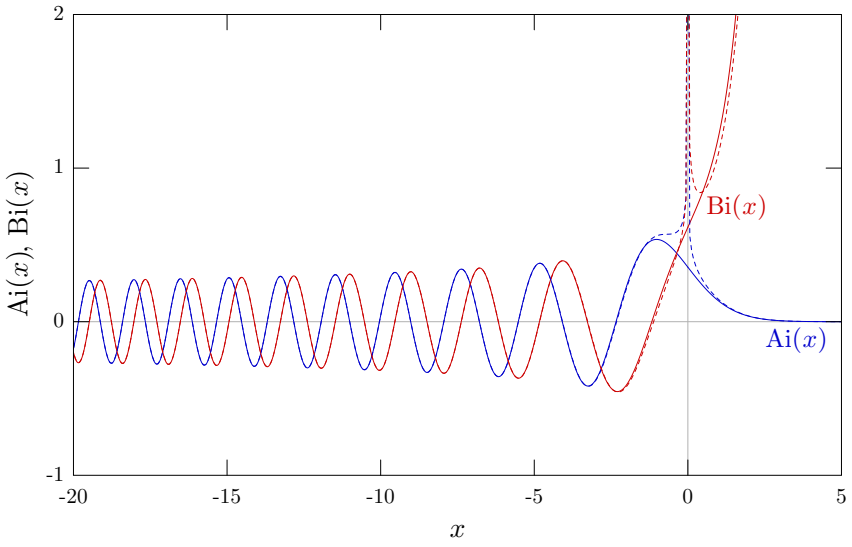
$$\begin{aligned} \mathrm{Ai}(z) &\approx \frac{1}{\sqrt{4\pi}}\, z^{-1/4}\, e^{-(2/3)z^{3/2}} \\ \mathrm{Bi}(z) &\approx \frac{1}{\sqrt{\pi}}\, z^{-1/4}\, e^{(2/3)z^{3/2}} \end{aligned} \qquad \begin{matrix} (6.69) \\ (\text{Airy asymptotics, } z \longrightarrow +\infty) \end{matrix}$$

while for large $z < 0$,

$$\begin{aligned} \mathrm{Ai}(z) &\approx \frac{1}{\sqrt{\pi}}\, |z|^{-1/4} \cos\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right) \\ \mathrm{Bi}(z) &\approx -\frac{1}{\sqrt{\pi}}\, |z|^{-1/4} \sin\left(\frac{2}{3}|z|^{3/2} - \frac{\pi}{4}\right) \end{aligned} \qquad \begin{matrix} (6.70) \\ (\text{Airy asymptotics, } z \longrightarrow -\infty) \end{matrix}$$

Note that these expressions are basically WKB approximations to the Airy functions. To see this, note that $p(x) \sim \sqrt{|V(x)|}$, which corresponds to $\sqrt{|z|}$ in this case; the prefactor in the WKB wave function (6.55) goes as $|p|^{-1/2}$, or as $|z|^{-1/4}$, which is the prefactor that we see in these expressions. We will see this connection to the WKB more explicitly in just a bit when we derive the form of these expressions.

The plot below shows the asymptotic expressions compared to the original functions. They are already good approximations for $|z| \gtrsim 2$.



6.3.6.2 Derivation

Before proceeding with the patching method, we will take a moment to derive the forms of the asymptotic expressions,[14] as an illustration of an alternative approach to the WKB approximation.

First, we will start by changing variables according to

$$\psi = e^{S(z)}. \tag{6.71}$$

There is no amplitude function as in the previous development of the WKB approximation, so clearly S must be a complex function, with the real part giving the amplitude and the imaginary part giving the phase of ψ. Then we will need the derivatives

$$\psi' = S'e^S, \qquad \psi'' = S''e^S + (S')^2 e^S \approx (S')^2 e^S. \tag{6.72}$$

In the second derivative we have already ignored S'' compared to $(S')^2$, in the spirit of the previous WKB approximation. Then the Airy equation

$$\psi''(z) = z\psi \tag{6.73}$$

becomes

$$(S')^2 e^S = z e^S, \tag{6.74}$$

which simplifies to

$$S' = \pm\sqrt{z}, \tag{6.75}$$

which integrates to

$$S(z) = S(0) \pm \frac{2}{3} z^{3/2}. \tag{6.76}$$

For now we will assume $z > 0$ and take care of $z < 0$ later. To obtain a better estimate, suppose we tack on a small correction $C(z)$ to the solution (6.76):

$$S(z) = S(0) \pm \frac{2}{3} z^{3/2} + C(z). \tag{6.77}$$

Then we have the derivatives

$$S' = \pm\sqrt{z} + C', \qquad S'' = \pm\frac{1}{2\sqrt{z}} + C'', \tag{6.78}$$

[14] There is a technical difficulty in calling these "asymptotic approximations," due to the zeros not coinciding between the exact and approximate expressions; for details see Carl M. Bender and Steven A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers*, (McGraw–Hill, 1978) (ISBN: 007004452X), Section 3.7, pp. 107–12.

and putting these into the derivatives (6.72) and then into the Airy equation (now keeping S'') gives

$$\left(\pm\frac{1}{2\sqrt{z}} + C''\right) e^S + \left(\pm\sqrt{z} + C'\right)^2 e^S = z e^S, \tag{6.79}$$

which simplifies to

$$C'' + (C')^2 \pm 2\sqrt{z}C' = \mp\frac{1}{2\sqrt{z}}. \tag{6.80}$$

Since z is large and C is a small correction, we will ignore the C'' and $(C')^2$ terms, so that the result simplifies to

$$C' = -\frac{1}{4z}. \tag{6.81}$$

Integrating this equation gives

$$C(z) = -\frac{1}{4}\log z, \tag{6.82}$$

where any constant of integration can be absorbed into $S(0)$. Putting this solution into Eq. (6.77) for $S(z)$, and putting that result into $\psi = e^S$ gives the desired asymptotic form

$$\psi(z) = c\, z^{-1/4}\, e^{\pm(2/3)z^{3/2}}, \tag{6.83}$$

where $c = e^{S(0)}$, which could in general be different for the two solutions. This remaining constant must be established by normalization (of the *exact* wave function), but the functional form is sufficient for our application to the WKB approximation.

In the treatment above, we assumed $z > 0$, but we should handle the case $z < 0$ carefully to avoid problems with the branch cut of the logarithm along the negative z-axis. For this case the above derivation goes through with a couple of modifications. First of all, where $\sqrt{z}$ appears, starting in Eq. (6.75), this quantity will change to $i\sqrt{-z}$. Since we will want to write the results in terms of $-z$, this will also effectively change the signs of S' and C'. In Eq. (6.75) the sign change doesn't matter, because we are tracking both signs anyway. The result (6.83) is the same, but we have the logarithm of a negative number; using $\log z = \log(-z) \pm i\pi$ for $z < 0$ [where the sign corresponds to the sign of the square root in Eq. (6.75), which fixes the branch of the square root and thus of the logarithm] changes Eq. (6.82) to

$$C(z) = -\frac{1}{4}\log(-z) \mp \frac{i\pi}{4}, \tag{6.84}$$

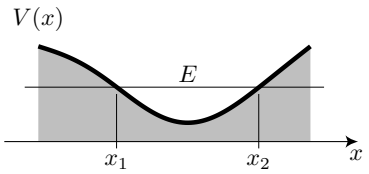
which changes Eq. (6.83) to

$$\psi(z) = c\,(-z)^{-1/4}\, e^{\pm i(2/3)(-z)^{3/2}} e^{\mp i\pi/4}. \tag{6.85}$$

The cos/sin asymptotic forms follow from taking linear combinations of the two complex exponentials in this case.

6.3.7 Soft-Wall Potential Well

Now back to analyzing the soft-wall potential—it's time to match the solutions. Again, we will start by matching the WKB solutions at the right-hand turning point x_2 in the diagram below.



To set up the calculation, we will first write down the WKB solutions on either side of the turning point,

$$\psi_{\text{WKB}}(x) = \begin{cases} \dfrac{A_{\text{W}}}{\sqrt{p(x)}} \exp\left[-\dfrac{i}{\hbar}\displaystyle\int_x^{x_2} p(x')\,dx'\right] + \dfrac{B_{\text{W}}}{\sqrt{p(x)}} \exp\left[\dfrac{i}{\hbar}\displaystyle\int_x^{x_2} p(x')\,dx'\right] & (x < x_2) \\ \dfrac{A_>}{\sqrt{|p(x)|}} \exp\left[-\dfrac{1}{\hbar}\displaystyle\int_{x_2}^{x} \bigl|p(x')\bigr|\,dx'\right] & (x > x_2), \end{cases} \tag{6.86}$$

where we have discarded the growing-exponential solution in the classically forbidden region (also, due to the setup of the integration limits, the A_{W} term is the one with the positive-exponential form $e^{ipx/\hbar}$). Often it's a good idea to work with shifted, scaled coordinates (like the z coordinate in Eq. (6.67) when we arrived at the Airy functions. However, there are multiple turning points and multiple regions, so we will be a little more explicit and notationally verbose than usual, to avoid getting mixed up. In any case, to patch the two WKB solutions together, we will use the interpolating Airy solution

$$\psi(x) \approx a\,\text{Ai}(\nu x) + b\,\text{Bi}(\nu x), \tag{6.87}$$

where

$$\nu := \sqrt[3]{\frac{2mV'(x_2)}{\hbar^2}} \tag{6.88}$$

was the coefficient in Eq. (6.67) of the scaled coordinate when we found the Airy functions. Now in the region $x > x_2$, but close to x_2, the same linearized potential (6.65) in the expression (6.56) defining $p(x)$ leads to

$$|p(x)| \approx \hbar\sqrt{\nu^3(x - x_2)}, \tag{6.89}$$

and the integral is

$$\int_{x_2}^{x} |p(x')|\,dx' \approx \hbar\nu^{3/2} \int_{x_2}^{x} \sqrt{x' - x_2}\,dx' = \frac{2\hbar}{3}\nu^{3/2}(x - x_2)^{3/2}. \tag{6.90}$$

Thus the WKB wave function for $x > x_2$ can be approximately written

$$\psi_{\text{WKB}}(x) \approx \frac{A_>}{\sqrt{\hbar}\nu^{3/4}(x - x_2)^{1/4}} \exp\left(-\frac{2}{3}\nu^{3/2}(x - x_2)^{3/2}\right). \tag{6.91}$$

At the same time, the asymptotic form of the patching function (6.87), using the asymptotic expressions (6.69) and (6.70), is

$$\psi(x) \approx \frac{a}{\sqrt{4\pi}\nu^{1/4}(x - x_2)^{1/4}} \exp\left(-\frac{2}{3}\nu^{3/2}(x - x_2)^{3/2}\right), \tag{6.92}$$

where we have already set $b = 0$ to match the WKB wave function. The expressions (6.91) and (6.92) are equivalent provided

$$a = \sqrt{\frac{4\pi}{\hbar\nu}}\,A_>, \tag{6.93}$$

since the functional dependence matched perfectly and thus canceled out.

On the other side of the turning point, for $x < x_2$, but close to x_2, we instead have

$$p(x) \approx \hbar\sqrt{\nu^3(x_2 - x)}, \tag{6.94}$$

and the integral becomes

$$-\int_x^{x_2} p(x')\,dx' \approx \hbar\nu^{3/2} \int_{x_2}^{x} \sqrt{x_2 - x'}\,dx' = -\frac{2\hbar}{3}\nu^{3/2}(x_2 - x)^{3/2}. \tag{6.95}$$

This has the same form as before except for the sign of $x - x_2$. The WKB wave function is thus approximately

$$\psi_{\text{WKB}}(x) \approx \frac{A_{\text{W}}}{\sqrt{\hbar}\nu^{3/4}(x_2 - x)^{1/4}} \exp\left(-i\frac{2}{3}\nu^{3/2}(x_2 - x)^{3/2}\right) + \frac{B_{\text{W}}}{\sqrt{\hbar}\nu^{3/4}(x_2 - x)^{1/4}} \exp\left(i\frac{2}{3}\nu^{3/2}(x_2 - x)^{3/2}\right), \tag{6.96}$$

while the asymptotic form of the patching wave function is

$$\psi(x) \approx \frac{a}{\sqrt{\pi}\nu^{1/4}(x_2-x)^{1/4}} \cos\left(\frac{2}{3}\nu^{3/2}(x_2-x)^{3/2} - \frac{\pi}{4}\right). \tag{6.97}$$

Note that we have used $b = 0$ here again for consistency with the $x > x_2$ solution. The expressions (6.96) and (6.97) are consistent if we split the cosine into complex exponentials and match them to the complex WKB exponentials. Thus, for example,

$$a = \sqrt{\frac{4\pi}{\hbar\nu}}\, e^{-i\pi/4} A_{\mathrm{W}}. \tag{6.98}$$

Eliminating a via Eq. (6.93), we find the connection formulae

$$\begin{aligned} A_{\mathrm{W}} &= e^{i\pi/4} A_{>} \\ B_{\mathrm{W}} &= A_{\mathrm{W}}^{*} = e^{-i\pi/4} A_{>}, \end{aligned} \tag{6.99}$$

(connection formulae, x_2)

where the formula for B_{W} follows from the observation that the complex exponentials forming the cosine are complex conjugates of each other, and we are assuming $A_>$ to be real.

To summarize the resulting wave function (6.86) after implementing the connection formulae (6.99), we have

$$\psi_{\mathrm{WKB}}(x) = \begin{cases} \dfrac{2A_{>}}{\sqrt{p(x)}} \cos\left[\dfrac{1}{\hbar}\displaystyle\int_x^{x_2} p(x')\,dx' - \dfrac{\pi}{4}\right] & (x < x_2) \\ \dfrac{A_{>}}{\sqrt{|p(x)|}} \exp\left[-\dfrac{1}{\hbar}\displaystyle\int_{x_2}^{x} \left|p(x')\right|\,dx'\right] & (x > x_2). \end{cases}$$

(connected WKB wave function, x_2) (6.100)

The solution at the left-hand turning point x_1 is essentially the same, but reflected in x; the solution is

$$\psi_{\mathrm{WKB}}(x) = \begin{cases} \dfrac{A_{<}}{\sqrt{|p(x)|}} \exp\left[-\dfrac{1}{\hbar}\displaystyle\int_x^{x_1} \left|p(x')\right|\,dx'\right] & (x < x_1) \\ \dfrac{2A_{<}}{\sqrt{p(x)}} \cos\left[\dfrac{1}{\hbar}\displaystyle\int_{x_1}^{x} p(x')\,dx' - \dfrac{\pi}{4}\right] & (x > x_1) \end{cases}$$

(connected WKB wave function, x_1) (6.101)

after implementing the analogous connection formulae.

In Eqs. (6.100) and (6.100), we have two cosine expressions for the well region $x_1 < x < x_2$, and we would like for them to be consistent. This is the case if $A_< = \pm A_>$, and

$$\cos\left[\frac{1}{\hbar}\int_x^{x_2} p(x')\,dx' - \frac{\pi}{4}\right] = \pm\cos\left[\frac{1}{\hbar}\int_{x_1}^{x} p(x')\,dx' - \frac{\pi}{4}\right], \tag{6.102}$$

where the variable sign here comes from $A_>/A_<$. Since we have an equation of the form $\cos\alpha = \pm\cos\beta$, the equality is satisfied if $\alpha+\beta$ or $\alpha-\beta$ is an integer multiple of π (positive or negative). The more promising case here is to work with $\alpha+\beta$, because then the integrals will combine to give the condition

$$\frac{1}{\hbar}\int_{x_1}^{x_2} p(x')\,dx' - \frac{\pi}{2} = n\pi, \tag{6.103}$$

where now we have nontrivial solutions for $n = 0, 1, 2, \ldots$ Cleaning this up a bit, we have

$$\int_{x_1}^{x_2} p(x')\,dx' = \left(n + \frac{1}{2}\right)\pi\hbar, \tag{6.104}$$

and identifying this expression as half the area enclosed by the trajectory in phase space, we can write the condition for the entire area by

$$\oint p(x)\,dx = \left(n + \frac{1}{2}\right) h.$$

(Bohr–Sommerfeld quantization condition) (6.105)

This is the same as the Bohr–Sommerfeld quantization condition (6.64), but with a correction of $1/2$ to the quantum number n. This correction which looks like a zero-point contribution like we found for the energy of the harmonic oscillator, came from the extra $\pi/4$ phases in the oscillatory parts of the WKB wave functions near the turning points. Practically speaking, however, this correction is probably not very significant. The WKB approximation is, after all, most accurate when the wave function varies quickly over the extent fo the potential—the semiclassical regime where $n \gg 1$.

6.4 Exercises

Problem 6.1

Consider particle in a potential $V(\mathbf{r}) = \lambda r^n$. Compute the commutator $[\mathbf{r}\cdot\mathbf{p}, H]$, where $H = p^2/2m + V(\mathbf{r})$. Use this to show that in an energy eigenstate, the relation

$$2\langle T\rangle = n\langle V\rangle\,, \tag{6.106}$$

holds, where $T = p^2/2m$ is the kinetic-energy operator. This is a special case of the **quantum virial theorem**, named for the analogous virial theorem in classical mechanics.

Problem 6.2

For an anharmonic oscillator,

$$H = \frac{p^2}{2m} + \alpha x^3, \tag{6.107}$$

calculate the equations of motion for the third-order expectation values $\langle x^3\rangle$, $\langle p^3\rangle$, $\langle x^2p + px^2\rangle$, and $\langle xp^2 + p^2x\rangle$. Which are coupled to fourth-order moments?

Problem 6.3

Suppose we define

$$\lambda(x) := \frac{\hbar}{p(x)} \tag{6.108}$$

as the spatially varying wavelength of a wave function. Show that the pair of "slowly varying wavelength" conditions

$$|\lambda'| \ll 1, \qquad |\lambda\lambda''| \ll 1 \tag{6.109}$$

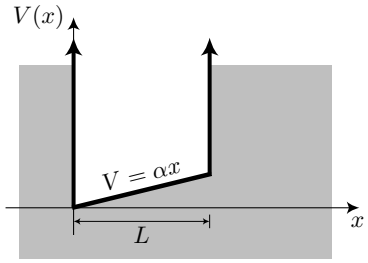
is sufficient to guarantee the validity of the WKB approximation in the context of one-dimensional energy eigenfunctions.

Problem 6.4

Use the WKB approximation to analyze the eigenenergies of the hard-wall potential well with

$$V(x) = \alpha x \qquad (0 < x < L), \tag{6.110}$$

as shown below.



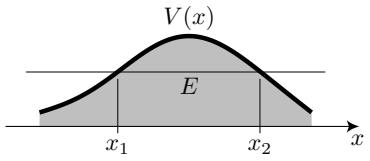
Since the resulting equation that determines the allowed energies is fairly complicated, assume a large energy, and give only the lowest-order correction to the energy.

Problem 6.5

Derive an expression for the energy levels of the harmonic oscillator within the WKB approximation.

Problem 6.6

In Section 6.3.6 we wrote down the WKB wave function in the three regions for a potential well with soft sides, and we derived the connection formulae for the piecewise solution in order to obtain a complete, consistent solution. Derive the analogous connection formulae for a potential barrier with soft sides, at classical turning points x_1 and x_2 as shown below. Use the sin/cos form of the WKB wave function in the regions outside the barrier in your setup. The solution to this problem will involve using both $\mathrm{Ai}(z)$ and $\mathrm{Bi}(z)$ in your patching function.



Problem 6.7

In Chapter 2 we also discussed the WKB estimate (6.59)

$$T_1 := \exp\left[-\frac{2}{\hbar}\int_{x_1}^{x_2} \left|p(x)\right| dx\right] = \exp\left[-\frac{2\sqrt{2m}}{\hbar}\int_{x_1}^{x_2} \sqrt{V(x)-E}\, dx\right] \tag{6.111}$$

for the barrier-tunneling probability. Use your solution to Problem 6.6 to obtain the improved WKB estimate

$$T = \frac{T_1}{(1+T_1/4)^2}. \tag{6.112}$$

Note that in the limit of small T_1 (a high, wide barrier), $T \approx T_1$.

What does this tunneling probability T account for that the simpler expression T_1 does not?

To carry out the calculation, start with the solution in the right-hand (transmission) region (in terms of sines and cosines). Use the connection formula to relate the solution to the under-barrier region. Changing the integration domain from $[x, x_2]$ to $[x_1, x]$ will prepare the solution to connect to region 1, and will introduce the amplitude $\tau_1 := \sqrt{T_1}$. Finally, connect the under-barrier solution to the solution in the incident region; reexpress the incident-region solution in terms of incident and reflected waves to find the transmission probability.

Problem 6.8

Consider a metal surface, with a static electric field $\mathscr{E}$ just outside the surface. An electron (of charge $-e$) thus sees a potential

$$V(x) = V_0 - e\mathscr{E}x \qquad x \geq 0, \tag{6.113}$$

where V_0 is the surface potential, the surface is located at $x = 0$, the metal occupies $x < 0$, and the region $x > 0$ is empty.

The most energetic electrons in the metal have an energy $E = V_0 - W$, where W is the **work function** of the metal. Use the WKB approximation to compute the tunneling probability T for an electron in the metal in terms of W and $\mathscr{E}$.

This problem serves, for example, as a simple model for cold electron emission from the sharp probe tip of a scanning tunneling microscope (STM). The tunneling current is proportional to the transmission

probability T. Since T varies exponentially with the electric field, the STM current is a sensitive measure of the distance from the STM tip to a nearby surface being probed.

Problem 6.9

Consider a particle incident on an inverted parabolic barrier,

$$V(x) = -\frac{1}{2}kx^2. \tag{6.114}$$

(a) For a below-the-barrier incident energy $E < 0$, compute the transmission probability in the WKB approximation.

(b) For the above-the-barrier case $E > 0$, there is a nice duality trick that will let you adapt your solution to part (a). The Schrödinger equation

$$\left(\frac{p^2}{2m} - \frac{1}{2}kx^2\right)|\psi\rangle = E|\psi\rangle \tag{6.115}$$

takes the form in the position representation

$$\left(-\frac{\hbar^2}{2m}\partial_x^2 - \frac{1}{2}kx^2\right)\psi(x) = E\psi(x), \tag{6.116}$$

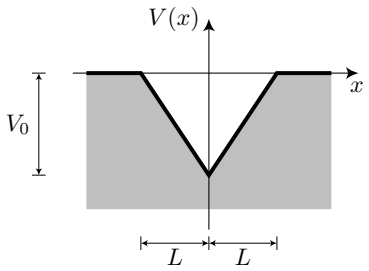
but in the momentum representation, the form can be written

$$\left(-\frac{\hbar^2 k}{2}\partial_p^2 - \frac{1}{2m}p^2\right)\phi(p) = -E\phi(p). \tag{6.117}$$

The latter form says that we can formally recast this problem as a particle of energy $-E$ incident, traveling in the positive momentum direction, on a "barrier" $-p^2/2m$. Note that "transmission" in the dual problem is equivalent to "reflection" in the original problem. So show explicitly how to handle mapping the parameters between the original and dual problems, and how to adapt your calculation from (a) to compute the reflection probability for the above-barrier case $E > 0$.

Problem 6.10

Consider the symmetric potential well sketched below, of depth $V_0 > 0$ and half-width (or full width at half depth) L.



(a) Use the WKB approximation to derive an expression for the bound-state energies.

(b) Estimate the number of bound states.

(c) Give an approximate condition for at least one bound state to exist.

(d) Do you expect the WKB approximation to underestimate or overestimate the true bound-state energies? Briefly justify your expectation.

Chapter 7

Angular Momentum

At this point we will develop the theory of angular momentum. This of course encompasses both ''real'' angular momentum in coordinate space as well as particle spin. However, before considering the physical manifestations of angular momentum we will start with a ''pure'' or minimalist approach to studying angular momentum in the form of a set of abstract operators, and show that we can infer a fair amount from just one commutator and a bunch of math. Then we'll return to physical manifestations, and after that proceed with some more advanced topics in angular momentum.

7.1 Axiomatic Angular Momentum

7.1.1 Operators and Eigenstates

To begin, suppose that we have a set of operators J_x, J_y, and J_z—the angular momentum operators. These operators are defined solely by the commutation relation

$$[J_\alpha, J_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}J_\gamma, \tag{7.1}$$
(angular-momentum commutator)

where $\epsilon_{\alpha\beta\gamma}$ is the **Levi-Civita symbol**.[1] This symbol acts as a completely antisymmetric ''tensor,'' though it is technically *not* a tensor because it doesn't transform correctly under rotations, hence ''symbol.'' This symbol takes the value $+1$ if $(\alpha\beta\gamma)$ is a cyclic permutation of (xyz) [equivalently for this case, an even permutation, which means it takes an even number of adjacent swaps to get back to (xyz)], -1 if an odd permutation [odd number of adjacent swaps to get back to (xyz)], and 0 otherwise (which occurs when one of the labels is repeated).

Note that in classical mechanics, angular momentum of a particle is defined in terms of the canonical coordinates by $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. It then turns out that the components of $\mathbf{L}$ satisfy the Poisson-bracket relation

$$[L_\alpha, L_\beta]_{\text{P}} = \epsilon_{\alpha\beta\gamma}L_\gamma. \tag{7.2}$$

It is then sensible to view the commutator (7.1) as the quantum counterpart of this Poisson bracket via canonical quantization. But by regarding the commutator (7.1) as the fundamental definition of angular momentum, we will obtain angular momentum without a classical counterpart (spin). We will show this when we explore the $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ definition in quantum mechanics in Section 7.2. Also, the canonical brackets of the form $[L_z, \phi]$ require extra care when taken over to quantum mechanics (see Section 21.2), and they are anyway specific to orbital angular momentum, so we will mostly avoid them here.

The notation for these operators suggest angular-momentum components associated with the three Cartesian axes, and so an obvious way to begin is to define an operator associated with the *total* angular momentum:

$$J^2 = J_x^2 + J_y^2 + J_z^2. \tag{7.3}$$

[1] Pronounced ''levee-tchiveeta,'' as best I can tell; Tullio Levi-Civita was an Italian mathematician.

We will assume these operators to correspond to observables, and are thus Hermitian. Out of the set of operators $\{J^2, J_x, J_y, J_z\}$, the above relations (7.1) and (7.3) show that the full set can be expressed in terms of only two (e.g., J_x and J_y). Thus, to completely span the space of angular momentum states, we can choose to have simultaneous eigenstates of any two such operators. This strategy is useful in spherically symmetric systems, where such eigenstates should exist, and so any component J_α is as good as any other. However, in view of the fundamental commutation relation, we can't have simultaneous eigenstates for J_α and J_β if $\alpha \neq \beta$. However, J^2 commutes with J_α:

$$[J_\alpha, J^2] = 0. \tag{7.4}$$
(angular-momentum commutator)

To see this, we can take $J_\alpha = J_x$ without loss of generality, in which case

$$\begin{aligned}[J_x, J^2] &= [J_x, J_y^2] + [J_x, J_z^2] \\ &= [J_x, J_y]J_y + J_y[J_x, J_y] + [J_x, J_z]J_z + J_z[J_x, J_z] \\ &= (i\hbar J_z)J_y + J_y(i\hbar J_z) + (-i\hbar J_y)J_z + J_z(-i\hbar J_y) \\ &= 0.\end{aligned} \tag{7.5}$$

Thus, we are free to construct simultaneous eigenstates of J^2 and J_α. We make the arbitrary but conventional choice of taking simultaneous eigenstates of J^2 and J_z. We will thus need two quantum numbers, which we call j and m, and define the eigenvalue λ_j of J^2 to be some function of j,

$$J^2|j\ m\rangle = \lambda_j|j\ m\rangle, \tag{7.6}$$

and the eigenvalue λ_m of J_z will similarly be some function of m,

$$J_z|j\ m\rangle = \lambda_m|j\ m\rangle. \tag{7.7}$$

To proceed, the goal is now to work out expressions for the angular-momentum eigenvalues λ_j and λ_m.

7.1.2 Ladder Operators and Eigenvalues

It is also useful to define two non-Hermitian operators, the **ladder operators**

$$J_\pm := J_x \pm iJ_y, \tag{7.8}$$

which will turn out to be somewhat more convenient than J_x and J_y separately. In fact, these will allow us to construct all the eigenstates in the same way that we used the ladder operators a and $a^\dagger$ to construct the states of the harmonic oscillator. Given the commutation relation (7.4), we immediately see that the ladder operators commute with J^2:

$$[J^2, J_\pm] = 0. \tag{7.9}$$
(ladder-operator commutator)

The commutators with J_z is not hard to work out,

$$[J_z, J_\pm] = [J_z, J_x] \pm i[J_z, J_y] = i\hbar J_y \pm \hbar J_x, \tag{7.10}$$

or

$$[J_z, J_\pm] = \pm\hbar J_\pm. \tag{7.11}$$
(ladder-operator commutator)

We can also readily compute the commutator of the two ladder operators as

$$[J_+, J_-] = -2i[J_x, J_y] = 2\hbar J_z. \tag{7.12}$$

Now, to put the ladder operators to use, we can consider the action of $J_\pm$ on an eigenstate state $|j\ m\rangle$. In particular, notice that since the J_α commute with J^2, they transform $|j\ m\rangle$ to a state $J_\alpha|j\ m\rangle$ such that

$$J^2(J_\alpha|j\ m\rangle) = J_\alpha J^2|j\ m\rangle = \lambda_j(J_\alpha|j\ m\rangle). \tag{7.13}$$

Thus, $J_\alpha|j\ m\rangle$ is an eigenstate of J^2 with the same eigenvalue as $|j\ m\rangle$, implying that j is unchanged. The same conclusion of course holds for $J_\pm$, and thus, since we will be considering the action of $J_{x,y,z,\pm}$ on the states $|j,m\rangle$ for the rest of this section, we can regard j as a fixed quantity.

We can then use the commutator (7.11) on $|j\ m\rangle$ to write

$$J_z J_\pm|j\ m\rangle = J_\pm J_z|j\ m\rangle \pm \hbar J_\pm|j\ m\rangle = (\lambda_m \pm \hbar)J_\pm|j\ m\rangle. \tag{7.14}$$

This shows that $J_\pm|j\ m\rangle$ is an eigenstate of J_z with eigenvalue $\lambda_m \pm \hbar$. Now we see the reason for the name "ladder operators," since J_+ acts to raise λ_m by $\hbar$, and J_- lowers it by the same amount. Now since m is an arbitrary label for the states, we may define it such that $\lambda_m = m\hbar$. That is, m represents the projection of angular momentum along the z-axis in multiples of $\hbar$. Then we may write

$$J_z|j\ m\rangle = m\hbar|j\ m\rangle \tag{7.15}$$
(J_z eigenvalues)

for the J_z eigenvalue equation, and for the ladder operators we have thus shown that

$$J_\pm|j\ m\rangle \propto |j\ m\pm1\rangle. \tag{7.16}$$

To establish the proper normalization, we note that

$$J_\mp J_\pm = J_x^2 + J_y^2 \pm i[J_x, J_y] = J^2 - J_z^2 \mp \hbar J_z = J^2 - J_z(J_z \pm \hbar), \tag{7.17}$$

and thus the norm of the raised/lowered state is

$$\langle j\ m|J_\mp J_\pm|j\ m\rangle = \langle j\ m|[J^2 - J_z(J_z \pm \hbar)]|j\ m\rangle = \lambda_j - m(m \pm 1)\hbar^2. \tag{7.18}$$

Note that the right-hand side becomes negative for sufficiently large m, assuming λ_j to be fixed. However, since $\langle j\ m|J_\mp J_\pm|j\ m\rangle \geq 0$, we can conclude that there is a maximum value of m, say $m_{\max}$, such that

$$J_+|j\ m_{\max}\rangle = 0. \tag{7.19}$$

Then applying Eq. (7.17) to $|j\ m_{\max}\rangle$,

$$J_- J_+|j\ m_{\max}\rangle = [J^2 - J_z(J_z + \hbar)]|j\ m_{\max}\rangle. \tag{7.20}$$

The left-hand side vanishes, so

$$J^2|j\ m_{\max}\rangle = J_z(J_z + \hbar)|j\ m_{\max}\rangle = m_{\max}(m_{\max} + 1)\hbar^2|j\ m_{\max}\rangle. \tag{7.21}$$

Since j is likewise an arbitrary label for the eigenvalue $\lambda_j = m_{\max}(m_{\max}+1)\hbar^2$, we may thus define $j := m_{\max}$, with $j \geq 0$, so that

$$J^2|j\ m\rangle = j(j+1)\hbar^2|j\ m\rangle. \tag{7.22}$$
(J^2 eigenvalue equation)

Repeating this argument, Eq. (7.18) implies a smallest (negative) value of m, say $m_{\min}$, so that

$$J_-|j\ m_{\min}\rangle = 0. \tag{7.23}$$

Again applying Eq. (7.17) to $|j\ m_{\min}\rangle$,

$$J_+ J_-|j\ m_{\min}\rangle = [J^2 - J_z(J_z - \hbar)]|j\ m_{\min}\rangle, \tag{7.24}$$

and since the left-hand side vanishes,

$$J^2|j\ m_{\min}\rangle = J_z(J_z - \hbar)|j\ m_{\min}\rangle = m_{\min}(m_{\min} - 1)\hbar^2|j\ m_{\min}\rangle. \tag{7.25}$$

Thus,

$$j(j+1) = m_{\min}(m_{\min} - 1), \tag{7.26}$$

which is satisfied by $m_{\min} = -j$ (the alternate solution, $m_{\min} = j + 1$, violates the definition $j = m_{\max}$). Thus, m is constrained to be within a bounded range,

$$-j \leq m \leq j. \tag{7.27}$$
(range constraint of m)

Recall that this followed from Eq. (7.18), to avoid a contradiction with the requirement $\langle j\ m|J_{\mp}J_{\pm}|j\ m\rangle \geq 0$. In particular, if we start with the state $|j\ {-j}\rangle$ and repeatedly apply J_+, we should eventually end up with (something proportional to) the $|j\ {+j}\rangle$ state. How do we know this? Referring again to Eq. (7.18), which we may rewrite now as

$$\langle j\ m|J_{\mp}J_{\pm}|j\ m\rangle = \Big[j(j+1) - m(m \pm 1)\Big]\hbar^2. \tag{7.28}$$

we see that the *only* state that vanishes when hit by J_+ is $|j\ (+j)\rangle$. Thus, the only way to avoid a contradiction (negative state norm) is for $J_+^n|j\ (-j)\rangle \propto |j\ (+j)\rangle$ for some integer n. Further, we may conclude that *every* state $|j\ m\rangle$ may be written as $J_+^n|j\ (-j)\rangle$ (up to a scalar factor) for some integer n; otherwise we would have a state that, when raised arbitrarily many times by J_+, would not vanish. Thus, we may conclude that m takes on discrete, integer-separated values, according to

$$m \in \{-j, -j+1, \ldots, j-1, j\} \qquad (2j+1 \text{ possible values}), \tag{7.29}$$
(range constraint of m)

which means that there are $2j+1$ possible values for m (i.e., because $m+j$ ranges from 0 to $2j$). Furthermore, $2j+1$ must be an integer, because $2j$ is the number of times J_+ must be applied to $|j\ (-j)\rangle$ to obtain $|j\ (+j)\rangle$. This implies that

$$j \in \mathbb{Z} \quad \text{or} \quad j + \frac{1}{2} \in \mathbb{Z}, \tag{7.30}$$
(integer/half-integer constraint)

with j also nonnegative, as we discussed before. That is, j is either an integer or a half-integer. As we will discuss later, only integer j can correspond to coordinate-space angular momenta; half-integer j are restricted to representing intrinsic particle *spin* angular momenta (which can also have integer j).

Finally, just to tidy up loose ends, we can use Eq. (7.28) to write down

$$\begin{aligned} J_{\pm}|j\ m\rangle &= \hbar\sqrt{j(j+1) - m(m \pm 1)}\ |j\ m{\pm}1\rangle \\ &= \hbar\sqrt{(j \pm m + 1)(j \mp m)}\ |j\ m{\pm}1\rangle \end{aligned} \tag{7.31}$$
(ladder operator effects)

as the properly normalized action of the ladder operators on the angular-momentum eigenstates.

7.2 Angular Momentum in Coordinate Space

In classical mechanics, angular momentum is defined by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \tag{7.32}$$

In quantum mechanics, we will use the same definition, and mostly we will work in the position representation:

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times \frac{\hbar}{i}\nabla. \tag{7.33}$$
(orbital angular momentum)

We will call this angular-momentum operator **orbital angular momentum** to distinguish it from other types we will introduce later (spin, composite).

7.2.1 Commutation Rules

First, we will want to establish that this is indeed an angular-momentum operator in the sense that we have already defined it, and so we will need to work out a bunch of commutators. To start, consider

$$[L_x, y] = [yp_z - zp_y, y] = -z[p_y, y] = -z(-i\hbar) = i\hbar z. \tag{7.34}$$

By the same argument, we have

$$[L_x, x] = 0. \tag{7.35}$$

Other cases follow by cyclic permutation of indices in the above two commutators, as well as in $[L_x, z] = -i\hbar y$, which follows from only a slight modification of the commutator calculation above. Together, we can write this as

$$[L_\alpha, r_\beta] = i\hbar\epsilon_{\alpha\beta\gamma} r_\gamma. \tag{7.36}$$
(commutator with position)

In a similar way we can work out the commutator with momentum. Starting with

$$[L_x, p_y] = [yp_z - zp_y, p_y] = p_z[y, p_y] = p_z(i\hbar) = i\hbar p_z = -[L_y, p_x] \tag{7.37}$$

and then

$$[L_x, p_x] = 0, \tag{7.38}$$

we have the general case

$$[L_\alpha, p_\beta] = i\hbar\epsilon_{\alpha\beta\gamma} p_\gamma. \tag{7.39}$$
(commutator with momentum)

Now we are in a position to compute commutators of angular-momentum operators. Starting with the specific case

$$[L_x, L_y] = [L_x, zp_x - xp_z] = [L_x, z]p_x - x[L_x, p_z] = (-i\hbar y)p_x - x(-i\hbar p_y) = i\hbar(xp_y - yp_x) = i\hbar L_z. \tag{7.40}$$

Clearly also $[L_y, L_x] = -i\hbar L_z$ and $[L_x, L_x] = 0$, so in the general case,

$$[L_\alpha, L_\beta] = i\hbar\epsilon_{\alpha\beta\gamma} L_\gamma.$$
(commutator of orbital angular momentum) (7.41)

Thus, orbital angular momentum satisfies the definition (7.1) that we started off with.

7.2.2 Application to Central-Force Problems

One of the primary applications of the $\mathbf{L}$ operator is to central potentials of the form

$$H(\mathbf{p}, \mathbf{r}) = \frac{p^2}{2m} + V(r), \tag{7.42}$$

so that the potential is only a function of $r = |\mathbf{r}|$. To see why this is useful, we will need yet more commutators. Because $[L_x, p_x] = 0$, it follows that

$$[L_x, p_x^2] = 0 \tag{7.43}$$

as well. Also, from $[L_x, p_y] = i\hbar p_z$, it follows that

$$[L_x, p_y^2] = p_y[L_x, p_y] + [L_x, p_y]p_y = i\hbar(p_y p_z + p_z p_y) = 2i\hbar(p_y p_z) \tag{7.44}$$

and thus also $[L_x, p_z^2] = -2i\hbar(p_y p_z)$. Putting together the three components of $p^2 = p_x^2 + p_y^2 + p_z^2$, we have

$$[L_x, p^2] = 0, \tag{7.45}$$

so any component of $\mathbf{L}$ commutes with the kinetic-energy operator. The same calculations lead to $[L_x, x^2] = 0$, $[L_x, y^2] = 2i\hbar yz$, and $[L_x, z^2] = -2i\hbar yz$, so that

$$[L_x, r^2] = 0. \tag{7.46}$$

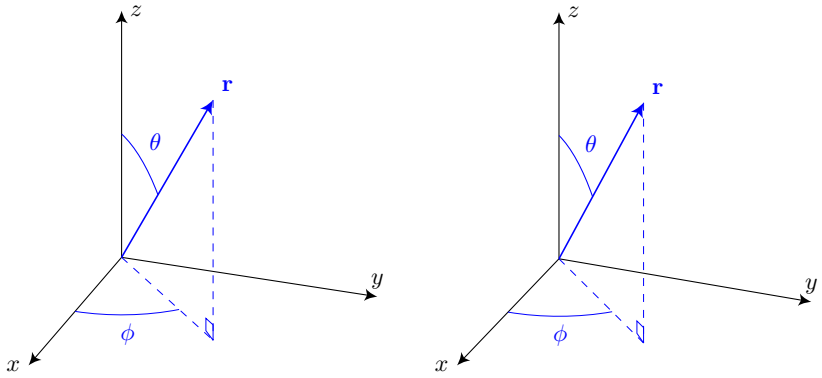
Then any component of $\mathbf{L}$ also commutes with any *function* of r^2, including $r = \sqrt{r^2}$, and any function of r like $V(r)$. Thus, any component of $\mathbf{L}$ commutes with the Hamiltonian,

$$[L_x, H] = 0, \tag{7.47}$$

in the case of a central potential. This is important, because the Hamiltonian will have simultaneous eigenstates with, say, L^2 and L_z. Thus, when we develop these eigenstates $|\ell\ m\rangle$, we will also be developing the angular dependence of the central-force problem.

7.2.3 Representation in Spherical Coordinates

Now the goal is to work out the representation of the eigenstates $|\ell\ m\rangle$ in spherical angles (θ, ϕ). Unfortunately, it's going to be something of a long slog to get there. To start, the convention for the spherical angles is shown in the diagram below.[2]



From the diagram we can read off the coordinate transformations

$$\begin{aligned} z &= r\cos\theta \\ x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi. \end{aligned} \tag{7.48}$$

Now we will need the gradient operator in spherical coordinates,

$$\nabla = \hat{r}\partial_r + \frac{\hat{\theta}}{r}\partial_\theta + \frac{\hat{\phi}}{r\sin\theta}\partial_\phi, \tag{7.49}$$

where the proof of this formula is left as an exercise (Problem 7.5). Using this expression, we can compute the angular momentum operator:

$$\mathbf{L} = -i\hbar\mathbf{r}\times\nabla = -i\hbar\left(\hat{r}\times\hat{\theta}\,\partial_\theta + \frac{1}{\sin\theta}\hat{r}\times\hat{\phi}\,\partial_\phi\right) = i\hbar\left(\frac{1}{\sin\theta}\hat{\theta}\,\partial_\phi - \hat{\phi}\,\partial_\theta\right). \tag{7.50}$$

More useful will be the projection of this form into Cartesian coordinates:

$$\begin{aligned} L_z &= -\sin\theta\, L_\theta = -i\hbar\partial_\phi \\ L_x &= \cos\phi\cos\theta\, L_\theta - \sin\phi\, L_\phi = i\hbar\Big(\cot\theta\cos\phi\,\partial_\phi + \sin\phi\,\partial_\theta\Big) \\ L_y &= \cos\phi\sin\theta\, L_\theta + \cos\phi\, L_\phi = i\hbar\Big(\cot\theta\sin\phi\,\partial_\phi - \cos\phi\,\partial_\theta\Big). \end{aligned} \tag{7.51}$$

The idea is to use these to calculate L^2, so we will have spherical representations of the operators L^2 and L_z to diagonalize. First, squaring the z component gives

$$L_z^2 = -\hbar^2\partial_\phi^2, \tag{7.52}$$

[2] Why are you seeing double in this figure? See the explanation in the usage chapter, starting on p. 20.

while squaring the x component gives the considerably messier expression

$$L_x^2 = -\hbar^2\Big[\cot^2\theta\cos\phi\,\partial_\phi\cos\phi\,\partial_\phi + \sin^2\phi\,\partial_\theta^2 + \cot\theta\cos\phi\,\partial_\phi\sin\phi\,\partial_\theta + \sin\phi\cos\phi\,\partial_\theta\cot\theta\,\partial_\phi\Big]. \tag{7.53}$$

Since this is only a step towards computing L^2, we can avoid the pain of writing down a similarly ugly expression for L_y^2 by realizing that $L_x^2 + L_y^2$ is azimuthally symmetric, so that it doesn't change under an average over ϕ. Thus, we can compute $L_x^2 + L_y^2$ by averaging L_x^2 over ϕ and then doubling the result. Making the replacements $\sin\phi\cos\phi \longrightarrow 0$; $\sin^2\phi$, $\cos^2\phi \longrightarrow 1/2$; $\cos\phi\,\partial_\phi\cos\phi\,\partial_\phi = \cos^2\phi\,\partial_\phi^2 - \cos\phi\sin\phi\,\partial_\phi \longrightarrow \partial_\phi^2/2$; and $\cos\phi\,\partial_\phi\sin\phi = \cos^2\phi - \cos\phi\sin\phi\,\partial_\phi \longrightarrow 1/2$, we have

$$L_x^2 + L_y^2 = -\hbar^2\Big[\cot^2\theta\,\partial_\phi^2 + \partial_\theta^2 + \cot\theta\,\partial_\theta\Big]. \tag{7.54}$$

Combining this result with Eq. (7.52), we have

$$L^2 = -\hbar^2\Big[(\cot^2\theta + 1)\partial_\phi^2 + \big(\partial_\theta + \cot\theta\big)\,\partial_\theta\Big]. \tag{7.55}$$

After a big more algebra, we have

$$\begin{aligned} L^2 &= -\hbar^2\left[\frac{1}{\sin\theta}\,\partial_\theta\Big(\sin\theta\,\partial_\theta\Big) + \frac{1}{\sin^2\theta}\,\partial_\phi^2\right] \\ L_z &= -i\hbar\partial_\phi, \end{aligned} \tag{7.56}$$

(operators to diagonalize)

including the operator L_z from Eqs. (7.51). Remember that the goal is to find simultaneous eigenfunctions of these two operators.

7.2.3.1 Azimuthal-Angle Solution

Recalling the general form of the J_z eigenvalue from Eq. (7.15),

$$L_z|\ell\ m\rangle = m\hbar|\ell\ m\rangle, \tag{7.57}$$

where m must be an integer or half-integer. If we project into the angular representation with $\langle\theta,\phi|$, we have

$$L_z\Phi(\phi) = -i\hbar\Phi'(\phi) = m\hbar\Phi(\phi), \tag{7.58}$$

where $\Phi(\phi)$ represents the functional dependence on ϕ in $\langle\theta,\phi|\ell\ m\rangle$, and we are dropping the θ dependence since there is no such dependence in L_z. This leads to the simple differential equation

$$\Phi'(\phi) = im\Phi(\phi), \tag{7.59}$$

which has solution

$$\Phi(\phi) = e^{im\phi}. \tag{7.60}$$

There is also technically an undetermined constant here that we are dropping, because we will normalize the entire state separately later, once the θ dependence is better established.

Note that the form of this wave function (7.60) implies a restriction on m. A shift of ϕ by 2π should leave the wave function unchanged; that is to say, since ϕ is an angle, it is subject to periodic boundary conditions. This requires that $e^{2\pi im} = 1$, which in turn requires m to be an integer, *not* a half-integer. This further implies that ℓ is an integer, not a half-integer. Half-integer angular momenta are possible, but do not correspond to orbital angular momentum.

7.2.3.2 Polar-Angle Solution: Differential Equation

Now for the remainder of the solution for the angular states. Recall that L^2 in Eqs. (7.56) has no ϕ-dependence (except via the operator ∂_ϕ). Therefore, introducing the notation

$$Y_\ell^m(\theta,\phi) := \langle\theta,\phi|\ell\ m\rangle \tag{7.61}$$

for the coordinate-space eigenfunction, this function separates into factors for the separate dependences on the two angles:

$$Y_\ell^m(\theta,\phi) = \Theta_\ell^m(\theta)\,\Phi_m(\phi) = \Theta_\ell^m(\theta)\,e^{im\phi}. \tag{7.62}$$

This is because L_z only depends on ϕ, and L^2 only contains θ dependence (it depends on ϕ only via its derivative, which we have seen amounts to dependence on m). We have already found the second factor $\Phi_m(\phi)$; what remains is to find the eigenfunction $\Theta_\ell^m(\theta)$ of the L^2 operator (which depends on m via the operator ∂_ϕ).

Recalling Eq. (7.22), we already have the eigenvalue equation

$$L^2|\ell\ m\rangle = \ell(\ell+1)\hbar^2|\ell\ m\rangle. \tag{7.63}$$

Projecting with $\langle\theta,\phi|$ gives

$$-\left[\frac{1}{\sin\theta}\,\partial_\theta\Big(\sin\theta\,\partial_\theta\Big) + \frac{1}{\sin^2\theta}\,\partial_\phi^2\right]\Theta_\ell^m(\theta)\,e^{im\phi} = \ell(\ell+1)\Theta_\ell^m(\theta)\,e^{im\phi}. \tag{7.64}$$

Carrying out the ϕ derivatives and simplifying leads to

$$\left[\frac{1}{\sin\theta}\,\partial_\theta\Big(\sin\theta\,\partial_\theta\Big) + \ell(\ell+1) - \frac{m^2}{\sin^2\theta}\right]\Theta_\ell^m(\theta) = 0. \tag{7.65}$$

This can be put into standard form by changing to the variable $\mu := \cos\theta$, so that $\sin^2\theta = 1-\mu^2$ and $\partial_\mu = -(1/\sin\theta)\partial_\theta$. The result is

$$\partial_\mu\Big[(1-\mu^2)\,\partial_\mu\Theta\Big] + \left[\ell(\ell+1) - \frac{m^2}{1-\mu^2}\right]\Theta = 0. \tag{7.66}$$

(general Legendre equation)

This differential equation is called the **general Legendre equation**, and the solutions are known as the **associated Legendre polynomials**. The approach here is to assume a power-series solution, show that it truncates, and work out a recursion relation for the coefficients (as was also possible for the Hermite polynomials). However, we will eschew this approach in favor of the more clever, fancy-schmancy method of using the ladder operators to construct solutions.

7.2.3.3 Polar-Angle Solution: Ladder Operators for Stretched States

To proceed, then, we will need the ladder operators (7.8):

$$L_\pm := L_x \pm iL_y. \tag{7.67}$$

Using L_x and L_y from Eqs. (7.51), we find

$$L_\pm = \hbar e^{\pm i\phi}\Big(i\cot\theta\,\partial_\phi \pm \partial_\theta\Big). \tag{7.68}$$

Now recall [Eq. (7.23)] that lowering the lowest state $|\ell\ (-\ell)\rangle$ must lead to a null result:

$$L_-|\ell\ (-\ell)\rangle = 0. \tag{7.69}$$

In the angular representation, this is a differential equation for the solution $\Theta_\ell^{-\ell}(\theta)$:

$$\hbar e^{-i\phi}\Big(i\cot\theta\,\partial_\phi - \partial_\theta\Big)\Theta_\ell^{-\ell}(\theta)\,e^{-i\ell\phi} = 0. \tag{7.70}$$

Simplifying a bit, we have

$$\Big(\ell\cot\theta - \partial_\theta\Big)\Theta_\ell^{-\ell}(\theta) = 0, \tag{7.71}$$

and the solution to this equation is

$$\Theta_\ell^{-\ell}(\theta) = \eta\,(\sin\theta)^\ell \tag{7.72}$$

for some normalization constant η. The normalization convention is to require

$$\int d\Omega\,\big|Y_\ell^m(\theta,\phi)\big|^2 = 1 \tag{7.73}$$

for any (ℓ, m), where $d\Omega = \sin\theta\,d\theta\,d\phi$. Putting in Eq. (7.72) into this condition (the ϕ dependence does not affect the normalization), we find

$$2\pi|\eta|^2\int_{-1}^{1} d\mu\,(1-\mu^2)^\ell = \frac{4\pi(2^\ell\ell!)^2}{(2\ell+1)!}|\eta|^2 = 1, \tag{7.74}$$

and thus we have

$$\Theta_\ell^{-\ell}(\theta) = \frac{1}{2^\ell\ell!}\sqrt{\frac{(2\ell+1)!}{4\pi}}\,(\sin\theta)^\ell \tag{7.75}$$

as the normalized, minimum-m solution, upon choosing a zero global phase angle. Note that the same argument, applying $L_+|\ell\;\ell\rangle = 0$, leads to the same solution for $\Theta_\ell^\ell(\theta)$.

7.2.3.4 Polar-Angle Solution: Ladder Operators for Arbitrary States

To construct the rest of the angular-space representations for the eigenstates $|\ell\;m\rangle$, we can iteratively apply the raising operator L_+ to $|\ell\;-\ell\rangle$ to end up with the desired state. The procedure is a little tricky because there is a lot involved, so we will break this into more manageable parts. First, from Eqs. (7.31), we have

$$L_+|\ell\;m\rangle = \hbar\sqrt{(\ell+m+1)(\ell-m)}\;|\ell\;(m+1)\rangle. \tag{7.76}$$

Shifting $m \longrightarrow m-1$ changes this to

$$L_+|\ell\;(m-1)\rangle = \hbar\sqrt{(\ell+m)(\ell-m+1)}\;|\ell\;m\rangle. \tag{7.77}$$

We can perform the same shift and then apply the raising operator again using the formula above; the result is

$$(L_+)^2|\ell\;(m-2)\rangle = \hbar^2\sqrt{(\ell+m)(\ell+m-1)(\ell-m+1)(\ell-m+2)}\;|\ell\;m\rangle. \tag{7.78}$$

Noticing the pattern of the factors, we can continue to k applications of the raising operator:

$$(L_+)^k|\ell\;(m-k)\rangle = \hbar^k\sqrt{\frac{(\ell+m)!}{(\ell+m-k)!}\frac{(\ell-m+k)!}{(\ell-m)!}}\;|\ell\;m\rangle. \tag{7.79}$$

Setting $k = \ell + m$ gives

$$(L_+)^{\ell+m}|\ell\;(-\ell)\rangle = \hbar^{\ell+m}\sqrt{\frac{(\ell+m)!(2\ell)!}{(\ell-m)!}}\;|\ell\;m\rangle, \tag{7.80}$$

and then solving for the desired state gives

$$|\ell\;m\rangle = \frac{1}{\hbar^{\ell+m}}\sqrt{\frac{(\ell-m)!}{(\ell+m)!(2\ell)!}}\,(L_+)^{\ell+m}|\ell\;(-\ell)\rangle. \tag{7.81}$$

Now from Eq. (7.68) we have

$$L_+ = \hbar e^{i\phi}\Big(i\cot\theta\,\partial_\phi + \partial_\theta\Big), \tag{7.82}$$

and if we assume this operator to act on $|\ell\, m\rangle$ (or Y_ℓ^m in coordinate space), then we may use the form

$$\begin{aligned} L_+ &= \hbar e^{i\phi}\Big(\partial_\theta - m\cot\theta\Big) \\ &= \hbar e^{i\phi}(\sin\theta)^m \partial_\theta (\sin\theta)^{-m} \\ &= -\hbar e^{i\phi}(1-\mu^2)^{(m+1)/2}\partial_\mu (1-\mu^2)^{-m/2}, \end{aligned} \tag{7.83}$$

using the same change of variables as before: $\mu = \cos\theta$, $\sin^2\theta = 1-\mu^2$, $\partial_\mu = -(1/\sin\theta)\partial_\theta$. Repeated application of L_+ is complicated somewhat by the observation that m is a moving target: it increases by 1 on each application. Applying it $\ell + m$ times to the edge state has the form

$$(L_+)^{\ell+m}|\ell\ (-\ell)\rangle = (-1)^{\ell+m}\hbar^{\ell+m}e^{i(\ell+m)\phi}(1-\mu^2)^{m/2}\partial_\mu^{\ell+m}(1-\mu^2)^{\ell/2}\,|\ell\ (-\ell)\rangle. \tag{7.84}$$

This can be seen by writing out the first couple of operations on the initial state, and noticing the pattern of factors (and the cancellation of factors of $(1-\mu^2)$ between the derivative operators):

$$\cdots\Big[(1-\mu^2)^{-(\ell-2)/2}\partial_\mu(1-\mu^2)^{(\ell-1)/2}\Big]\Big[(1-\mu^2)^{-(\ell-1)/2}\partial_\mu(1-\mu^2)^{\ell/2}\Big]\,|\ell\ (-\ell)\rangle. \tag{7.85}$$

Putting Eq. (7.84) into Eq. (7.80) and then projecting into coordinate space, we find

$$\hbar^{\ell+m}\sqrt{\frac{(\ell+m)!(2\ell)!}{(\ell-m)!}}\,Y_\ell^m = (-1)^{\ell+m}\hbar^{\ell+m}e^{i(\ell+m)\phi}(1-\mu^2)^{m/2}\partial_\mu^{\ell+m}(1-\mu^2)^{\ell/2}\,Y_\ell^{-\ell}. \tag{7.86}$$

Using Eq. (7.75) with a factor $e^{-i\ell\phi}$ for $Y_\ell^{-\ell}$ and then simplifying everything, we find

$$Y_\ell^m = (-1)^{\ell+m}\frac{1}{2^\ell\ell!}\sqrt{\frac{2\ell+1}{4\pi}}\sqrt{\frac{(\ell-m)!}{(\ell+m)!}}\,(1-\mu^2)^{m/2}\partial_\mu^{\ell+m}(1-\mu^2)^\ell\,e^{im\phi}. \tag{7.87}$$

To summarize and clean up the notation a little bit, while breaking the result up into simpler factors, we have the **spherical harmonics**

$$Y_\ell^m(\theta,\phi) = (-1)^m\sqrt{\frac{2\ell+1}{4\pi}}\sqrt{\frac{(\ell-m)!}{(\ell+m)!}}\,P_\ell^m(\cos\theta)\,e^{im\phi}, \tag{7.88}$$
(spherical harmonics)

which are the coordinate-space representation of the eigenstates $|\ell\, m\rangle$. Here, it is conventional to define the **associated Legendre polynomials**

$$P_\ell^m(\mu) := (1-\mu^2)^{m/2}\partial_\mu^m P_\ell(\mu), \tag{7.89}$$
(associated Legendre polynomials)

which are written as derivative of the **Legendre polynomials**

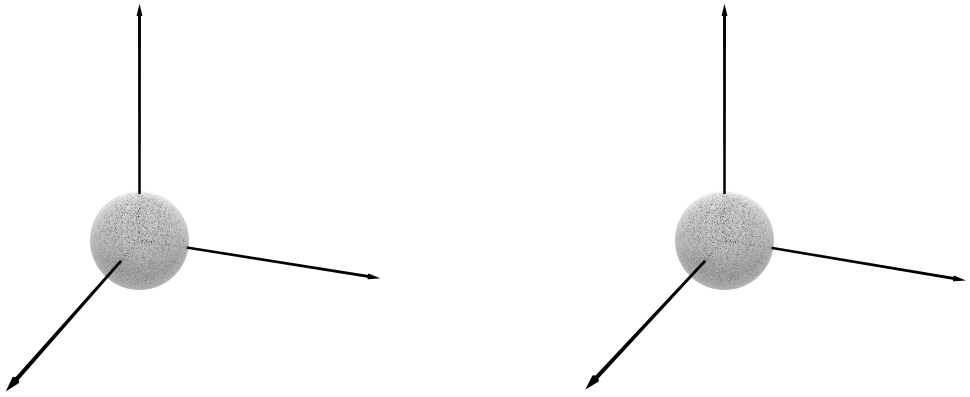
$$P_\ell(\mu) := \frac{1}{2^\ell\ell!}\partial_\mu^\ell(\mu^2-1)^\ell. \tag{7.90}$$
(Legendre polynomials)

As usual, $\mu = \cos\theta$ here. For handy reference, some of the lower-order spherical harmonics are listed below

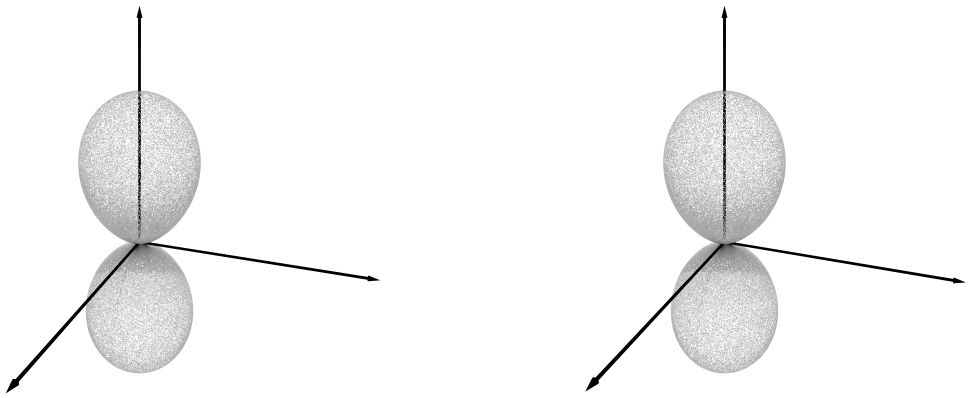
$$
\begin{aligned}
Y_0^0(\theta,\phi) &= \frac{1}{\sqrt{4\pi}} \\
Y_1^0(\theta,\phi) &= \sqrt{\frac{3}{4\pi}}\,\cos\theta \\
Y_1^{\pm 1}(\theta,\phi) &= \mp\sqrt{\frac{3}{8\pi}}\,\sin\theta\, e^{\pm i\phi} \\
Y_2^0(\theta,\phi) &= \sqrt{\frac{5}{16\pi}}\,\left(3\cos^2\theta - 1\right) \\
Y_2^{\pm 1}(\theta,\phi) &= \mp\sqrt{\frac{15}{8\pi}}\,\sin\theta\,\cos\theta\, e^{\pm i\phi} \\
Y_2^{\pm 2}(\theta,\phi) &= \sqrt{\frac{15}{32\pi}}\,\sin^2\theta\, e^{\pm 2i\phi}.
\end{aligned}
\tag{7.91}
$$

(example spherical harmonics)

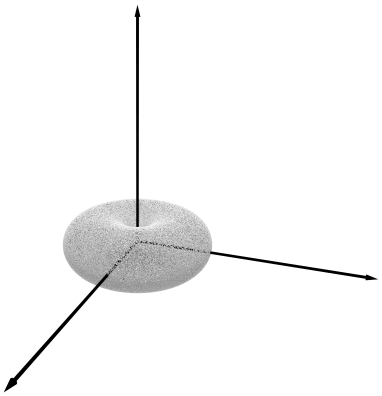
And here are corresponding plots of the same spherical harmonics:
$|Y_0^0(\theta,\phi)|^2$:

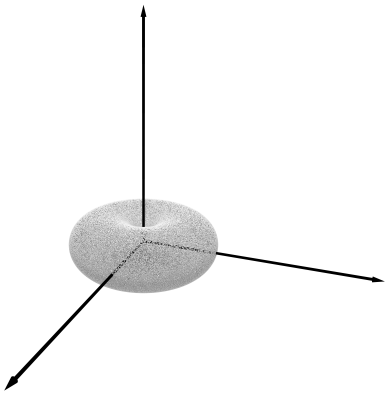


$|Y_1^0(\theta,\phi)|^2$:

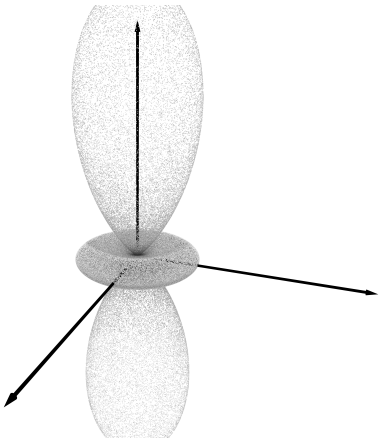


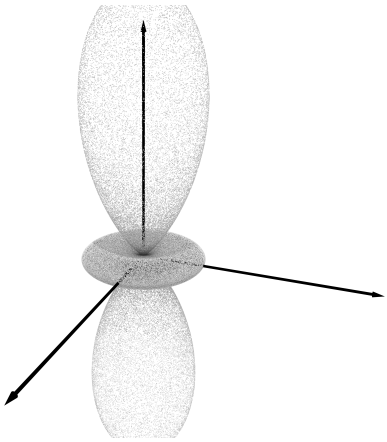
$|Y_1^{\pm 1}(\theta,\phi)|^2$:



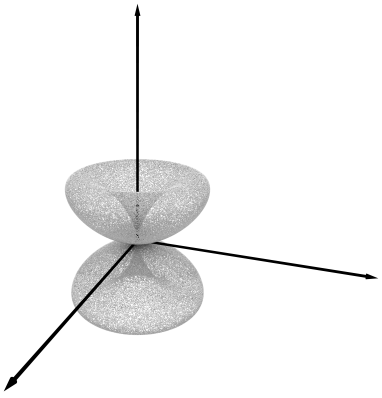


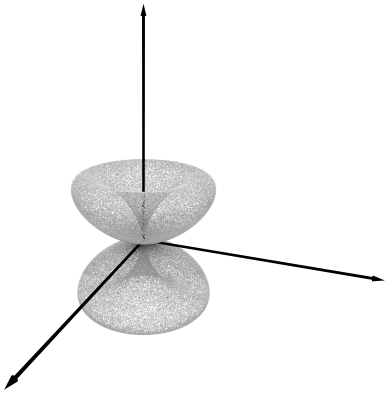
$|Y_2^0(\theta,\phi)|^2$:



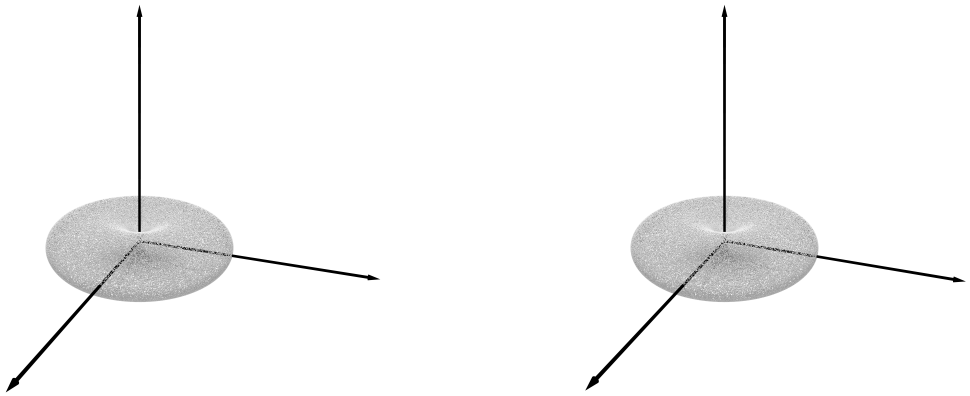


$|Y_2^{\pm 1}(\theta,\phi)|^2$:





$|Y_2^{\pm 2}(\theta,\phi)|^2$:



These spherical harmonics will be useful in later calculations.

7.3 Addition of Angular Momenta

7.3.1 Basis States

Suppose we have two angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$, and we want to consider their sum $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$. This is useful in describing the interaction with multiple quantum systems, where the interation can't distinguish the individual systems (for example, an optical field interacting with a cloud of atoms could see all the angular momenta of the individual atoms as one ''super'' angular momentum), or the interactions of two particles with angular momentum. We assume these angular momenta to correspond to independent degrees of freedom (different particles, different aspects of the same particle, etc.), and thus they commute:

$$[J_{1\alpha}, J_{2\beta}] = 0 \qquad \forall_{\alpha,\beta}. \tag{7.92}$$

Treating the two angular momenta as separate entities, we can construct simultaneous eigenstates of J_1^2, J_2^2, J_{1z}, and J_{2z}, since everybody here commutes. We will denote these eigenstates by $|j_1\ m_1; j_2\ m_2\rangle \equiv |j_1\ m_1\rangle|j_2\ m_2\rangle$, so that

$$\begin{aligned} J_1^2|j_1\ m_1; j_2\ m_2\rangle &= j_1(j_1+1)\hbar^2|j_1\ m_1; j_2\ m_2\rangle \\ J_2^2|j_1\ m_1; j_2\ m_2\rangle &= j_2(j_2+1)\hbar^2|j_1\ m_1; j_2\ m_2\rangle \\ J_{1z}|j_1\ m_1; j_2\ m_2\rangle &= m_1\hbar|j_1\ m_1; j_2\ m_2\rangle \\ J_{2z}|j_1\ m_1; j_2\ m_2\rangle &= m_2\hbar|j_1\ m_1; j_2\ m_2\rangle. \end{aligned} \tag{7.93}$$

Now note that the total angular momentum $\mathbf{J}$ has the characteristics of an angular momentum operator, since

$$[J_\alpha, J_\beta] = [J_{1\alpha} + J_{2\alpha}, J_{1\beta} + J_{2\beta}] = [J_{1\alpha}, J_{1\beta}] + [J_{2\alpha}, J_{2\beta}] = i\hbar\epsilon_{\alpha\beta\gamma}J_{1\gamma} + i\hbar\epsilon_{\alpha\beta\gamma}J_{2\gamma} = i\hbar\epsilon_{\alpha\beta\gamma}J_\gamma. \tag{7.94}$$

Thus, we may have simultaneous eigenstates of J^2 and J_z. Also, it is easy to see that J_1^2 and J_2^2 both commute with J^2 and J_z (but J_{1z} and J_{2z} don't commute with J^2), so that we can represent our states in terms of simultaneous eigenstates of J_1^2, J_2^2, J^2, and J_z, which we will label by $|j_1, j_2; j\ m\rangle$, so that

$$\begin{aligned} J_1^2|j_1, j_2; j\ m\rangle &= j_1(j_1+1)\hbar^2|j_1, j_2; j\ m\rangle \\ J_2^2|j_1, j_2; j\ m\rangle &= j_2(j_2+1)\hbar^2|j_1, j_2; j\ m\rangle \\ J^2|j_1, j_2; j\ m\rangle &= j(j+1)\hbar^2|j_1, j_2; j\ m\rangle \\ J_z|j_1, j_2; j\ m\rangle &= m\hbar|j_1, j_2; j\ m\rangle. \end{aligned} \tag{7.95}$$

Sometimes, the state $|j_1, j_2; j\ m\rangle$ is written more succinctly as $|j, m\rangle$ if j_1 and j_2 are clear from the context.

7.3.2 Transformation between Bases and Clebsch–Gordan Coefficients

Now we have two distinct bases by which to represent a general state. The basic problem of angular-momentum addition is thus to express any basis state in terms of a superposition of states from the other basis. This is easy to do by using the representations of the identity in each basis:

$$\begin{aligned} |j_1, j_2; j\ m\rangle &= \sum_{j_1' j_2' m_1 m_2} |j_1'\ m_1; j_2'\ m_2\rangle\langle j_1'\ m_1; j_2'\ m_2|j_1, j_2; j\ m\rangle \\ |j_1\ m_1; j_2\ m_2\rangle &= \sum_{j_1' j_2' j m} |j_1', j_2'; j\ m\rangle\langle j_1', j_2'; j\ m|j_1\ m_1; j_2\ m_2\rangle. \end{aligned} \tag{7.96}$$

The inner products on the right-hand sides of the above equations are **Clebsch–Gordan coefficients**. Note that J_1^2 and J_2^2 are Hermitian, and thus

$$\begin{aligned} \langle j_1', j_2'; j\ m|J_1^2|j_1\ m_1; j_2\ m_2\rangle &= j_1'(j_1'+1)\hbar^2\langle j_1', j_2'; j\ m|j_1\ m_1; j_2\ m_2\rangle \\ &= j_1(j_1+1)\hbar^2\langle j_1', j_2'; j\ m|j_1\ m_1; j_2\ m_2\rangle, \end{aligned} \tag{7.97}$$

so that the Clebsch–Gordan coefficient vanishes unless $j_1 = j_1'$ (and similarly $j_2 = j_2'$). Additionally, $J_z = J_{1z} + J_{2z}$, so

$$\begin{aligned} \langle j_1, j_2; j\ m|J_z|j_1\ m_1; j_2\ m_2\rangle &= (m_1+m_2)\hbar\langle j_1, j_2; j\ m|j_1\ m_1; j_2\ m_2\rangle \\ &= m\hbar\langle j_1, j_2; j\ m|j_1\ m_1; j_2\ m_2\rangle, \end{aligned} \tag{7.98}$$

and thus we must have

$$m = m_1 + m_2 \tag{7.99}$$
(angular-momentum conservation)

for the Clebsch–Gordan coefficient to be nonvanishing. Thus, we may rewrite the transformation relations (7.96) as

$$\begin{aligned} |j_1, j_2; j\ m\rangle &= \sum_{\substack{m_1 m_2 \\ (m_1+m_2=m)}} |j_1\ m_1; j_2\ m_2\rangle\langle j_1\ m_1; j_2\ m_2|j_1, j_2; j\ m\rangle \\ |j_1\ m_1; j_2\ m_2\rangle &= \sum_{\substack{jm \\ (m_1+m_2=m)}} |j_1, j_2; j\ m\rangle\langle j_1, j_2; j\ m|j_1\ m_1; j_2\ m_2\rangle, \end{aligned} \tag{7.100}$$

or omitting the redundant labels,

$$\begin{aligned} |j\ m\rangle &= \sum_{\substack{m_1 m_2 \\ (m_1+m_2=m)}} |j_1\ m_1; j_2\ m_2\rangle\langle j_1\ m_1; j_2\ m_2|j\ m\rangle \\ |j_1\ m_1; j_2\ m_2\rangle &= \sum_{\substack{jm \\ (m_1+m_2=m)}} |j\ m\rangle\langle j\ m|j_1\ m_1; j_2\ m_2\rangle, \end{aligned} \tag{7.101}$$
(transformation rules)

The other important constraint is

$$|j_1 - j_2| \le j \le j_1 + j_2 \tag{7.102}$$
(triangular condition)

(recall that $j_1, j_2 \ge 0$). To see this, first note that since $m = m_1 + m_2$, and the maximum value of m is the maximum value of j, but is also given by $j_1 + j_2$. Thus, $j_{\max} = j_1 + j_2$. To find the minimum value of j, note that in the $|j_1\ m_1; j_2\ m_2\rangle$ basis, there are $2j_1 + 1$ states associated with the the $|j_1\ m_1\rangle$ space and $2j_2 + 1$ states associated with the the $|j_2\ m_2\rangle$ space, and thus the composite space is spanned by $(2j_1 + 1)(2j_2 + 1)$

states. In the other basis, we get the correct number of states if $j_{\min} = |j_1 - j_2|$. That is, $j_{\min}$ is the solution to

$$\sum_{j=j_{\min}}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1), \tag{7.103}$$

which we can see because, assuming without loss of generality that $j_1 \geq j_2$,

$$\sum_{j=j_1-j_2}^{j_1+j_2} (2j+1) = \sum_{j=-j_2}^{j_2} [2(j_1+j)+1] = \sum_{j=-j_2}^{j_2} (2j_1+1) + \sum_{j=-j_2}^{j_2} 2j = (2j_1+1)(2j_2+1). \tag{7.104}$$

The cases $j = |j_1 - j_2|$ and $j = j_1 + j_2$ clearly correspond to antialigned and aligned constituent momentum vectors, respectively.

The Clebsch–Gordan coefficients obey orthogonality relations as follows. From the second transformation rule in Eqs. (7.101),

$$\langle j_1\ m_1'; j_2\ m_2' | j_1\ m_1; j_2\ m_2 \rangle = \sum_{jm} \langle j_1\ m_1'; j_2\ m_2' | j\ m \rangle \langle j\ m | j_1\ m_1; j_2\ m_2 \rangle, \tag{7.105}$$

The left-hand side is zero unless $m_1' = m_1$ and $m_2' = m_2$, so

$$\sum_{jm} \langle j_1\ m_1'; j_2\ m_2' | j\ m \rangle \langle j\ m | j_1\ m_1; j_2\ m_2 \rangle = \delta_{m_1 m_1'} \delta_{m_2 m_2'}.$$

(Clebsch–Gordan orthogonality relation) (7.106)

Similarly, the other transformation rule leads to

$$\sum_{m_1 m_2} \langle j\ m | j_1\ m_1; j_2\ m_2 \rangle \langle j_1\ m_1; j_2\ m_2 | j'\ m' \rangle = \delta_{jj'} \delta_{mm'},$$

(Clebsch–Gordan orthogonality relation) (7.107)

which are reasonably obvious applications of different representations of the identity operator.

7.3.3 Calculation of Clebsch–Gordan Coefficients

To determine the Clebsch–Gordan coefficients, we make use of the raising and lowering operators

$$\begin{aligned} J_{1\pm} &= J_{1x} \pm i J_{1y} \\ J_{2\pm} &= J_{2x} \pm i J_{2y} \\ J_\pm &:= J_{1\pm} + J_{2\pm}. \end{aligned} \tag{7.108}$$

Then by writing out $\langle j_1\ m_1; j_2\ m_2 | J_\pm | j\ m \rangle = \langle j_1\ m_1; j_2\ m_2 | (J_{1\pm} + J_{2\pm}) | j\ m \rangle$, we find

$$\begin{aligned} \sqrt{j(j+1) - m(m\pm1)}\, \langle j_1\ m_1; j_2\ m_2 | j\ m\pm1 \rangle = {} & \sqrt{j_1(j_1+1) - m_1(m_1\mp1)}\, \langle j_1\ m_1\mp1; j_2\ m_2 | j\ m \rangle \\ & + \sqrt{j_2(j_2+1) - m_2(m_2\mp1)}\, \langle j_1\ m_1; j_2\ m_2\mp1 | j\ m \rangle \end{aligned}$$

(Clebsch–Gordan recursion relation) (7.109)

This recursion relation, in addition to some initial conditions, is sufficient to compute the coefficients. The basic idea is as follows: Setting $m = j$ and taking the upper sign option in Eq. (7.109) gives

$$\begin{aligned} & \sqrt{j_1(j_1+1) - m_1(m_1-1)}\, \langle j_1\ m_1-1; j_2\ m_2 | j\ j \rangle \\ & \qquad + \sqrt{j_2(j_2+1) - m_2(m_2-1)}\, \langle j_1\ m_1; j_2\ m_2-1 | j\ j \rangle = 0, \end{aligned} \tag{7.110}$$

which together with the special cases of Eq. (7.107)

$$\sum_{\substack{m_1 m_2 \\ (m_1+m_2=j)}} |\langle j_1\ m_1; j_2\ m_2 | j\ j \rangle|^2 = 1 \tag{7.111}$$

that pin down the normalization, all coefficients of the form $\langle j_1\ m_1 - 1; j_2\ m_2 | j\ j\rangle$ can be determined up to an arbitrary phase. It is conventional to take the coefficients $\langle j_1\ j_1; j_2\ j - j_1 | j\ j\rangle$ to be real and positive.[3] The recursion relation (7.110) can then generate all the rest of the Clebsch–Gordon coefficients from these "basis cases," and an important consequence of the recursion relation (which only involves real recursion coefficients) and the phase convention is that by convention **all Clebsch–Gordon coefficients are real** (though not necessarily positive).

7.3.4 Explicit Formula

The above recursion procedure is fairly cumbersome, although sometimes useful. In a numerical calculation, it is convenient to have explicit formulae to implement any of the coupling coefficients. Fortunately, the Clebsch–Gordan coefficient may be computed according to the rather complicated formula[4]

$$\begin{aligned}
&\langle j_1, m_1; j_2, m_2 | j_3, m_3\rangle \\
&\quad = \delta_{(m_1+m_2),m_3} \sqrt{\frac{(j_1+j_2-j_3)!(j_1+j_3-j_2)!(j_2+j_3-j_1)!}{(j_1+j_2+j_3+1)!}} \\
&\qquad \times \sqrt{(2j_3+1)(j_1+m_1)!(j_1-m_1)!(j_2+m_2)!(j_2-m_2)!(j_3+m_3)!(j_3-m_3)!} \\
&\qquad \times \sum_{n=n_{\min}}^{n_{\max}} \frac{(-1)^n}{(j_1-m_1-n)!(j_3-j_2+m_1+n)!(j_2+m_2-n)!(j_3-j_1-m_2+n)!n!(j_1+j_2-j_3-n)!},
\end{aligned} \tag{7.112}$$

(Clebsch–Gordan coefficient: explicit formula)

where the summation limits

$$\begin{aligned}
n_{\min} &= \max\{j_2 - j_3 - m_1, j_1 + m_2 - j_3, 0\} \\
n_{\max} &= \min\{j_1 - m_1, j_2 + m_2, j_1 + j_2 - j_3\}
\end{aligned} \tag{7.113}$$

are chosen such that no factorial arguments are negative. For a nonzero result, we reiterate that we must have $m_1 + m_2 = m_3$, $|j_1 - j_2| \le j_3 \le |j_1 + j_2|$, $j_\alpha \ge 0$, and $|m_\alpha| \le j_\alpha$.

7.3.5 Symmetry Relations and Wigner 3-*j* Symbols

Now that we can compute the Clebsch–Gordan coefficients, we can ask, what are the shortcuts to relating them if we just want to permute some symbols? For example, recall that the coupling of two angular momenta according to

$$\mathbf{J}_1 + \mathbf{J}_2 = \mathbf{J}_3 \tag{7.114}$$

is represented by the coefficient $\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle$. However, $\mathbf{J}_1$ and $\mathbf{J}_2$ are on equal footing in being added together to form $\mathbf{J}_3$, and so we should be able to switch them without a problem, at least up to an overall phase. It turns out that according to the sign convention we have chosen,

$$\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle = (-1)^{j_1+j_2-j_3} \langle j_2\ m_2; j_1\ m_1 | j_3\ m_3\rangle. \tag{7.115}$$

(symmetry relation)

We can see this by redefining the index n in the explicit formula (7.112) according to $n \longrightarrow (j_1 + j_2 - j_3) - n$, with the limits redefined appropriately to avoid any negative factorials, together with the simultaneous exchanges $j_1 \longleftrightarrow j_2$ and $m_1 \longleftrightarrow m_2$. This transformation leaves the sum invariant, except for the sign $(-1)^{j_1+j_2-j_3}$ (the same exchanges leave the prefactor of the sum invariant as well).

We can go even farther than this. The addition (7.114) is clearly equivalent to the addition

$$\mathbf{J}_3 - \mathbf{J}_1 = \mathbf{J}_2, \tag{7.116}$$

[3] This is known as the **Condon–Shortley phase convention**. See, e.g., D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Oxford, 1968), Section 2.7.2, p. 33.

[4] D. M. Brink and G. R. Satchler, op. cit., p. 34, Eq. (2.34).

and thus we expect

$$\langle j_1\ -m_1; j_3\ m_3|j_2\ m_2\rangle \propto \langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle. \tag{7.117}$$

In fact, we can see that this is the case by noting that the recursion relation (7.109)

$$\begin{aligned}\sqrt{j_3(j_3+1)-m_3(m_3\pm1)}\,\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\pm1\rangle \\ = \sqrt{j_1(j_1+1)-m_1(m_1\mp1)}\,\langle j_1\ m_1\mp1; j_2\ m_2|j_3\ m_3\rangle \\ + \sqrt{j_2(j_2+1)-m_2(m_2\mp1)}\,\langle j_1\ m_1; j_2\ m_2\mp1|j_3\ m_3\rangle,\end{aligned} \tag{7.118}$$

upon the substitutions $|j_3\, m_3\rangle \longrightarrow |j_2\ m_2\rangle$, $|j_2\, m_2\rangle \longrightarrow |j_1\ -m_1\rangle$, $|j_1\, m_1\rangle \longrightarrow |j_3\ m_3\rangle$, and $\pm \longleftrightarrow \mp$, and multiplying through by $(-1)^{-m_1}$, becomes

$$\begin{aligned}(-1)^{-m_1}\sqrt{j_3(j_3+1)-m_3(m_3\pm1)}\,\langle j_3\ m_3\pm1; j_1\ -m_1|j_2\ m_2\rangle \\ = (-1)^{-(m_1\mp1)}\sqrt{j_1(j_1+1)-(-m_1)[-(m_1\mp1)]}\,\langle j_3\ m_3; j_1\ -(m_1\mp1)|j_2\ m_2\rangle \\ + (-1)^{-m_1}\sqrt{j_2(j_2+1)-m_2(m_2\mp1)}\,\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\mp1\rangle.\end{aligned} \tag{7.119}$$

This recursion relation has the same form as the original, and indicates that $(-1)^{-m_1}\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\rangle$ obeys the same recursion relation as $\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle$. Since the recursion relation determines the m-dependence of the Clebsch–Gordan coefficients, we conclude that these two coefficients are proportional,

$$\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle \propto (-1)^{-m_1}\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\rangle, \tag{7.120}$$

with the remaining proportionality constant to be determined depends only on the j's. To get the j-dependent amplitude, note that from Eq. (7.107) we may write

$$\begin{aligned}\sum_{m_1 m_2} |\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle|^2 = 1 \\ \sum_{m_1 m_3} |\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\rangle|^2 = 1.\end{aligned} \tag{7.121}$$

but since $m_1 + m_2 = m_3$ holds in either case, the sums simplify to

$$\begin{aligned}\sum_{m_2} |\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle|^2 = 1 \\ \sum_{m_3} |\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\rangle|^2 = 1.\end{aligned} \tag{7.122}$$

Noting that the coefficients are equivalent in each case and that we have already taken care of the m-dependence, we count $2j_2 + 1$ terms in the first sum and $2j_3 + 1$ in the second. Thus, for the sums to be equivalent, we require

$$\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle \propto (-1)^{-m_1}\sqrt{\frac{2j_3+1}{2j_2+1}}\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\rangle \tag{7.123}$$

where the remaining proportionality constant is a j-dependent phase. This we establish by noting the convention we already mentioned that $\langle j_1\ j_1; j_2\ (j_3 - j_1)|j_3\ j_3\rangle$ is always positive. In this case, we need a factor of $(-1)^{j_1}$ to cancel the factor of $(-1)^{-m_1}$ for this case, and so we can finally write the symmetry relation

$$\langle j_1\ m_1; j_2\ m_2|j_3\ m_3\rangle = (-1)^{j_1-m_1}\sqrt{\frac{2j_3+1}{2j_2+1}}\langle j_3\ m_3; j_1\ -m_1|j_2\ m_2\rangle.$$

(Clebsch–Gordan symmetry rule) (7.124)

We can then take $\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle$, apply Eq. (7.115), apply Eq. (7.124), and apply Eq. (7.115) again to find

$$\begin{aligned}\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle &= (-1)^{j_1+j_2-j_3}\langle j_2\ m_2; j_1\ m_1 | j_3\ m_3\rangle \\ &= (-1)^{j_1+j_2-j_3}(-1)^{j_2-m_2}\sqrt{\frac{2j_3+1}{2j_1+1}}\langle j_3\ m_3; j_2\ -m_2 | j_1\ m_1\rangle \\ &= (-1)^{j_1+j_2-j_3}(-1)^{j_2-m_2}(-1)^{j_3+j_2-j_1}\sqrt{\frac{2j_3+1}{2j_1+1}}\langle j_2\ -m_2; j_3\ m_3 | j_1\ m_1\rangle \\ &= (-1)^{j_2+m_2}(-1)^{2(j_2-m_2)}\sqrt{\frac{2j_3+1}{2j_1+1}}\langle j_2\ -m_2; j_3\ m_3 | j_1\ m_1\rangle,\end{aligned} \tag{7.125}$$

and noting that $j_2 - m_2$ is always an integer, so $(-1)^{2(j_2-m_2)} = 1$, we find the alternate symmetry relation

$$\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle = (-1)^{j_2+m_2}\sqrt{\frac{2j_3+1}{2j_1+1}}\langle j_2\ -m_2; j_3\ m_3 | j_1\ m_1\rangle. \tag{7.126}$$

(Clebsch–Gordan symmetry rule)

Noting that this rule amounts to a cyclic permutation of the angular momenta while flipping the orientation of one, we can apply this rule three times to find

$$\begin{aligned}\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle &= (-1)^{j_2+m_2}\sqrt{\frac{2j_3+1}{2j_1+1}}\langle j_2\ -m_2; j_3\ m_3 | j_1\ m_1\rangle \\ &= (-1)^{j_2+j_3+m_2+m_3}\sqrt{\frac{2j_3+1}{2j_2+1}}\langle j_3\ -m_3; j_1\ m_1 | j_2\ -m_2\rangle \\ &= (-1)^{j_1+j_2+j_3+m_1+m_2+m_3}\langle j_1\ -m_1; j_2\ -m_2 | j_3\ -m_3\rangle.\end{aligned} \tag{7.127}$$

Noting that $j_3 - m_3$ and $m_1 + m_2 - j_3$ are both integers, we can rewrite this as the final symmetry rule

$$\langle j_1\ m_1; j_2\ m_2 | j_3\ m_3\rangle = (-1)^{j_1+j_2-j_3}\langle j_1\ -m_1; j_2\ -m_2 | j_3\ -m_3\rangle. \tag{7.128}$$

(Clebsch–Gordan symmetry rule)

A nice way to summarize the symmetry relations here is to define the **Wigner 3-*j* symbol** in terms of the Clebsch–Gordan coefficient as

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} := \frac{(-1)^{j_1-j_2-m_3}}{\sqrt{2j_3+1}}\langle j_1, m_1; j_2, m_2 | j_3, -m_3\rangle. \tag{7.129}$$

(Wigner 3-j symbol)

Then the symmetries are as follows: The symbol on the left-hand side of Eq. (7.129) is invariant under *even* permutations of the columns, but *odd* permutations are accompanied by a factor $(-1)^{j_1+j_2+j_3}$. The simultaneous, triple replacement $m_{1,2,3} \longrightarrow -m_{1,2,3}$ is similarly accompanied by the same factor. Finally, the symbol is only nonvanishing if $m_1 + m_2 + m_3 = 0$, and if j_1, j_2, and j_3 obey the usual triangle condition.

7.4 Rotations and Irreducible Tensor Operators

7.4.1 Rotation Operator

What is the operator that induces a rotation in quantum mechanics? Rather than deduce it directly, we will ''cheat'' and simply quantize the classical version of a rotation. Consider the classical angle (generalized coordinate) ζ, with conjugate (angular) momentum J. The Hamiltonian $H = J$ leads to Hamilton's equations $\partial_t \zeta = 1$ and $\partial_t J = 0$. That is, J is a constant of the motion, and ζ evolves linearly in time as $\zeta(t) = t$.

Thus, time evolution according to this Hamiltonian is equivalent to a rotation through an angle t. Quantum mechanically, since this Hamiltonian is time-independent, the time-evolution operator is

$$U(t,0) = \exp\left(-\frac{iHt}{\hbar}\right) = \exp\left(-\frac{iJ\zeta}{\hbar}\right) =: R(\zeta), \tag{7.130}$$

then we have the rotation operator (for a two-dimensional system) for a rotation through angle ζ. Generalizing the Hamiltonian to $H = aJ_x + bJ_y + cJ_z$ (where $a^2 + b^2 + c^2 = 1$), a rotation by angle $\boldsymbol{\zeta}$ (that is, a rotation about the $\boldsymbol{\zeta}$-axis by angle ζ) is induced by the unitary rotation operator

$$R(\boldsymbol{\zeta}) := \exp\left(-\frac{i\mathbf{J}\cdot\boldsymbol{\zeta}}{\hbar}\right). \tag{7.131}$$
(rotation operator)

Note that a rotation of an angular-momentum state $|j\ m\rangle$ about the z-axis (the quantization axis) is particularly simple, as

$$R(\zeta\hat{z})|j\ m\rangle = \exp\left(-\frac{iJ_z\zeta}{\hbar}\right)|j\ m\rangle = e^{-im\zeta}|j\ m\rangle. \tag{7.132}$$
(rotation operator)

Physically, this is sensible because such a rotation cannot change the projection of the angular momentum vector onto the z axis. However, a rotation about any other axis is more complicated, as the result will in general be a superposition of angular-momentum states. Being a rotation, the j quantum number must be left unchanged (following directly from $[J^2, \mathbf{J}] = 0$, since this implies $[J^2, R(\boldsymbol{\zeta})] = 0$), but the superposition will involve states of other m values. This is a good way to see that the angular orientation of a state is encoded in the m quantum number; the j quantum number by itself doesn't tell you about orientation.

7.4.1.1 Rotation Matrix

To formalize the transformation of $|j\ m\rangle$ into a superposition of states $|j\ m'\rangle$ by a rotation we can write out an explicit rotation matrix in the basis of angular-momentum states. Wigner's convention is to write such a matrix as

$$R(\boldsymbol{\zeta})|j\ m\rangle = \sum_{m'=-j}^{j} |j\ m'\rangle\, d^{(j)}_{m'm}(\boldsymbol{\zeta}), \tag{7.133}$$
(action of rotation matrix)

where

$$d^{(j)}_{m'm}(\boldsymbol{\zeta}) := \langle j\ m'|R(\boldsymbol{\zeta})|j\ m\rangle = \langle j\ m'|e^{-i\mathbf{J}\cdot\boldsymbol{\zeta}/\hbar}|j\ m\rangle. \tag{7.134}$$
(rotation matrix)

Note the ''backwards'' convention for the matrix indices for the matrix-vector product in Eq. (7.133). The point is that there is a $(2j+1)\times(2j+1)$ rotation matrix $\mathbf{d}^{(j)}(\boldsymbol{\zeta})$ associated with the rotation operator $R(\boldsymbol{\zeta})$ when it acts on a subspace of angular-momentum states with fixed quantum number j.

If we follow one rotation $R(\boldsymbol{\alpha})$ by another rotation $R(\boldsymbol{\beta})$, we can represent the total rotation by a composite rotation operator R:

$$R = R(\boldsymbol{\beta})R(\boldsymbol{\alpha}). \tag{7.135}$$

Projecting into the angular-momentum representation and using the completeness relation,

$$\langle j\ m|R|j\ m'\rangle = \sum_{m''}\langle j\ m|R(\boldsymbol{\beta})|j\ m''\rangle\langle j\ m''|R(\boldsymbol{\alpha})|j\ m'\rangle. \tag{7.136}$$

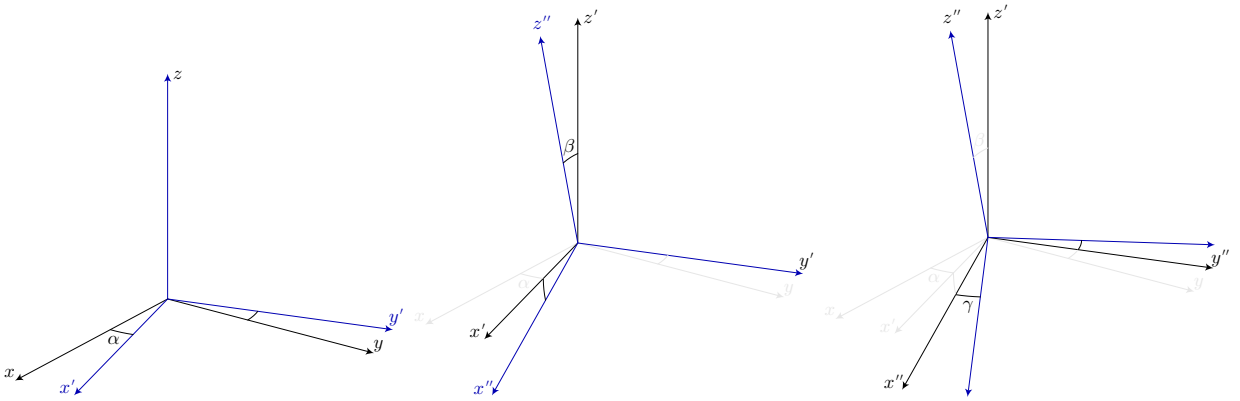
The corresponding rotation matrices thus compose by normal matrix multiplication, so long as the first rotation to operate is the rightmost:

$$\mathbf{d}^{(j)} = \mathbf{d}^{(j)}(\boldsymbol{\beta})\,\mathbf{d}^{(j)}(\boldsymbol{\alpha}). \tag{7.137}$$
(composition of rotations)

This property is very useful in decomposing arbitrary rotations, as we now discuss.

7.4.1.2 Euler Angles

As in classical mechanics, a general rotation may be represented as a composition of rotations through the three **Euler angles**: first rotate about the z-axis by angle α, then rotate about the new y-axis by angle β, and finally rotate about the new z-axis by angle γ. These angles are illustrated in the diagrams below. Note that the rotation operators act on the *state*, not the coordinate system; however, we are *also* considering rotations of the axes solely to define the second and third rotations.



Thus an arbitrary rotation R may always decomposed in the form

$$R(\alpha,\beta,\gamma) = R(\boldsymbol{\gamma})R(\boldsymbol{\beta})R(\boldsymbol{\alpha}), \tag{7.138}$$

where again $\boldsymbol{\alpha} = \alpha\hat{z}$, $\boldsymbol{\beta} = \beta\hat{y}'$, where $\hat{y}'$ is along the new y-direction after the $\boldsymbol{\alpha}$ rotation, and $\boldsymbol{\gamma} = \gamma\hat{z}''$, where $\hat{z}''$ is along the new z-direction after the $\boldsymbol{\beta}$ rotation. Clearly, $R(\boldsymbol{\alpha})$ is written to the right since it is the first rotation, and thus must operate first on the state vector. (The order is important, because in general rotation operators for different axes do not commute.) Writing these operators out explicitly,

$$R(\alpha,\beta,\gamma) = e^{-i\gamma J_{z''}/\hbar}\, e^{-i\beta J_{y'}/\hbar}\, e^{-i\alpha J_z/\hbar}. \tag{7.139}$$

But now, since $R(\boldsymbol{\beta})$ is written in terms of the coordinate system after the $R(\boldsymbol{\alpha})$ rotation, we can write this rotation as a rotated version of the operator in the original coordinate system:

$$e^{-i\beta J_{y'}/\hbar} = R(\boldsymbol{\alpha})\, e^{-i\beta J_y/\hbar}\, R^\dagger(\boldsymbol{\alpha}) = e^{-i\alpha J_z/\hbar}\, e^{-i\beta J_y/\hbar}\, e^{i\alpha J_z/\hbar}. \tag{7.140}$$

Similarly, for the last rotation, we can write

$$e^{-i\gamma J_{z''}/\hbar} = R(\boldsymbol{\beta})\, e^{-i\gamma J_{z'}/\hbar}\, R^\dagger(\boldsymbol{\beta}) = e^{-i\beta J_{y'}/\hbar}\, e^{-i\gamma J_{z'}/\hbar}\, e^{i\beta J_{y'}/\hbar}, \tag{7.141}$$

and putting this into Eq. (7.139), we find

$$R(\alpha,\beta,\gamma) = e^{-i\beta J_{y'}/\hbar}\, e^{-i\gamma J_{z'}/\hbar}\, e^{-i\alpha J_z/\hbar}. \tag{7.142}$$

Now putting in Eq. (7.140) and the analogous result with $J_{z'}$,

$$\boxed{R(\alpha,\beta,\gamma) = e^{-i\alpha J_z/\hbar}\, e^{-i\beta J_y/\hbar}\, e^{-i\gamma J_z/\hbar}.} \tag{7.143}$$
(rotation operator, Euler angles)

Conveniently, then, a rotation according to the Euler angles may be implemented solely in the original coordinate system, if the order of the rotations is *reversed*. (Of course, this result has to hold classically, as well.)

Now to return to the rotation matrix. Using the definition (7.134) for the matrix corresponding to this rotation operator,

$$D^{(j)}_{m'm}(\alpha,\beta,\gamma) = \langle j\ m'|R|j\ m\rangle = \langle j\ m'|e^{-i\alpha J_z/\hbar}\, e^{-i\beta J_y/\hbar}\, e^{-i\gamma J_z/\hbar}|j\ m\rangle. \tag{7.144}$$

(The convention is to capitalize the "D" for the composite rotation of the three Euler angles, leaving "d" to denote simple rotations.) The first and last rotations are thus easy to represent, leaving the second rotation as the only nontrivial one:

$$D^{(j)}_{m'm}(\alpha,\beta,\gamma) = e^{-im'\alpha}\, d^{(j)}_{m'm}(\beta\hat{y})\, e^{-im\gamma}. \tag{7.145}$$

(rotation matrix, Euler angles)

Wigner's explicit expression for the remaining rotation matrix is[5]

$$d^{(j)}_{m'm}(\beta\hat{y}) = \sqrt{(j+m)!(j-m)!(j+m')!(j-m')!} \times \sum_s \frac{(-1)^s}{(j-m'-s)!(j+m-s)!(s+m'-m)!s!} \left(\cos\frac{\beta}{2}\right)^{2j+m-m'-2s} \left(-\sin\frac{\beta}{2}\right)^{m'-m+2s}, \tag{7.146}$$

(middle rotation matrix, explicit form)

where the sum is over all values of s where the factorials are nonnegative. This form is particularly useful for computer implementation of the rotation matrices. We can also see from this formula that under the replacement $\beta \longrightarrow -\beta$, only the sin factor changes sign, so that

$$d^{(j)}_{m'm}(-\beta\hat{y}) = (-1)^{m'-m} d^{(j)}_{m'm}(\beta\hat{y}), \tag{7.147}$$

since the $2s$ part never contributes a minus sign. Furthermore, this formula is invariant under the replacements $m \longrightarrow -m'$ and $m' \longrightarrow -m$,

$$d^{(j)}_{-m,-m'}(\beta\hat{y}) = d^{(j)}_{m'm}(\beta\hat{y}). \tag{7.148}$$

Finally, since the rotation by $-\beta$ is the transpose of the rotation by β (this rotation matrix is orthogonal),

$$d^{(j)}_{m,m'}(-\beta\hat{y}) = d^{(j)}_{m'm}(\beta\hat{y}). \tag{7.149}$$

Combining these last three expressions, we find

$$d^{(j)}_{mm'}(\beta\hat{y}) = (-1)^{m'-m} d^{(j)}_{-m,-m'}(\beta\hat{y}). \tag{7.150}$$

This last expression may be generalized to arbitrary axes. Combining it with Eq. (7.145) gives

$$d^{(j)}_{m'm}(\boldsymbol{\zeta}) = (-1)^{m-m'} d^{(j)*}_{-m',-m}(\boldsymbol{\zeta}), \tag{7.151}$$

(rotation matrix conjugation)

where the complex conjugation "undoes" the minus signs of m and m' in the exponents of the general rotation matrix.

7.4.1.3 Active and Passive Rotations

When discussing rotations, there are generally *two* types. An **active rotation** rotates a vector (in this case, a state), as you might expect, with respect to a static coordinate system. On the other hand, a **passive rotation** is a rotation of a coordinate system, while leaving the vector fixed. Classically, an active rotation by an angle θ is equivalent to a passive rotation by angle $-\theta$, with respect to the relative orientation of vector and axis system. So, the question is, what kind of rotation are we dealing with in quantum mechanics? The fact that we used the rotation operator to rotate the axis system in the derivation of Eq. (7.143) suggests a passive rotation, but on the other hand the definition (7.133) of the rotation matrix involved an operation on a state $|j\ m\rangle$.

The correct interpretation is best seen in the matrix transformation of a state. Consider a rotated version $|\tilde{\psi}\rangle$ of $|\psi\rangle$:

$$|\tilde{\psi}\rangle = R|\psi\rangle. \tag{7.152}$$

[5] M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, 1957), p. 52.

Assuming $|\psi\rangle$ can be represented in terms of eigenstates $|j\ m\rangle$ with fixed j, we can project with $\langle j\ m|$:

$$\langle j\ m|\tilde{\psi}\rangle = \langle j\ m|R|\psi\rangle = \sum_{m'}\langle j\ m|R|j\ m'\rangle\langle j\ m'|\psi\rangle. \tag{7.153}$$

Then in terms of the rotation matrix (7.134), this transformation becomes

$$\langle j\ m|\tilde{\psi}\rangle = \sum_{m'} d^{(j)}_{mm'}\langle j\ m'|\psi\rangle. \tag{7.154}$$
(active rotation)

This is the transformation of the coefficients in the angular-momentum representation—in other words, the usual matrix-vector multiplication. Indeed, the rotation matrix acts in the usual matrix way, in contrast to Eq. (7.133), where the *transpose* of the rotation matrix acts on the $|j\ m\rangle$. (Remember that a transpose of a rotation matrix is a rotation in the opposite direction, at least in the case of a *real* matrix.) Thus, Eq. (7.154) is the active rotation, while the defining relation (7.133) for the rotation operator,

$$R(\boldsymbol{\zeta})|j\ m\rangle = \sum_{m'=-j}^{j} |j\ m'\rangle\, d^{(j)}_{m'm}(\boldsymbol{\zeta}), \tag{7.155}$$
(passive rotation)

being the transformation of a *basis vector* defining the standard angular-momentum representation, is the passive counterpart to the active rotation (7.154). This also explains Wigner's convention of the rotation matrix in Eq. (7.155).

Correspondingly, Eq. (7.154) came from Eq (7.152), so R itself is an active rotation when acting on a state vector. Recall that when considering an expectation value (which is invariant under rotations), it can be computed in either the unrotated or rotated frame, in view of

$$\langle\psi|A|\psi\rangle = \langle\psi|R^\dagger(RAR^\dagger)R|\psi\rangle, \tag{7.156}$$

provided we interpret $RAR^\dagger$ as the rotated operator. This is analogous to the passive transformation in the general case, and it is *clearly* a passive transformation in the case where A is a coordinate operator or an angular-momentum operator. This is why we could use the rotation operator to transform out of the new Euler-angle coordinate systems in the proof of the backwards form (7.143) of the rotation operator. The rotated scalar product here is rotation-invariant precisely because the effects of the active and passive rotations cancel. A good example of the importance of distinguishing active and passive rotations is the mapping of the rotation matrix between the Cartesian and spherical bases (see Problem 7.21).

7.4.1.4 Simple Rotation Matrix Examples

The rotation matrices are still a bit abstract at this point, and while Eq. (7.146) is handy for calculations, it doesn't do much to make the matrices intuitive. Writing out the simplest three cases aids intuition a little bit, but even more so when writing these out in detail. Ignoring for the moment the simpler α and γ rotations, the β rotation has the form for $j = 0$

$$\left[d^{(0)}_{m'm}(\beta\hat{y})\right] = \left[\ 1\ \right]. \tag{7.157}$$

You probably could have guessed this. This is a 1×1 unitary matrix, and the phases are only associated with rotations about the z-axis, which pretty much leaves unity.

For $j = 1/2$, the rotation matrix has the form (see Problem 9.1 for a general representation of the spin-½ rotation matrix)

$$\left[d^{(1/2)}_{m'm}(\beta\hat{y})\right] = \begin{bmatrix} \cos(\beta/2) & -\sin(\beta/2) \\ \sin(\beta/2) & \cos(\beta/2) \end{bmatrix}. \tag{7.158}$$

We have to be careful now to specify the matrix convention here.[6] The m index labels the columns, and *decreases* from $+1/2$ to $-1/2$ going towards the right-hand side of the matrix; while the m' index labels the rows, and decreases going towards the bottom side. Thus, the lower-right matrix element is $m' = -1/2, m = -1/2$. This is the normal matrix convention in terms of index order, but the matrix indices usually increase going down or to the right. Note that this $j = 1/2$ rotation matrix has the (further) odd property that a rotation through 2π gives the negative identity matrix (the same happens with the phase factors for a 2π rotation in α or γ). It is only a 4π rotation that leaves the state untouched. Again, this means that half-integer angular momenta don't have coordinate-space representations; it doesn't mean they aren't allowed. Otherwise, this rotation matrix has the expected form for a classical rotation matrix confined to the plane, although the rotation angle is $\beta/2$ instead of β.

For $j = 1$, the rotation matrix has the form

$$\left[d^{(1)}_{m'm}(\beta\hat{y})\right] = \begin{bmatrix} \dfrac{1+\cos\beta}{2} & \dfrac{-\sin\beta}{\sqrt{2}} & \dfrac{1-\cos\beta}{2} \\ \dfrac{\sin\beta}{\sqrt{2}} & \cos\beta & \dfrac{-\sin\beta}{\sqrt{2}} \\ \dfrac{1-\cos\beta}{2} & \dfrac{\sin\beta}{\sqrt{2}} & \dfrac{1+\cos\beta}{2} \end{bmatrix}. \tag{7.159}$$

This is beginning to be complicated for a general rotation angle, but is easier to interpret for specific cases (Problem 7.13). In each of the rotation matrices, the generalization to the three Euler angles means multiplying the matrix rows by $e^{-im\alpha}$ and the matrix columns by $e^{-im'\gamma}$ (again, with m' or m decreasing, respectively, moving downward or rightward, with the matrix convention we are using). (See Problem 7.21 for the exact form.)

7.4.1.5 Rotation of Spherical Harmonics

An important relation comes from considering the sum of products of spherical harmonics,

$$\sum_m \langle\theta_2,\phi_2|\ell\ m\rangle\langle\ell\ m|\theta_1,\phi_1\rangle = \sum_m Y_\ell^{m*}(\theta_1,\phi_1)\,Y_\ell^m(\theta_2,\phi_2), \tag{7.160}$$

for two spherical angles (θ_1,ϕ_1) and (θ_2,ϕ_2). We now intend to show that this expression is independent of orientation (i.e., it is a scalar under rotations) by showing it is equivalent to the rotated version

$$\sum_m \langle\theta_2,\phi_2|R|\ell\ m\rangle\,\langle\ell\ m|R^{-1}|\theta_1,\phi_1\rangle = \sum_m Y_\ell^{m*}(\theta_1',\phi_1')\,Y_\ell^m(\theta_2',\phi_2'), \tag{7.161}$$

for some rotation operator R, where $R|\ell,m\rangle$ is the rotated state. Recall that there are two ways to think of a rotation: the first is that the rotation operator acts on (and rotates) the state vector, while the other is that the rotation operator acts on the basis vectors $|\theta,\phi\rangle$ and rotates the coordinate system in the opposite sense. Thus, the rotated angles (θ_1',ϕ_1') and (θ_2',ϕ_2') are defined by $|\theta_\alpha',\phi_\alpha'\rangle := R^{-1}|\theta_\alpha,\phi_\alpha\rangle$. The rotation operator has a matrix representation that we will denote by $d^{(\ell)}_{m'm}$, which is a unitary matrix. Thus, Eq. (7.161) becomes

$$\sum_m Y_\ell^{m*}(\theta_1',\phi_1')\,Y_\ell^m(\theta_2',\phi_2') = \sum_{mm'm''} d^{(\ell)}_{m'm}\,d^{(\ell)*}_{mm''}\langle\theta_2,\phi_2|\ell\ m'\rangle\,\langle\ell\ m''|\theta_1,\phi_1\rangle, \tag{7.162}$$

where we have used the unitarity of the rotation matrix. We can carry out the sum over m by again using the unitarity of the rotation matrix, which we may write as

$$\sum_m d^{(\ell)}_{m'm}\,d^{(\ell)*}_{mm''} = \delta_{m'm''}, \tag{7.163}$$

[6] To wit: these matrices are conveniently computed by *Mathematica*, but it's important to keep track of the sign convention there. For example, `WignerD[{j, -m, -n]}, α, β, γ]` gives the matrix element $D^{(j)}_{mn}(\alpha,\beta,\gamma)$, but to display the $j = 1/2$ rotation matrix in the form (7.158), the command is `Table[WignerD[{j, m, n}, 0, β, 0], {m, -j, j}, {n, -j, j}] /. j -> 1/2 // MatrixForm`, because *Mathematica*'s convention is for the index value to increase down and to the right, which undoes the reversed index-sign convention.

so that we arrive at

$$\sum_m Y_\ell^{m*}(\theta_1', \phi_1')\, Y_\ell^m(\theta_2', \phi_2') = \sum_m \langle \theta_2, \phi_2 | \ell\ m\rangle\, \langle \ell\ m | \theta_1, \phi_1\rangle, \tag{7.164}$$

after dropping primes from the remaining dummy index. Then comparing to Eq. (7.160), we now see the independence of the sum under rotations:

$$\sum_m Y_\ell^{m*}(\theta_1', \phi_1')\, Y_\ell^m(\theta_2', \phi_2') = \sum_m Y_\ell^{m*}(\theta_1, \phi_1)\, Y_\ell^m(\theta_2, \phi_2). \tag{7.165}$$

In particular, we may choose the rotation such that (θ_1', ϕ_1') point along the z-axis, and $\phi_2' = 0$. Now we use the fact that $P_l^m(\cos 0) = P_l^m(1) = \delta_{m0}$, and so from Eq. (7.88), we have

$$Y_\ell^m(0, \phi) = \sqrt{\frac{2\ell + 1}{4\pi}}\, \delta_{m0}. \tag{7.166}$$

Thus we arrive at the **spherical-harmonic addition theorem**

$$Y_\ell^0(\theta, 0) = \sqrt{\frac{4\pi}{2\ell + 1}} \sum_m Y_\ell^{m*}(\theta_1, \phi_1)\, Y_\ell^m(\theta_2, \phi_2), \tag{7.167}$$
(addition theorem)

where $\theta = \theta_2'$ is the angle between the radial vectors corresponding to the two directions (θ_1, ϕ_1) and (θ_2, ϕ_2).

Taking $\theta_1 = \theta_2$ and $\phi_1 = \phi_2$, so that $\theta = 0$ in the addition theorem, we can drop the subscripts and write the sum rule

$$\sum_{m=-\ell}^{\ell} |Y_\ell^m(\theta, \phi)|^2 = \frac{2\ell + 1}{4\pi}, \tag{7.168}$$
(sum rule)

where we have again used Eq. (7.166). This sum rule is essentially just another statement of the rotational invariance of products of spherical harmonics when summed over m. This statement indicates indirectly that the m quantum number determines the orientation of the modes; summing over it results in an isotropic angular distribution.

7.4.2 Irreducible Tensor Operators

Now that we have defined and worked with rotation operators, it's a good time to talk about things that get rotated. Yes, angular-momentum eigenstates, but operators on these states *also* rotate. These rotatable things include operators like the position vector, which as we noted before, wants to rotate in the same way as $|1\ m\rangle$. These transformations under rotations will lead us to the general (and formidably named) notion of irreducible tensor operators.

7.4.2.1 Spherical Basis

As a prelude to introducing irreducible tensor operators, we will examine the **spherical basis**, which is a relatively simple special case of tensor operators. The spherical basis is simply an alternative to the Cartesian vector basis that is especially convenient when dealing with angular momentum. In terms of the Cartesian basis vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$, the spherical basis vectors are defined as

$$\begin{aligned} \hat{\mathrm{e}}_{\pm 1} &:= \mp \frac{1}{\sqrt{2}}(\hat{x} \pm i\hat{y}) = -(\hat{\mathrm{e}}_{\mp 1})^* \\ \hat{\mathrm{e}}_0 &:= \hat{z} = (\hat{\mathrm{e}}_0)^*, \end{aligned} \tag{7.169}$$
(spherical basis vectors)

The signs may be a little odd here, but the basis vectors here are more or less what you expect, for example, from taking the vector $|j\ m\rangle = |1\ 0\rangle$, and rotating it to point along the x and y directions (Problem 7.13). Likewise, if the Cartesian components of a vector $\mathbf{A}$ are defined such that $\mathbf{A} = A_x\hat{x} + A_y\hat{y} + A_z\hat{z}$, so that for

example $A_x = \hat{x}\cdot\mathbf{A}$, then the components of $\mathbf{A}$ in the spherical basis are given analogously by $A_q := \hat{\mathrm{e}}_q\cdot\mathbf{A}$, so that

$$\begin{aligned} A_{\pm1} &= \mp\frac{1}{\sqrt{2}}(A_x \pm iA_y) \\ A_0 &= A_z, \end{aligned} \qquad \text{(vector components in spherical basis)} \tag{7.170}$$

and thus

$$\mathbf{A} = \sum_q (-1)^q A_q \hat{\mathrm{e}}_{-q} = \sum_q \hat{\mathrm{e}}_q^* A_q. \qquad \text{(vector in spherical basis)} \tag{7.171}$$

This funny form for the vector in spherical components comes about because $\hat{\mathrm{e}}_q^*\cdot\hat{\mathrm{e}}_{q'} = \delta_{qq'}$, so we really need to think about products of vectors, where one of them is conjugated (which is, of course, a natural idea in quantum mechanics). Inverting Eqs. (7.170) gives

$$\begin{aligned} A_x &= -\frac{1}{\sqrt{2}}(A_1 - A_{-1}) \\ A_y &= \frac{i}{\sqrt{2}}(A_1 + A_{-1}) \\ A_z &= A_0, \end{aligned} \tag{7.172}$$

with, of course, the same relations for the Cartesian basis vectors in terms of the spherical basis vectors. Note that the choice of minus signs may seem kind of odd here, but it is dictated by the natural way that $j = 1$ objects rotate (Problem 7.13). In the spherical basis, the dot product of two vectors is given by

$$\mathbf{A}\cdot\mathbf{B} = \sum_q (-1)^q A_q \hat{\mathrm{e}}_{-q}\cdot\mathbf{B} = \sum_q (-1)^q A_q B_{-q} = \sum_q A_q (\mathbf{B}^*)_q^*, \qquad \text{(dot product in spherical basis)} \tag{7.173}$$

so that $\mathbf{A}^*\cdot\mathbf{B} = \sum_q (A_q)^* B_q$ and $|\mathbf{A}|^2 = \sum_q |A_q|^2$. [Note that the quantity $(\mathbf{B}^*)_q \equiv \hat{\mathrm{e}}_q\cdot(\mathbf{B}^*)$ appearing in the above equation refers to conjugation of the *Cartesian* vector components, $\mathbf{B}^* = B_x^*\hat{x} + B_y^*\hat{y} + B_z^*\hat{z}$.] Finally, we note that the components of the position vector $\mathbf{r}$ can be written

$$\begin{aligned} r_{\pm1} &= \mp\frac{r}{\sqrt{2}}\sin\theta\, e^{\pm i\phi} \\ r_0 &= r\cos\theta, \end{aligned} \qquad \text{(position operator in spherical basis)} \tag{7.174}$$

or more compactly,

$$r_q = r\sqrt{\frac{4\pi}{3}}\, Y_1^q(\theta,\phi). \qquad \text{(position operator as spherical harmonic)} \tag{7.175}$$

That is, the position operator is in some sense an expression of spherical harmonics—it *wants* to transform like angular momentum states $|1\ m\rangle$.

7.4.2.2 General Definition

The position vector here (as with any Cartesian three-vector) in the spherical basis is a **vector operator**, because of the way the three components transform among each other under rotations. We will now generalize this notion of sets of operators that are closed under rotations. An **irreducible tensor operator** of rank k (specifically, a spherical tensor operator), which we denote by $\mathbf{T}^{(k)}$ is a set of $2k+1$ operators that transform among themselves under rotations in the same way as the angular-momentum states $|j\ m\rangle$, where $j = k$:

$$R(\boldsymbol{\zeta})T_q^{(k)}R^\dagger(\boldsymbol{\zeta}) = \sum_{q'=-k}^{k} T_{q'}^{(k)} d_{q'q}^{(k)}(\boldsymbol{\zeta}). \qquad \text{(spherical tensor operator)} \tag{7.176}$$

Equivalently, they transform in the same way under rotations as the spherical harmonics,

$$Y_\ell^m(\theta',\phi') = \sum_{m'} Y_\ell^{m'}(\theta,\phi)\, d^{(\ell)}_{m'm}, \tag{7.177}$$

where $\langle\theta,\phi|\ell\ m\rangle = Y_\ell^m(\theta,\phi)$ is the unrotated function, and $\langle\theta,\phi|R|\ell\ m\rangle = Y_\ell^m(\theta',\phi')$ is the rotated form. In this context, *irreducible* means that there is no proper subset of the component operators that transform among themselves in a similar way. This is already guaranteed by the definition, as the set of angular-momentum basis states $|j\ m\rangle$ is irreducible in the same sense.

This definition actually introduces **spherical tensors** in general: that is, sets of components that transform into each other. Since again we require that they transform as the spherical harmonics, then the spherical harmonics Y_ℓ^m give a particular example of a spherical tensor of rank ℓ. The tensor *operator* comes about when we take each component of the tensor to be an operator. Since we have already seen that the position operator in the spherical basis is proportional to Y_1^m, as in Eq. (7.175), we know that $\mathbf{r}$ transforms as a spherical tensor of rank 1. Thus, $\mathbf{r}$ is an example of a rank-1 irreducible tensor operator according to the definition here, which is again also a vector operator.

7.4.2.3 Cartesian Tensors

The more familiar type of tensor is the **Cartesian tensor**, of the form $M_{\alpha\beta}$, for example, for a rank-2 tensor, where α and β range from 1 to 3 (or x to z). A rank-k Cartesian tensor is generally represented by k indices, and transforms under rotations according to

$$\tilde{M}_{\alpha_1\alpha_2\cdots\alpha_k} = R_{\alpha_1\beta_1}R_{\alpha_2\beta_2}\cdots R_{\alpha_k\beta_k}M_{\beta_1\beta_2\cdots\beta_k}, \tag{7.178}$$

where

$$R_{\alpha\beta} = \langle\alpha|R|\beta\rangle \tag{7.179}$$

is the rotation operator expressed in Cartesian coordinates. That is, the rotation operator is applied to each dimension, represented by each index.

How is the Cartesian tensor related to the irreducible tensors? Well, returning to the rank-2 example, the Cartesian tensor operator has nine independent component operators, whereas the irreducible, rank-2 tensor has only five. The Cartesian tensor must be reducible, and we can reduce it as follows. We may construct a scalar, or rank-0 operator, by computing the trace,

$$M^{(0)} = \mathrm{Tr}[M_{\alpha\beta}] = M_{\alpha\alpha}. \tag{7.180}$$
(scalar part)

This is invariant under rotations, since computing the trace after a rotation gives $\mathrm{Tr}[R\mathbf{M}R^\dagger] = \mathrm{Tr}[\mathbf{M}]$ after cyclic permutation under the trace. We can then form a vector (rank-1) operator as

$$M^{(1)}_\mu = \epsilon_{\mu\alpha\beta}(M_{\alpha\beta} - M_{\beta\alpha}), \tag{7.181}$$
(vector part)

which has three independent components and is clearly related to the antisymmetric part of $M_{\alpha\beta}$. To see that it transforms as a vector under rotations, we can compute the vector after rotation of the tensor, with the result

$$\begin{aligned}\tilde{M}^{(1)}_\mu &= \epsilon_{\mu\alpha\beta}[R_{\alpha\sigma}M_{\sigma\tau}(R^\dagger)_{\tau\beta} - R_{\beta\tau}M_{\tau\sigma}(R^\dagger)_{\sigma\alpha}] \\ &= \epsilon_{\mu\alpha\beta}(R_{\alpha\sigma}R_{\beta\tau}M_{\sigma\tau} - R_{\beta\tau}R_{\alpha\sigma}M_{\tau\sigma}).\end{aligned} \tag{7.182}$$

Now note that the cross product $\mathbf{A}\times\mathbf{B}$ of two vectors, after rotating each vector, is the same as the rotation of the cross product itself, or

$$(\mathbf{RA})\times(\mathbf{RB}) = \mathbf{R}(\mathbf{A}\times\mathbf{B}), \tag{7.183}$$

where $\mathbf{R}$ is the rotation matrix. Expressed in components, this becomes

$$\epsilon_{\mu\alpha\beta}(R_{\alpha\sigma}A_\sigma)(R_{\beta\tau}B_\tau) = R_{\mu\nu}(\epsilon_{\nu\sigma\tau}A_\sigma B_\tau). \tag{7.184}$$

Since this holds for any $\mathbf{A}$ and $\mathbf{B}$, we may drop them and write

$$\epsilon_{\mu\alpha\beta}R_{\alpha\sigma}R_{\beta\tau} = R_{\mu\nu}\epsilon_{\nu\sigma\tau}. \tag{7.185}$$

Putting this into Eq. (7.182),

$$\tilde{M}^{(1)}_{\mu} = R_{\mu\nu}\epsilon_{\nu\sigma\tau}(M_{\sigma\tau} - M_{\tau\sigma}), \tag{7.186}$$

which is the proper vector rotation of Eq. (7.181). Obviously, this vector operator is still expressed in Cartesian components, but can be transformed to a spherical tensor by Eqs. (7.170).

Finally, the reduced (now irreducible) rank-2 tensor is what remains, or is in other words the original tensor with the trace and antisymmetric parts subtracted away,

$$M^{(2)}_{\alpha\beta} = M_{(\alpha\beta)} - \frac{1}{3}M_{\mu\mu}\delta_{\alpha\beta}, \tag{7.187}$$
(irreducible tensor part)

where $M_{(\alpha\beta)} = (M_{\alpha\beta} + M_{\beta\alpha})/2$ denotes the symmetrized Cartesian tensor. The resulting tensor is clearly symmetric and traceless, and has only 5 independent components, as is consistent with the irreducible rank-2 form. It is also still obviously a rank-2 tensor, since it is a linear combination of $M_{\alpha\beta}$, $M_{\beta\alpha}$, and $\delta_{\alpha\beta}$, which are all rank-2 tensors. However, the transformation of the remaining components to a spherical rank-2 tensor is more complicated than for the vector-operator case.

In any case, we may now write the original tensor in terms of its irreducible components as

$$M_{\alpha\beta} = \frac{1}{3}M^{(0)}\delta_{\alpha\beta} + \frac{1}{4}M^{(1)}_{\mu}\epsilon_{\mu\alpha\beta} + M^{(2)}_{\alpha\beta}. \tag{7.188}$$
(reduced Cartesian tensor)

We can see this by using Eqs. (7.180), (7.181), and (7.187) to write

$$\begin{aligned}
\frac{1}{3}M^{(0)}\delta_{\alpha\beta} + \frac{1}{4}M^{(1)}_{\mu}\epsilon_{\mu\alpha\beta} + M^{(2)}_{\alpha\beta} &= \frac{1}{3}M_{\mu\mu}\delta_{\alpha\beta} + \frac{1}{4}\Big[\epsilon_{\mu\sigma\tau}(M_{\sigma\tau} - M_{\tau\sigma})\Big]\epsilon_{\mu\alpha\beta} + \left[M_{(\alpha\beta)} - \frac{1}{3}M_{\mu\mu}\delta_{\alpha\beta}\right] \\
&= \frac{1}{4}\epsilon_{\mu\alpha\beta}\epsilon_{\mu\sigma\tau}(M_{\sigma\tau} - M_{\tau\sigma}) + M_{(\alpha\beta)} \\
&= \frac{1}{4}(\delta_{\alpha\sigma}\delta_{\beta\tau} - \delta_{\alpha\tau}\delta_{\beta\sigma})(M_{\sigma\tau} - M_{\tau\sigma}) + M_{(\alpha\beta)} \\
&= \frac{1}{4}\Big[(M_{\alpha\beta} - M_{\beta\alpha}) - (M_{\beta\alpha} - M_{\alpha\beta})\Big] + \frac{1}{2}(M_{\alpha\beta} + M_{\beta\alpha}) \\
&= M_{\alpha\beta},
\end{aligned} \tag{7.189}$$

where we have used the relation

$$\epsilon_{\mu\alpha\beta}\epsilon_{\mu\sigma\tau} = \delta_{\alpha\sigma}\delta_{\beta\tau} - \delta_{\alpha\tau}\delta_{\beta\sigma}, \tag{7.190}$$

which is essentially the "bac-cab" vector identity $\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) = \mathbf{B}(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}(\mathbf{A}\cdot\mathbf{B})$ written in tensor notation (Problem 7.6).

7.4.3 Wigner–Eckart Theorem

Now we come to an extremely important result in angular momentum algebra. Consider the action of a tensor-operator component on an angular-momentum state,

$$T^{(k)}_{q}|\alpha'\ j'\ m'\rangle, \tag{7.191}$$

where α' represents other (i.e., radial) quantum numbers that do not represent angular dependence of the state. How does this state transform under a rotation? Since we may write the rotated form as

$$RT^{(k)}_{q}|\alpha'\ j'\ m'\rangle = (RT^{(k)}_{q}R^{\dagger})\,R|\alpha'\ j'\ m'\rangle, \tag{7.192}$$

evidently $T_q^{(k)}$ and $|\alpha'\ j'\ m'\rangle$ transform separately. In particular, by definition the state $|\alpha'\ j'\ m'\rangle$ transforms as the ket $|j'\ m'\rangle$, while by comparing Eq. (7.176) to Eq. (7.133) we recall that $T_q^{(k)}$ transforms via the rotation matrix in the same way as the angular-momentum ket $|k\ q\rangle$. Then heuristically, the state $T_q^{(k)}|\alpha'\ j'\ m'\rangle$ should transform in a way similar to the composite state $|k\ q\rangle|j'\ m'\rangle$. This statement is really the key to the upcoming famous theorem, which is a primary motivation for introducing irreducible tensor operators.

Let's work out the transformation properties of $T_q^{(k)}|\alpha'\ j'\ m'\rangle$ explicitly. Consider the following linear combination of states of this type:

$$|\tilde{\alpha}\ j\ m\rangle = \sum_{qm'} T_q^{(k)}|\alpha'\ j'\ m'\rangle\langle j'\ m';k\ q|j\ m\rangle. \tag{7.193}$$

At this point, the ket on the left is just a name for this superposition, with $\tilde{\alpha}$ representing the linear combinations of $|\alpha'\rangle$. It remains to show that this is also a simultaneous eigenstate of J^2 and J_z with respective eigenvalues $\hbar^2 j(j+1)$ and $m\hbar$. To prove this, consider an arbitrary rotation R:

$$R|\tilde{\alpha}\ j\ m\rangle = \sum_{qm'}(RT_q^{(k)}R^\dagger)R|\alpha'\ j'\ m'\rangle\langle j'\ m';k\ q|j\ m\rangle. \tag{7.194}$$

Then using Eq. (7.176) for the rotation of the tensor operators and Eq. (7.133) for the rotation of the states, we have

$$R|\tilde{\alpha}\ j\ m\rangle = \sum_{q'm''} T_{q'}^{(k)}|\alpha'\ j'\ m''\rangle \sum_{qm'} d_{q'q}^{(k)} d_{m''m'}^{(j')}\langle j'\ m';k\ q|j\ m\rangle \tag{7.195}$$

in terms of a pair of rotation matrices. We can proceed by writing out the rotation matrices in terms of a single rotation on the composite state:

$$\begin{aligned}
R|\tilde{\alpha}\ j\ m\rangle &= \sum_{q'm''} T_{q'}^{(k)}|\alpha'\ j'\ m''\rangle \sum_{qm'}\langle j'\ m'';k\ q'|R|j'\ m';k\ q\rangle\langle j'\ m';k\ q|j\ m\rangle \\
&= \sum_{q'm''} T_{q'}^{(k)}|\alpha'\ j'\ m''\rangle\langle j'\ m'';k\ q'|R|j\ m\rangle \\
&= \sum_{q'm'm''} T_{q'}^{(k)}|\alpha'\ j'\ m''\rangle\langle j'\ m'';k\ q'|j\ m'\rangle\langle j\ m'|R|j\ m\rangle \\
&= \sum_{q'm'm''} T_{q'}^{(k)}|\alpha'\ j'\ m''\rangle\langle j'\ m'';k\ q'|j\ m'\rangle\, d_{m'm}^{(j)} \\
&= \sum_{m'} |\tilde{\alpha}\ j\ m'\rangle\, d_{m'm}^{(j)},
\end{aligned} \tag{7.196}$$

where we used Eq. (7.193) in the last step. This is the proper rotation behavior for an angular-momentum eigenstate $|j\ m\rangle$.

Now by comparison to the transformation rules (7.101), we can invert the linear combination in Eq. (7.193) to write

$$T_q^{(k)}|\alpha'\ j'\ m'\rangle = \sum_{k'q'} |\tilde{\alpha}\ k'\ q'\rangle\langle k'\ q'|j'\ m';k\ q\rangle, \tag{7.197}$$

where we have relabeled $j \longrightarrow k'$ and $m \longrightarrow q'$. Now we can operate from the left with $\langle\alpha\ j\ m|$ to find the matrix element

$$\begin{aligned}
\langle\alpha\ j\ m|T_q^{(k)}|\alpha'\ j'\ m'\rangle &= \sum_{k'q'}\langle\alpha\ j\ m|\tilde{\alpha}\ k'\ q'\rangle\ \langle k'\ q'|j'\ m';k\ q\rangle \\
&= \langle\alpha|\tilde{\alpha}\rangle\ \langle j\ m|j'\ m';k\ q\rangle,
\end{aligned} \tag{7.198}$$

where we have used the orthogonality of the angular-momentum states to obtain the second equality. Now, note that the inner product $\langle\alpha\ j\ m|\tilde{\alpha}\ j\ m\rangle$ is, in fact, independent of m, just as the inner product $\langle j\ m|j\ m\rangle = 1$ is m-independent. We may thus define the m-independent **reduced matrix element**

$$\langle\alpha\ j\|\mathbf{T}^{(k)}\|\alpha'\ j'\rangle := (-1)^{2k}\langle\alpha|\tilde{\alpha}\rangle, \tag{7.199}$$

(reduced matrix element)

where the dependence on j, j', and $\mathbf{T}^{(k)}$ comes in via the way α transforms into $\tilde{\alpha}$. (The transformation $\alpha \longrightarrow \tilde{\alpha}$ of course introduces no m-dependence because by assumption α represented the radial and thus orientation-independent part of the quantum state.) Note that the reduced matrix element, while using the notation of a tensor, is in fact a scalar quantity, as is clear from the right-hand side of the definition. The double bars indicate that this is *not* a regular matrix element, although it represents a portion (the orientation-independent part) of one.

Finally, using the reduced matrix element in Eq. (7.198), we arrive at the **Wigner–Eckart theorem**[7,8]

$$\langle \alpha\ j\ m|T_q^{(k)}|\alpha'\ j'\ m'\rangle = (-1)^{2k}\langle \alpha\ j\|\mathbf{T}^{(k)}\|\alpha'\ j'\rangle\ \langle j\ m|j'\ m';k\ q\rangle. \quad \text{(Wigner–Eckart theorem)} \tag{7.200}$$

The Wigner–Eckart theorem thus factors a matrix element of a component of an irreducible tensor operator into an orientation-independent part (the reduced matrix element) and a Clebsch–Gordan coefficient (which encapsulates *all* the orientation dependence of the matrix element).

The Clebsch–Gordan coefficient in Eq. (7.200) requires that j take values between $|k - j'|$ and $k + j'$. In particular, this indicates that $T_q^{(k)}$ can only be of integer rank k. A tensor of half-integer rank would have the awkward consequence of inducing transitions between integer and half-integer states (i.e., between bosonic and fermionic states, which would only be acceptable if particles are changing or being created/destroyed). Such half-integer tensor operators are rare but possible, explaining the k-dependent phase factor in Eq. (7.200).

7.4.3.1 Projection Theorem

A useful special case of the Wigner–Eckart theorem arises[9] if we consider the scalar product of a vector operator $\mathbf{A}$ with angular momentum $\mathbf{J}$. Considering a matrix element of the scalar combination and expanding in the spherical basis using the scalar product (7.173),

$$\begin{aligned}\langle \alpha\ j\ m|\mathbf{J}\cdot\mathbf{A}|\alpha'\ j\ m\rangle &= \sum_q (-1)^q \langle \alpha\ j\ m|J_q A_{-q}|\alpha'\ j\ m\rangle \\ &= \langle \alpha\ j\ m|\Big(J_0A_0 - J_1A_{-1} - J_{-1}A_1\Big)|\alpha'\ j\ m\rangle.\end{aligned} \tag{7.201}$$

Then comparing Eqs. (7.8) and (7.170) to identify the spherical components of $\mathbf{J}$ in terms of the ladder operators,

$$J_{\pm 1} = \mp\frac{1}{\sqrt{2}}J_\pm, \tag{7.202}$$

we can use the action (7.31) of the ladder operators on angular-momentum eigenstates (with $J_\pm^\dagger = J_\mp$) to write

$$\begin{aligned}\langle \alpha\ j\ m|\mathbf{J}\cdot\mathbf{A}|\alpha'\ j\ m\rangle = m\hbar\langle \alpha\ j\ m|A_0|\alpha'\ j\ m\rangle &+ \frac{\hbar}{\sqrt{2}}\sqrt{(j+m)(j-m+1)}\langle \alpha\ j\ m{-}1|A_{-1}|\alpha'\ j\ m\rangle \\ &- \frac{\hbar}{\sqrt{2}}\sqrt{(j-m)(j+m+1)}\langle \alpha\ j\ m{+}1|A_1|\alpha'\ j\ m\rangle.\end{aligned} \tag{7.203}$$

The point of this expression is to show that the matrix elements of $\mathbf{J}\cdot\mathbf{A}$ here can be expressed solely in terms of matrix elements of $\mathbf{A}$. If we apply the Wigner–Eckart theorem (7.200) to each term on the right-hand side of Eq. (7.203), we will find that the whole right-hand side of Eq. (7.203) will have the form $c_{jm}\langle \alpha\ j\|\mathbf{A}\|\alpha'\ j\rangle$,

[7] Carl Eckart, "The Application of Group Theory to the Quantum Dynamics of Monatomic Systems," *Reviews of Modern Physics* **2**, 305 (1930) (doi: 10.1103/RevModPhys.2.305); Eugene P. Wigner, "Group Theory and Its Application to Quantum Mechanics of Atomic Spectra," (Academic Press, 1959).

[8] Many sign and normalization conventions abound, particularly for the Wigner–Eckart theorem and the reduced matrix elements. Here we are following the normalization convention of D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd ed. (Oxford, 1968), Section 4.7, p. 56 (ISBN: 0198514190).

[9] Here we are following J. J. Sakurai and Jim Napolitano, *Modern Quantum Mechanics*, 2nd ed. (Cambridge, 2017), pp. 254-5 (ISBN: 9781108422413).

where c_{jm} involves the factors like $m\hbar$ on the right-hand side of Eq. (7.203) and Clebsch–Gordan coefficients of the form $\langle j\ m|j\ m, 1\ q\rangle$. We can apply the Wigner–Eckart theorem *again* to the matrix element of the *scalar* operator $\mathbf{J}\cdot\mathbf{A}$ in Eq. (7.203). This matrix element must be orientation-independent (and thus m-independent). Putting all this together, the conclusion is that

$$\langle\alpha\ j\ m|\mathbf{J}\cdot\mathbf{A}|\alpha'\ j\ m\rangle =: c_j\langle\alpha\ j\|\mathbf{A}\|\alpha'\ j\rangle\,, \tag{7.204}$$

where c_j is a constant independent of m, α, and α'; c_j is also independent of $\mathbf{A}$, except for the fact that it is a vector operator.

Now to compute c_j, we take advantage of the $\mathbf{A}$-independence of this last relation, setting $\mathbf{A}\longrightarrow\mathbf{J}$ and $\alpha'\longrightarrow\alpha$ to obtain

$$c_j\langle\alpha\ j\|\mathbf{J}\|\alpha\ j\rangle = \langle\alpha\ j\ m|J^2|\alpha\ j\ m\rangle = \hbar^2 j(j+1). \tag{7.205}$$

Using this relation to eliminate c_j in Eq. (7.204), we have

$$\frac{\langle\alpha\ j\ m|\mathbf{J}\cdot\mathbf{A}|\alpha'\ j\ m\rangle}{\hbar^2 j(j+1)} = \frac{\langle\alpha\ j\|\mathbf{A}\|\alpha'\ j\rangle}{\langle\alpha\ j\|\mathbf{J}\|\alpha\ j\rangle}. \tag{7.206}$$

Applying the Wigner–Eckart theorem (7.200) again but now for $k=1$, the last ratio transforms to

$$\frac{\langle\alpha\ j\ m|\mathbf{J}\cdot\mathbf{A}|\alpha'\ j\ m\rangle}{\hbar^2 j(j+1)} = \frac{\langle\alpha\ j\ m|A_q|\alpha'\ j\ m'\rangle}{\langle\alpha\ j\ m|J_q|\alpha\ j\ m'\rangle}, \tag{7.207}$$

assuming that the J_q matrix element does not vanish. Rearranging, we come to

$$\langle\alpha\ j\ m|A_q|\alpha'\ j\ m'\rangle = \frac{\langle\alpha\ j\ m|\mathbf{J}\cdot\mathbf{A}|\alpha'\ j\ m\rangle}{\hbar^2 j(j+1)}\langle\alpha\ j\ m|J_q|\alpha\ j\ m'\rangle, \tag{7.208}$$

(projection theorem)

which is known as the **projection theorem**. This is sometimes a handy special case of the Wigner–Eckart theorem where the reduced matrix element has already been eliminated. It will be useful later, for example, when we discuss the Zeeman effect (Section 12.9.4).

7.4.4 Application to Multipole Radiation

An important application of the above formalism is to scattering problems. In particular here we will consider the implications of angular momentum for the radiation of an atom.[10]

7.4.4.1 Matter–Field Coupling

To start, we'll need to understand just a bit about how an atom couples to the electromagnetic field. It is specifically the electrons—or more generically, the electron charge density of the atom—that couples to the field. This is something of a deep subject, so we'll only go just far enough to obtain the coupling that we need.

The Lagrangian for the electromagnetic field is written in terms of both the vector potential $\mathscr{A}$ and the scalar potential ϕ:

$$\begin{aligned} L &= L_{\text{free}} + L_{\text{source}} \\ L_{\text{free}} &= \frac{\epsilon_0}{2}\int d^3r\left[(\nabla\phi + \dot{\mathscr{A}})^2 - c^2(\nabla\times\mathscr{A})^2\right] \\ L_{\text{source}} &= -\int d^3r\,[\rho\phi - \mathbf{j}\cdot\mathscr{A}]\,. \end{aligned}$$

(electromagnetic Lagrangian) (7.209)

[10] Once we get into the hardcore angular-momentum stuff below, we'll be following Gordon Baym, *Lectures on Quantum Mechanics* (Benjamin/Cummings, 1969), pp. 376–80 (ISBN: 0805306641). See also M. E. Rose, *Multipole Fields* (Wiley, 1955).

This Lagrangian is split into the free part and a source part that represents the coupling to the source fields ρ (charge) and $\mathbf{j}$ (current density). The vector and scalar potentials are the generalized coordinates in this Lagrangian, which fundamentally defines the structure of the electromagnetic field. Note that the form of the Lagrangian motivates the definitions

$$\begin{aligned} \mathscr{E} &:= -\nabla\phi - \dot{\mathscr{A}} \\ \mathscr{B} &:= \nabla \times \mathscr{A} \end{aligned} \qquad \text{(electromagnetic fields)} \tag{7.210}$$

for the electric and magnetic fields. Then in terms of these fields, the simple quadratic nature of the Lagrangian is more apparent:

$$L_{\text{free}} = \frac{\epsilon_0}{2}\int d^3r \left[\mathscr{E}^2 - c^2\mathscr{B}^2\right].$$

(free electromagnetic Lagrangian) (7.211)

It turns out that the electric field is again essentially the momentum field conjugate to the coordinate field $\mathscr{A}$. The minus sign in the definition of the electric field simply makes the gradient of the potential agree with the usual mechanical potential, $\dot{\mathbf{p}} = -\nabla V(\mathbf{q})$.

The point of this section is to treat the interaction embodied by L_{source}. There are two interactions here, the interaction of ρ with ϕ, and the interaction of $\mathbf{j}$ with $\mathscr{A}$. Without going too much into the details, if we choose Coulomb gauge (with condition $\nabla\cdot\mathscr{A} = 0$), the scalar field will not have any radiative component; $\mathscr{A}$ will handle all the aspects of radiation. Hence, we can drop the coupling to the charge density ρ (which will just consist of the ordinary Coulomb field of the electron charge, which serves to bind the electron to the nucleus. (An alternate argument is to note that for time-dependent sources, the source charge is redundant in view of the continuity equation $\dot{\rho} = -\nabla\cdot\mathbf{j}$.) The remaining interaction corresponds to the Hamiltonian

$$H_{\text{int}} = -\int d^3r\, \mathbf{j}\cdot\mathscr{A}. \qquad \text{(charge–field interaction)} \tag{7.212}$$

Note that the sign here changes as compared to the Lagrangian, because it functions as linear potential (and a Lagrangian $L = T - V$ maps to a Hamiltonian $H = T + V$ if T is quadratic in the derivative of the coordinate).

The above interaction Hamiltonian was what we needed, but let's run quickly through the math to show that the above Lagrangian generates the classical Maxwell equations. We haven't introduced the math necessary to properly handle this (in particular differentiation with respect to a function), so this is just the scenic-drive derivation to establish some plausibility for the above interaction. For the vector-potential degree of freedom, the Euler–Lagrange equation is

$$\frac{\delta L}{\delta\mathscr{A}} - \frac{d}{dt}\frac{\delta L}{\delta\dot{\mathscr{A}}} = 0. \tag{7.213}$$

The derivatives here are **functional derivatives**, and the results are

$$\frac{\delta L}{\delta(\dot{\mathscr{A}})} = \epsilon_0(\dot{\mathscr{A}} + \nabla\phi), \qquad \frac{\delta L}{\delta\mathscr{A}} = \mathbf{j} - \epsilon_0 c^2\nabla\times(\nabla\times\mathscr{A}). \tag{7.214}$$

These derivatives more or less correspond to ordinary vector derivatives after discarding the integration, but the functional derivative for the cross product must be handled carefully to obtain the proper sign. Putting these derivatives in the Euler–Lagrange equation, we find that $\mathscr{A}$ satisfies a wave equation

$$\nabla\times(\nabla\times\mathscr{A}) + \frac{1}{c^2}\partial_t(\dot{\mathscr{A}} + \nabla\phi) = \frac{1}{\epsilon_0 c^2}\mathbf{j}, \tag{7.215}$$

and hence supports radiation. Identifying $c^2 = 1/\mu_0\epsilon_0$, and using the above definitions for the electromagnetic fields, we find the Maxwell equation

$$\nabla\times\mathscr{B} = \frac{1}{c^2}\dot{\mathscr{E}} + \mu_0\mathbf{j}. \tag{7.216}$$

The other Euler–Lagrange equation for the scalar potential reads

$$\frac{\delta L}{\delta \phi} - \nabla \cdot \frac{\delta L}{\delta \nabla \phi} = 0. \tag{7.217}$$

The associated functional derivatives are

$$\frac{\delta L}{\delta \phi} = -\rho, \qquad \frac{\delta L}{\delta \nabla \phi} = \epsilon_0 (\nabla \phi + \dot{\boldsymbol{\mathcal{A}}}), \tag{7.218}$$

and using these in the Euler–Lagrange equation gives

$$\nabla \cdot (\nabla \phi + \dot{\boldsymbol{\mathcal{A}}}) = -\frac{\rho}{\epsilon_0}. \tag{7.219}$$

Note that with the Coulomb-gauge condition, this becomes

$$\nabla^2 \phi = -\frac{\rho}{\epsilon_0}, \tag{7.220}$$

which is a nondynamical (i.e., constraint) equation, which is why the scalar field does not support radiation. (It is possible to make other gauge choices where the scalar wave is radiative, however.) In terms of the field, this equation becomes

$$\nabla \cdot \boldsymbol{\mathcal{E}} = \frac{\rho}{\epsilon_0}, \tag{7.221}$$

independent of the gauge, giving Gauss' law. The other two Maxwell equations ($\nabla \cdot \boldsymbol{\mathcal{B}} = 0$ and $\nabla \times \boldsymbol{\mathcal{E}} = -\dot{\boldsymbol{\mathcal{B}}}$) simply follow from the definitions of the fields and ordinary vector identities.

7.4.4.2 Plane-Wave Form of the Interaction

To decompose the interaction energy into plane-wave form, we can use the spatial Fourier transforms of the current-density and vector-potential fields, defined by

$$\tilde{\mathbf{j}}(\mathbf{k}) = \int d^3r\, \mathbf{j}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}, \qquad \tilde{\boldsymbol{\mathcal{A}}}(\mathbf{k}) = \int d^3r\, \boldsymbol{\mathcal{A}}(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}. \tag{7.222}$$

Putting the inverse transforms

$$\mathbf{j}(\mathbf{r}) = \frac{1}{2\pi} \int d^3k\, \tilde{\mathbf{j}}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}, \qquad \boldsymbol{\mathcal{A}}(\mathbf{r}) = \frac{1}{2\pi} \int d^3k\, \tilde{\boldsymbol{\mathcal{A}}}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{7.223}$$

into the interaction (7.212), we obtain

$$H_{\text{int}} = -\frac{1}{4\pi^2} \int d^3r \int d^3k' \int d^3k\, \tilde{\mathbf{j}}(\mathbf{k}') \cdot \tilde{\boldsymbol{\mathcal{A}}}(\mathbf{k})\, e^{i(\mathbf{k}'+\mathbf{k})\cdot\mathbf{r}}. \tag{7.224}$$

The $\mathbf{r}$ integration will change the exponential into the delta function $2\pi\delta^3(\mathbf{k}+\mathbf{k}')$, and one of the remaining $\mathbf{k}$ integrals removes the delta function, with the result

$$H_{\text{int}} = -\frac{1}{2\pi} \int d^3k\, \tilde{\mathbf{j}}(-\mathbf{k}) \cdot \tilde{\boldsymbol{\mathcal{A}}}(\mathbf{k}) = -\frac{1}{2\pi} \int d^3k\, \tilde{\mathbf{j}}^*(\mathbf{k}) \cdot \tilde{\boldsymbol{\mathcal{A}}}(\mathbf{k}). \tag{7.225}$$

(charge–field interaction)

Thus, in the plane-wave basis, the conjugate Fourier transform

$$\tilde{\mathbf{j}}^*(\mathbf{k}) = \tilde{\mathbf{j}}(-\mathbf{k}) = \int d^3r\, \mathbf{j}(\mathbf{r})\, e^{i\mathbf{k}\cdot\mathbf{r}} \tag{7.226}$$

of the current density represents the atomic operator responsible for emission of the electromagnetic field into the $\mathbf{k}$ direction.

7.4.4.3 Partial-Wave Expansion of the Plane Wave

An atom is highly localized, and we must handle the possibility of radiation to occur in any direction. The spherical harmonics offer a handy way to characterize the angular dependence of the radiation. To change to this representation we will need the expression of a plane wave $e^{i\mathbf{k}\cdot\mathbf{r}}$ in terms of spherical harmonics. Since the spherical harmonics span the angular Hilbert space, we can write the expansion

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_{\ell m} c_{\ell m} Y_\ell^m(\theta,\phi) \tag{7.227}$$

in terms of expansion coefficients $c_{\ell m}$ (''constants'' that depend on $\mathbf{k}$ and $\mathbf{r}$). To work out the coefficients it is simplest to orient the coordinate system such that $\mathbf{r}$ is along the z axis, so that the expansion becomes

$$e^{ikr\cos\theta} = \sum_{\ell} c_\ell Y_\ell^0(\theta,0), \tag{7.228}$$

where now θ is the angle between $\mathbf{k}$ and $\mathbf{r}$, and we have discarded the $m \neq 0$ terms in the expansion due to the lack of any dependence on ϕ. Since the orthonormality condition for the spherical harmonics reads

$$\int d\Omega \left(Y_\ell^m\right)^* Y_{\ell'}^{m'} = \delta_{\ell\ell'}\delta_{mm'}, \tag{7.229}$$

we can find the coefficients by multiplying by $(Y_\ell^m)^*$ and integrating over all angles:

$$c_\ell = \int d\Omega\, e^{ikr\cos\theta}\, Y_\ell^{0*}(\theta,0) = 2\pi\sqrt{\frac{2\ell+1}{4\pi}}\int_{-1}^{1} d\mu\, e^{ikr\mu}\, P_\ell(\mu). \tag{7.230}$$

Here, we have used Eqs. (7.87)–(7.90) to write the spherical harmonic in terms of a Legendre polynomial. The integral here can be evaluated using the integral representation

$$j_\ell(z) = \frac{1}{2i^\ell}\int_{-1}^{1} d\mu\, e^{iz\mu}\, P_\ell(\mu) \tag{7.231}$$

for the spherical Bessel functions $j_\ell(z)$ [to be discussed later; see Eq. (8.29) and Problem 8.2], giving

$$c_\ell = 4\pi i^\ell \sqrt{\frac{2\ell+1}{4\pi}} j_\ell(kr). \tag{7.232}$$

Thus, we have the expansion

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}} j_\ell(kr) Y_\ell^0(\theta,0) = \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) j_\ell(kr) P_\ell(\cos\theta),$$

(plane wave, partial-wave expansion) (7.233)

where again θ is the angle between $\mathbf{k}$ and $\mathbf{r}$. Now using the addition theorem (7.167) for $Y_\ell^0(\theta,0)$, we find

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{\ell=0}^{\infty} i^\ell j_\ell(kr) \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\hat{k})\, Y_\ell^m(\hat{r}),$$

(plane wave, partial-wave expansion) (7.234)

where we are indicating the angular dependence of the spherical harmonics according to the orientation of the appropriate unit vectors. These last two expressions are called **partial-wave expansions** of the plane wave (referring to a method for solving scattering problems by decomposing an incident plane wave into components of definite angular momentum). Of course, that *is* the idea of what we're up to.

7.4.4.4 Reduction of the Tensor

Now using the partial-wave expansion (7.234) in the expression (7.226) for the current density, we find

$$\tilde{\mathbf{j}}^*(\mathbf{k}) = 4\pi \sum_{\ell=0}^{\infty} i^\ell \int d^3r\, \mathbf{j}(\mathbf{r})\, j_\ell(kr) \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\hat{k})\, Y_\ell^m(\hat{r}). \tag{7.235}$$

(Sorry about the double use of j for both the current density and spherical Bessel function! Make sure to pay attention to the arguments to sort out which is which.) Projecting into spherical-basis components with $\hat{\mathbf{e}}_q\cdot$, we have

$$j_{-q}^*(\mathbf{k}) = (-1)^q 4\pi \sum_{\ell=0}^{\infty} i^\ell \int d^3r\, j_q(\mathbf{r})\, j_\ell(kr) \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(\hat{k})\, Y_\ell^m(\hat{r}), \tag{7.236}$$

where we used $(A^*)_q = (-1)^q A_{-q}^*$, which follows by starting with the definition $A_q := \hat{\mathbf{e}}_q \cdot \mathbf{A}$, changing the sign of q and conjugating, and then a bit of algebra:

$$A_{-q}^* = \hat{\mathbf{e}}_{-q}^* \cdot \mathbf{A}^* = (-1)^q \hat{\mathbf{e}}_q \cdot \mathbf{A}^* = (-1)^q (A^*)_q. \tag{7.237}$$

Grouping factors in Eq. (7.236), we can write

$$j_{-q}^*(\mathbf{k}) = (-1)^q 4\pi \sum_{\ell m} i^\ell \left[\int d^3r\, j_q(\mathbf{r})\, j_\ell(kr)\, Y_\ell^m(\hat{r}) \right] Y_\ell^{m*}(\hat{k}), \tag{7.238}$$

where the bracketed factor is a weighted integral over the current density [i.e., the atomic contribution to $j_{-q}^*(\mathbf{k})$], while the last factor is the only orientation factor, representing an angular probability amplitude at fixed (ℓ, m). Unfortunately things are not so simple, because the atomic contribution involves a reducible product of the tensors j_q and Y_ℓ^m. To reduce this product, we can introduce an extra sum $\sum_{m''q''} \delta_{mm''}\delta_{qq''}$ in the summand without changing anything, and then use the Clebsch–Gordan orthogonality relation (7.106) in the form

$$\delta_{mm''}\delta_{qq''} = \sum_{\ell' m'} \langle \ell\ m''; 1\ q'' | \ell'\ m' \rangle \langle \ell'\ m' | \ell\ m; 1\ q \rangle, \tag{7.239}$$

with the result

$$j_{-q}^*(\mathbf{k}) = (-1)^q 4\pi \sum_{\ell\ell' m'} i^\ell \sum_{mm''q''} \left[\int d^3r\, j_{q''}(\mathbf{r})\, j_\ell(kr)\, Y_\ell^{m''}(\hat{r})\, \langle \ell\ m''; 1\ q'' | \ell'\ m' \rangle \right] \langle \ell'\ m' | \ell\ m; 1\ q \rangle\, Y_\ell^{m*}(\hat{k}). \tag{7.240}$$

Now explicitly separating the current-density and angular-distribution components, we can define a factor encompassing the integral over the current density,

$$\mathscr{J}_{m'}^{(\ell')}(\ell) = \sum_{m''q''} \int d^3r\, j_{q''}(\mathbf{r})\, j_\ell(kr)\, Y_\ell^{m''}(\hat{r})\, \langle \ell\ m''; 1\ q'' | \ell'\ m' \rangle, \tag{7.241}$$

and a factor with the orientation dependence,

$$\Phi_{m'}^{(\ell')}(\ell, \hat{k}, q) = \sum_m Y_\ell^{m*}(\hat{k})\, \langle \ell'\ m' | \ell\ m; 1\ q \rangle, \tag{7.242}$$

such that Eq. (7.240) becomes

$$j_{-q}^*(\mathbf{k}) = (-1)^q 4\pi \sum_{\ell\ell' m'} i^\ell\, \mathscr{J}_{m'}^{(\ell')}(\ell) \left[\Phi_{m'}^{(\ell')}(\ell, \hat{k}, q) \right]^*. \tag{7.243}$$

Here, ℓ' is summed over the range

$$|\ell - 1| \le \ell' \le \ell + 1, \tag{7.244}$$

due to the triangularity of the Clebsch–gordan coefficients.

Now is the crucial point: The quantity in Eq. (7.241) was motivated because the product of spherical tensors $j_q(\mathbf{r})$ and $Y_\ell^m(\hat{r})$ formed a reducible tensor. So have we managed to reduce it? In fact, yes, since Eq. (7.241) has the same form as Eq. (7.193), and we proved that the latter transformed correctly under rotations. We can also see this another way: Recalling the addition rule (7.101) for two angular momenta, and then projecting the first one into angular states $|\theta,\phi\rangle$, we find that the combination of two spherical harmonics is

$$Y_\ell^m(\theta,\phi) = \sum_{\substack{m_1 m_2 \\ (m_1+m_2=m)}} Y_{\ell_1}^{m_1}(\theta,\phi)\, Y_{\ell_2}^{m_2}(\theta,\phi)\, \langle \ell_1\ m_1; \ell_2\ m_2 | \ell\ m\rangle, \tag{7.245}$$

where $|\ell_1 - \ell_2| \le \ell \le \ell_1 + \ell_2$. The spherical harmonics here provide the prototype for how products of spherical tensors transform. The current density is a vector *operator*, but remember that irreducible tensor operators are defined such that they transform in the same way as spherical tensors. Thus, $\mathscr{J}_{m'}^{(\ell')}(\ell)$ in Eq. (7.241) transforms as an irreducible tensor operator of rank ℓ'. In fact, have another look at Eq. (7.241) and try to read this off directly from the Clebsch–Gordan coefficient: It says we are adding angular momenta $|\ell\ m''\rangle$ and $|1\ q''\rangle$ (i.e., spherical tensors $Y_\ell^{m''}$ and $j_{q''}$) to form an angular momentum of the form $|\ell'\ m'\rangle$. Note that the same argument does *not* apply to the quantity $\Phi_{m'}^{(\ell')}(\ell,\hat{k},q)$ in Eq. (7.242); we will comment further on this below.

7.4.4.5 Electric Multipole Moments

Although we know now that $\mathscr{J}_{m'}^{(\ell')}(\ell)$ transforms as an irreducible tensor, what remains is to figure out what it *means*. First, a simplification is in order. Generally speaking, when this relation is applied to atoms, the wavelength $(2\pi/k)$ of the emitted radiation is much larger than the extend of the current density. Thus, we make the **long-wavelength approximation**, which amounts to taking $kr \ll 1$ (i.e., this relation applies wherever the integrand is significant). It follows that we can apply the small-argument expansion

$$j_\ell(kr) \approx \frac{(kr)^\ell}{(2\ell+1)!!} \tag{7.246}$$

for the spherical Bessel function, where $(n+1)!! = (n+1)(n-1)(n-3)\cdots$. Using this approximation in Eq. (7.247) we have

$$\mathscr{J}_{m'}^{(\ell')}(\ell) \approx \frac{k^\ell}{(2\ell+1)!!} \sum_{m''q''} \int d^3r\, j_{q''}(\mathbf{r})\, r^\ell\, Y_\ell^{m''}(\hat{r})\, \langle \ell\ m''; 1\ q'' | \ell'\ m'\rangle, \tag{7.247}$$

for a simpler weighted integral of the current density.

This quantity divides into three cases: $\ell' = \ell - 1$, $\ell' = \ell$, and $\ell' = \ell + 1$. First we will work with the case $\ell = \ell' - 1$:

$$\mathscr{J}_{m'}^{(\ell')}(\ell = \ell' - 1) \approx \frac{k^\ell}{(2\ell+1)!!} \sum_{m''} \int d^3r\, j_{m'-m''}(\mathbf{r})\, r^\ell\, Y_\ell^{m''}(\hat{r})\, \langle \ell\ m''; 1\ m'-m'' | \ell+1\ m'\rangle, \tag{7.248}$$

It is a bit difficult to see how to proceed, so let's guess the general behavior of this quantity by examining the simplest case $\ell = 0$ ($\ell' = 1$):

$$\mathscr{J}_{m'}^{(\ell'=1)}(\ell = 0) = \sum_{m''} \int d^3r\, j_{m'-m''}(\mathbf{r})\, Y_0^{m''}(\hat{r})\, \langle 0\ m''; 1\ m'-m'' | 1\ m'\rangle. \tag{7.249}$$

The only possible value for m'' is 0, and the resulting Clebsch–Gordan coefficient is simply unity (without any sign). Then using $Y_0^0 = 1/\sqrt{4\pi}$, we can write

$$\mathscr{J}_{m'}^{(\ell'=1)}(\ell = 0) = \frac{1}{\sqrt{4\pi}} \int d^3r\, j_{m'}(\mathbf{r}). \tag{7.250}$$

Now integrating by parts, using $\nabla \cdot (r_{m'}\mathbf{j}) = r_{m'}\nabla\cdot\mathbf{j} + \mathbf{j}\cdot\nabla r_{m'} = r_{m'}\nabla\cdot\mathbf{j} + j_{m'}$, we find

$$\mathscr{J}_{m'}^{(\ell'=1)}(\ell=0) = -\frac{1}{\sqrt{4\pi}}\int d^3r\, r_{m'}\nabla\cdot\mathbf{j}(\mathbf{r}) \tag{7.251}$$

after dropping the surface integral (by assuming the current density is localized, and thus drops off sufficiently quickly at large $\mathbf{r}$). The continuity equation gives $\nabla\cdot\mathbf{j} = -\dot\rho = i\omega\rho = ick\rho$, and thus

$$\mathscr{J}_{m'}^{(\ell'=1)}(\ell=0) = -i\frac{ck}{\sqrt{4\pi}}\int d^3r\, r_{m'}\,\rho(\mathbf{r}) \tag{7.252}$$
(electric dipole contribution)

in terms of the charge density ρ. The integral here is the (m' component of the) electric dipole moment of the charge density. The cases of $\ell' = 2, 3, \ldots$ are the higher-order electric multipoles (quadrupole, octupole, hexadecapole, etc.). In the general multipole case, it must work out such that the integral is of the form $\int d^3r\, r^{\ell'}\, Y_{\ell'}^{m'}(\hat r)\,\rho(\mathbf{r})$, which defines the electric multipole of order ℓ'.

Now let's look at the case $\ell = \ell' + 1$:

$$\mathscr{J}_{m'}^{(\ell')}(\ell=\ell'+1) \approx \frac{k^\ell}{(2\ell+1)!!}\sum_{m''}\int d^3r\, j_{m'-m''}(\mathbf{r})\, r^\ell\, Y_\ell^{m''}(\hat r)\,\langle \ell\ m''; 1\ m'-m'' | \ell-1\ m'\rangle. \tag{7.253}$$

For a given ℓ', this equation has a similar form to the previous case (7.248), but with a couple of changes. First, the Clebsch–Gordan coefficient is different, but may be brought into a form similar to the previous case via the application of a symmetry relation. The other main difference is an extra factor of $(kr)^2$. This means that a higher order multipole is coupling to the same field as in the $\ell = \ell' - 1$ (for example, the octupole moment is coupling to the dipole-radiated field), but this coupling is much weaker (long-wavelength approximation), so this factor is generally ignored compared to the contribution (7.248).

7.4.4.6 Magnetic Multipole Moments

Finally we should consider the remaining case of Eq. (7.241), where $\ell = \ell'$:

$$\mathscr{J}_{m'}^{(\ell')}(\ell=\ell') \approx \frac{k^\ell}{(2\ell+1)!!}\sum_{m''}\int d^3r\, j_{m'-m''}(\mathbf{r})\, r^\ell\, Y_\ell^{m''}(\hat r)\,\langle \ell\ m''; 1\ m'-m'' | \ell\ m'\rangle. \tag{7.254}$$

Again, the Clebsch–Gordan coefficient obscures the behavior of this quantity, so let's simplify and consider the simplest case. Note that the case $\ell = \ell' = 0$ is excluded because the Clebsch–Gordan coefficient in Eq. (7.242) vanishes (you can't add a $j = 1$ to $j = 0$ and expect to get $j = 0$ back, because one of these is spherically symmetric and the other isn't)—this is basically saying that there is no monopole radiation. So, let's go ahead with $\ell = \ell' = 1$:

$$\mathscr{J}_{m'}^{(\ell'=1)}(\ell=1) \approx \frac{k}{3}\sum_{m''}\int d^3r\, j_{m'-m''}(\mathbf{r})\, r\, Y_1^{m''}(\hat r)\,\langle 1\ m''; 1\ m'-m'' | 1\ m'\rangle. \tag{7.255}$$

We'll have to work out the integrand here piece by piece (including the sum over m''), because we haven't yet written down how this works out. Using $rY_1^{m''} = \sqrt{3/4\pi}\, r_{m''}$ from Eq. (7.175), we can write out the various possibilities for $\sum_{m''} r_{m''} j_{m'-m''}\langle 1\ m''; 1\ m'-m'' | 1\ m'\rangle$ as

$$\begin{aligned}
m'=+1: &\quad \frac{1}{\sqrt{2}}\Big[r_1\, j_0(\mathbf{r}) - r_0\, j_1(\mathbf{r})\Big]\\
m'=0: &\quad \frac{1}{\sqrt{2}}\Big[r_1\, j_{-1}(\mathbf{r}) - r_{-1}\, j_1(\mathbf{r})\Big]\\
m'=-1: &\quad \frac{1}{\sqrt{2}}\Big[r_0\, j_{-1}(\mathbf{r}) - r_{-1}\, j_0(\mathbf{r})\Big].
\end{aligned} \tag{7.256}$$

These are just the spherical components of the cross product $i\sqrt{1/2}(\mathbf{r}\times\mathbf{j})_{m'}$ (see Problem 7.22), so that

$$\mathscr{J}_{m'}^{(\ell'=1)}(\ell=1)\approx\frac{ik}{\sqrt{24\pi}}\int d^3r\,(\mathbf{r}\times\mathbf{j})_{m'}. \qquad (7.257)$$
(magnetic dipole contribution)

The cross product is sensible here, because we essentially had a product of two rank-1 tensors, and we needed to end up with a tensor of rank 1; the natural way to form a vector out of two vectors is via the cross product (see Problem 7.22). The integral here is (twice) the magnetic dipole moment of the current density (note that due to the cross product, this integral gives a sense of how the current density is circulating). In general, for increasing ℓ', these cases correspond to magnetic multipoles of increasing order. Notice that the magnetic-dipole contribution lacks a factor of c that appears in the electric-dipole contribution (7.252); in general, magnetic-dipole radiation is much weaker than electric-dipole radiation (and the strength decays as you go to higher-order multipoles, as they pick up more and more factors of k).

7.4.4.7 Field Emission Amplitude

Now returning to the quantity $\Phi_{m'}^{(\ell')}(\ell,\hat{k},q)$ in Eq. (7.242), we noted above that it does not transform like a spherical tensor. However suppose that we multiply by the component of a unit vector $\hat{\varepsilon}_q^*$ and sum over the components:

$$\sum_q\hat{\varepsilon}_q^*\Phi_{m'}^{(\ell')}(\ell,\hat{k},q)=\sum_{mq}Y_\ell^{m*}(\hat{k})\,\hat{\varepsilon}_q^*\,\langle\ell'\ m'|\ell\ m;1\ q\rangle. \qquad (7.258)$$

This quantity now matches the template of Eq. (7.245), and thus transforms as a tensor operator of rank ℓ'. Keeping in mind that it is the conjugate of this quantity that appears in Eq. (7.243), in a scalar product of $\mathbf{j}^*(\mathbf{k})$ with $\hat{\epsilon}$, we can interpret this quantity as follows. Since it contains all the dependence on the outgoing radiation, and none of the details of the current density, this is a relative amplitude for the field emission, *given* that the atom has emitted a photon. The amplitude dictates the polarization ($\hat{\epsilon}$), emission direction ($\hat{k}$), total angular momentum (quantum number ℓ'), and z-component of the total angular momentum (m'). The Clebsch–Gordan coefficient says that the total angular momentum is a sum of orbital angular momentum (quantum number ℓ, z-projection quantum number m) and a "spin," or intrinsic angular momentum associated with the photon polarization (quantum number 1, z-projection quantum number q; thus a photon is a massless, spin-1 particle).

The tensor addition of the spherical harmonic and the polarization vector that appears in Eq. (7.258),

$$\mathbf{Y}_{L\ell1}^{m_L}(\hat{r}):=\sum_{mq}Y_\ell^m(\hat{r})\,\hat{\varepsilon}_q\,\langle L\ m_{\text{L}}|\ell\ m;1\ q\rangle, \qquad (7.259)$$
(vector spherical harmonic)

is an important quantity in radiation and scattering problems called the **vector spherical harmonic**.[11] The unit index suggests that these tensors are a special case of the more general **vector solid harmonics**. The interpretation of this expression as a vector spherical harmonic may be somewhat confusing, as there is an alternate set of vector spherical harmonics (more common in classical electrodynamics), taken to be a radial vector field and two fields tangent to the sphere, all mutually orthogonal:

$$\begin{aligned}\mathbf{Y}_{LM}^{(-1)}(\hat{r})&=\hat{r}Y_L^M(\hat{r})\\ \mathbf{Y}_{LM}^{(0)}(\hat{r})&=-\frac{i}{\sqrt{L(L+1)}}\mathbf{r}\times\nabla Y_L^M(\hat{r})\\ \mathbf{Y}_{LM}^{(1)}(\hat{r})&=-\frac{1}{\sqrt{L(2L+1)}}\hat{r}\times(\mathbf{r}\times\nabla)Y_L^{m_L}(\hat{r}).\end{aligned} \qquad (7.260)$$

[11] John M. Blatt and Victor F. Weisskopf, *Theoretical Nuclear Physics* (Wiley, 1952) (ISBN: 0486668274) p. 797, Eq. (1.5).

In terms of these, the vector spherical harmonics (7.259) have the more explicit expressions[12]

$$\begin{aligned}
\mathbf{Y}^{m_L}_{L(L-1)1}(\hat{r}) &= \sqrt{\frac{L+1}{2L+1}}\mathbf{Y}^{(1)}_{Lm_L}(\hat{r}) + \sqrt{\frac{L}{2L+1}}\mathbf{Y}^{(-1)}_{Lm_L}(\hat{r}) \\
\mathbf{Y}^{m_L}_{LL1}(\hat{r}) &= \mathbf{Y}^{(0)}_{Lm_L}(\hat{r}) \\
\mathbf{Y}^{m_L}_{L(L+1)1}(\hat{r}) &= \sqrt{\frac{L}{2L+1}}\mathbf{Y}^{(1)}_{Lm_L}(\hat{r}) - \sqrt{\frac{L+1}{2L+1}}\mathbf{Y}^{(-1)}_{Lm_L}(\hat{r})
\end{aligned} \tag{7.261}$$

Again, these functions define the angular patterns into which the vector potential radiates for the various multipoles.

It is worth reiterating that it is not possible to have $\ell = \ell' = 0$, since the corresponding Clebsch–Gordan coefficient vanishes—the orbital and total angular momenta would both correspond to spherical symmetry, but the problem is that, except for the physically irrelevant case of purely radial polarization, there is no way for the polarization to be spherically symmetric [this also follows from Eq. (7.128)]. This would correspond to a spherically symmetric emission (i.e., $Y^0_0(\hat{k})$ is angle-independent), and thus no monopole radiation is allowed.

7.4.4.8 Wigner–Eckart Theorem and Selection Rules

Now suppose that we compute matrix elements of Eq. (7.243) with respect to atomic states of the form $|\alpha\ J\ m_J\rangle$,

$$\langle \alpha\ J\ m_J|\hat{\varepsilon}\cdot\mathbf{j}^*(\mathbf{k})|\alpha'\ J'\ m'_J\rangle = 4\pi\sum_{\ell\ell' m' q}(-1)^q i^\ell\left[\hat{\epsilon}_q\Phi^{(\ell')}_{m'}(\ell,\hat{k},q)\right]^*\langle \alpha\ J\ m_J|\mathscr{J}^{(\ell')}_{m'}(\ell)|\alpha'\ J'\ m'_J\rangle, \tag{7.262}$$

where we are now including the polarization vector. Here, J and m_J are angular-momentum quantum numbers for the atomic states, and α represents other (i.e., radial) degrees of freedom for the atom. Now applying the Wigner–Eckart theorem (7.200) with tensor rank $k = \ell'$, we find

$$\begin{aligned}
&\langle \alpha\ J\ m_J|\hat{\varepsilon}\cdot\mathbf{j}^*(\mathbf{k})|\alpha'\ J'\ m'_J\rangle \\
&\qquad = 4\pi\sum_{\ell\ell' m' q} i^\ell(-1)^{2\ell'+q}\left[\hat{\epsilon}_q\Phi^{(\ell')}_{m'}(\ell,\hat{k},q)\right]^*\langle \alpha\ J\|\mathscr{J}^{(\ell')}(\ell)\|\alpha'\ J'\rangle\,\langle J\ m_J|J'\ m'_J;\ell'\ m'\rangle.
\end{aligned}$$

(atomic matrix element) (7.263)

This says that the matrix element connecting $|\alpha'\ J'\ m'_J\rangle$ to $|\alpha\ J\ m_J\rangle$ via the atomic operator $\hat{\varepsilon}\cdot j^*(\mathbf{k})$ is the product of a field-emission amplitude, an atomic reduced matrix element (which is orientation-independent), and a Clebsch–Gordan coefficient (which contains all of the orientation dependence of the atom).

We can now read off a bunch of useful information from the Clebsch–Gordan coefficient, without knowing any real details about the atom (other than it should be isotropic to admit wave functions in terms of spherical harmonics). First, the quantum numbers must satisfy

$$|J'-\ell'| \le J \le J'+\ell'. \tag{7.264}$$

(selection rule for multipole radiation)

Since ℓ' is the order of the multipole radiation, it represents the most by which the atomic quantum number J may change in that multipole transition. For example, in a dipole ($\ell' = 1$) transition, J may change by at most 1. The Clebsch–Gordan coefficient similarly says that the projection quantum numbers must add up:

$$m_J = m'_J + m'. \tag{7.265}$$

(selection rule for multipole radiation)

Since $|m'|$ is at most ℓ', this also says that m_J may change by at most ℓ' in a multipole transition of order ℓ'. It is also a simple statement of conservation of (the z component of) angular momentum, such that

[12] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum*, (World Scientific, 1988) (ISBN: 9971501074), p. 210.

the initial atomic angular atom matches the sum of the angular momenta of the final atomic state and the emitted field.

There is one more transition that can be excluded on the basis of the above expression. As a result of the symmetry rule (7.128) of Clebsch–Gordan coefficients, if $J' = J$ and $m'_J = m_J = 0$ (so that necessarily $m' = 0$), the coefficient will vanish if ℓ' is odd:

$$\text{if } m_J = m'_J = 0 \text{ and } \ell' \text{ is odd, then } J \neq J'. \tag{7.266}$$

(selection rule for multipole radiation)

This applies to electric and magnetic dipole transitions ($\ell' = 1$), but not electric or magnetic quadrupole transitions ($\ell' = 2$), for example. (See also Problem 7.16.)

It is worth reiterating that for fixed J and J', the relative strengths of the remaining allowed transitions are then given by simply evaluating a Clebsch–Gordan coefficient. To compute relative strengths of transitions of varying J and J', it is necessary to compute a reduced matrix element. It is possible to compute this directly, but an accurate calculation is difficult except in the case of hydrogen. It is generally easier to relate the matrix element to a spontaneous emission rate, which can be measured experimentally.

7.4.4.9 Parity Selection Rules

The parity of the atomic state further constrains the possible transitions. Recall that the parity operator Π induces the transformation $\mathbf{r} \longrightarrow -\mathbf{r}$, and hence $\mathbf{p} \longrightarrow -\mathbf{p}$. We haven't yet considered the parity of angular-momentum states, so as a prototype let's work out the parity of the spherical harmonics. Combining Eqs. (7.62) and (7.72) gives the expression for the stretched state $|\ell\ -\ell\rangle$

$$Y_\ell^{-\ell}(\theta, \phi) = \eta\,(\sin\theta)^\ell e^{-i\ell\phi}, \tag{7.267}$$

where η is the normalization constant that won't matter here. In spherical coordinates, the parity transformation corresponds to changing the angles by $\theta \longrightarrow \pi - \theta$ and $\phi \longrightarrow \phi + \pi$, so the parity-flipped spherical harmonic is

$$\Pi\, Y_\ell^{-\ell}(\theta, \phi) = \eta\big[\sin(\pi - \theta)\big]^\ell e^{-i\ell(\phi+\pi)} = \eta\,(\sin\theta)^\ell e^{-i\ell\phi} e^{-i\ell\pi} = (-1)^\ell Y_\ell^{-\ell}(\theta, \phi). \tag{7.268}$$

Thus, the parity eigenvalue of this state is $(-1)^\ell$. To fill in the other states, note that $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is invariant under a parity change, and thus so is every component (we just saw that m didn't change for the stretched state, for example). In particular, $L_\pm = L_x \pm iL_y$ is invariant under a parity change, so can write

$$\Pi\, Y_\ell^m(\theta, \phi) = (-1)^\ell Y_\ell^m(\theta, \phi), \tag{7.269}$$

(spherical-harmonic parity)

which is to say *all* the spherical harmonics have parity $(-1)^\ell$.

Now to apply parity to multipole radiation, we can start by referring to Eq. (7.241) for $\mathscr{J}_{m'}^{(\ell')}(\ell)$. The two factors that change under a parity transformation are the current density [which transforms as $\mathbf{j}(\mathbf{r}) \longrightarrow -\mathbf{j}(-\mathbf{r})$] and the spherical harmonic $Y_\ell^{m''}(\hat{r})$. Thus the parity of $\mathscr{J}_{m'}^{(\ell')}(\ell)$ is $(-1)^{\ell+1}$, and the corresponding matrix element will vanish unless the initial and final states differ in parity by $(-1)^{\ell+1}$. (If the combined parity is odd, the matrix element amounts to an odd integral over symmetric limits.)

For electric multipoles, the multipole order is $\ell' = \ell + 1$, so the parity of the initial and final states must differ by $(-1)^{\ell'}$. For magnetic multipoles, with $\ell' = \ell$, the parity of the initial and final states must differ by $(-1)^{\ell'+1}$. Mathematically, we can summarize these statements as

$$\begin{aligned} \pi_J \pi_{J'} &= (-1)^{\ell'} && \text{(electric multipole)} \\ \pi_J \pi_{J'} &= (-1)^{\ell'+1} && \text{(magnetic multipole),} \end{aligned} \tag{7.270}$$

(parity selection rules)

where π_J is the parity eigenvalue of the state $|\alpha\ J\ m_J\rangle$. Thus, for example, for electric dipole transitions ($\ell' = 1$), the initial and final states must have opposite parity—this is the most important selection rule,

because electric dipole transitions are the strongest ones. For magnetic dipole ($\ell' = 1$) or electric quadrupole transitions ($\ell' = 2$), the initial and final states must have the same parity.

As a further example, suppose we have a simple, one-electron atom (hydrogen-like, so this applies to the alkali atoms). In the case of an electric dipole transition, ignoring any electronic or nuclear spin, so the states are just defined by orbital angular momentum (i.e., the angular momentum quantum numbers J and m_J correspond to L and m_L), the angular momentum of the initial and final states must differ by at most 1, so $L' = L, L \pm 1$ according to the Wigner–Eckart theorem. But because of parity, $L' = L$ is excluded, so the selection rule is $L' = L \pm 1$. On the other hand, if J and m_J refer to some composite quantum numbers (with spin mixing with orbit, or two electrons mixing), then it could be that $J' = J$ in an electric dipole transition.

7.5 Exercises

Problem 7.1

If we define the vector $\mathbf{J} := \hat{x}J_x + \hat{y}J_y + \hat{z}J_z$, where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are the usual unit vectors, show that

$$\mathbf{J} \times \mathbf{J} = i\hbar\mathbf{J}. \tag{7.271}$$

This is really just a component-free restatement of the defining commutation relations for angular momentum.

Problem 7.2

Consider an operator A, which satisfies $[A, J_x] = [A, J_y] = 0$. Show that $[A, J_z] = 0$.

Problem 7.3

Remember that the trace is a sum over all diagonal matrix elements, which is true in any basis; in the context here the matrix elements run over a basis corresponding to a particular j, so that for example

$$\mathrm{Tr}[A] = \sum_m \langle j\ m|A|j\ m\rangle \tag{7.272}$$

for any operator A. Let J_α denote the Cartesian components of the angular momentum vector $\mathbf{J}$.

(a) Show that $\mathrm{Tr}[J_\alpha] = 0$.

(b) Show that

$$\mathrm{Tr}[J_\alpha J_\beta] = \frac{\hbar^2 j(j+1)(2j+1)}{3}\delta_{\alpha\beta}. \tag{7.273}$$

(c) Show that

$$\mathrm{Tr}[J_\alpha J_\beta J_\gamma] = \frac{i\hbar^3 j(j+1)(2j+1)}{6}\epsilon_{\alpha\beta\gamma}. \tag{7.274}$$

Problem 7.4

The idea behind Schwinger's representation of an angular momentum in terms of a pair of harmonic oscillators[13] is that J_z is represented by the difference in energy quanta of the two oscillators, J_+ creates a quantum in the first oscillator and removes one from the second, and J_- removes a quantum from the first and creates one in the second. Each oscillator is basically an ensemble of spin-$1/2$ systems, and a total angular momentum j is represented by a total of $2j$ spin-$1/2$'s (note that the number of spin-$1/2$'s is conserved).

Thus, consider a pair of independent, identical, uncoupled harmonic oscillators, with Hamiltonian

$$H = \hbar\omega_+\big(a_+^\dagger a_+ + 1/2\big) + \hbar\omega_-\big(a_-^\dagger a_- + 1/2\big). \tag{7.275}$$

That is, their operators are distinguished by the $\pm$ labels. Now suppose that we define the vector operator

$$\mathbf{J} := \frac{\hbar}{2}\sum_{mm'} a_m^\dagger \langle m|\boldsymbol{\sigma}|m'\rangle\, a_{m'}, \tag{7.276}$$

where the sums m and m' run over $\{+,-\}$, and $\langle m|\boldsymbol{\sigma}|m'\rangle$ refer to the matrix elements of the Pauli matrix (σ_x, σ_y, or σ_z) matching components of $\mathbf{J}$.

[13] J. Schwinger, "On Angular Momentum,". US Atomic Energy Commission report NYO-3071 (1952) (doi: 10.2172/4389568). A more readable version is available online at `https://www.ifi.unicamp.br/~cabrera/teaching/paper_schwinger.pdf`.

Note that the equations

$$J_z = \frac{\hbar}{2}\Big(a_+^\dagger a_+ - a_-^\dagger a_-\Big), \qquad J_\pm = \hbar a_\pm^\dagger a_\mp \tag{7.277}$$

give an equivalent expression of Eq. (7.276).

Show that **J** is an angular-momentum vector. The easier way to do this is in terms of the equations (7.277), but of course the cool and awesome way to do this is directly in terms of the definition (7.276).

Problem 7.5

Derive the formula [Eq. (7.49)]

$$\nabla = \hat{r}\,\partial_r + \frac{\hat{\theta}}{r}\,\partial_\theta + \frac{\hat{\phi}}{r\sin\theta}\,\partial_\phi \tag{7.278}$$

for the gradient operator in spherical coordinates by considering the differential

$$df(r,\theta,\phi) = d\mathbf{r}\cdot\nabla f(\mathbf{r}) \tag{7.279}$$

for an arbitrary scalar function $f(\mathbf{r})$, and working out the effect of infinitesimal displacements in different directions. Note the suggestive forms of the (equivalent) arguments on both sides.

Problem 7.6

Prove the identity

$$\epsilon_{\mu\alpha\beta}\epsilon_{\mu\sigma\tau} = \delta_{\alpha\sigma}\delta_{\beta\tau} - \delta_{\alpha\tau}\delta_{\beta\sigma} \tag{7.280}$$

for the Levi-Civita symbol by writing out the "bac-cab" vector identity $\mathbf{A}\times(\mathbf{B}\times\mathbf{C}) = \mathbf{B}(\mathbf{A}\cdot\mathbf{C}) - \mathbf{C}(\mathbf{A}\cdot\mathbf{B})$, in terms of components.

Problem 7.7

We argued that the requirement that the azimuthal phase be single-valued for an eigenstate $Y_\ell^m(\theta,\phi)$ of orbital angular momentum rules out the possibility of half-integer values for m (and thus ℓ). Another way to rule out the case $\ell = 1/2$ is to consider the function $\Theta_\ell^{-\ell}(\theta)$ in the case $\ell = 1/2$. From the development of the spherical harmonics, we know that

$$\Theta_\ell^{-\ell}(\theta) = \Theta_\ell^{\ell}(\theta), \tag{7.281}$$

and

$$(L_+)^{2\ell}\Theta_\ell^{-\ell}(\theta)\,e^{-i\ell\phi} \propto \Theta_\ell^{\ell}(\theta)\,e^{i\ell\phi}. \tag{7.282}$$

Show that these two statements form a contradiction in the case $\ell = 1/2$.

Problem 7.8

(a) Show that

$$[J_x^2, J_y^2] = [J_y^2, J_z^2] = [J_z^2, J_x^2]. \tag{7.283}$$

Hint: start with the observation that $[J^2, J_z] = 0$.

(b) Show that if $j = 0$, $j = 1/2$, or $j = 1$, then all these commutators vanish.
Hint: start by computing an expression for $J_+^2 + J_-^2$.

Problem 7.9

Show that a general rotation operator on a $j = 1$ Hilbert space may be written in the form

$$e^{-i\boldsymbol{\zeta}\cdot\mathbf{J}/\hbar} = 1 - i\frac{\hat{\zeta}\cdot\mathbf{J}}{\hbar}\sin\zeta + \left(\frac{\hat{\zeta}\cdot\mathbf{J}}{\hbar}\right)^2(\cos\zeta - 1). \tag{7.284}$$

(For the analogous expression in the case $j = 1/2$, see Problem 9.1.)

Problem 7.10

In the case $j = 1$, derive the explicit matrix expressions for J_x, J_y, and J_z (in the representation of J_z's eigenstates).

Problem 7.11

(a) The Wigner rotation matrix for a composite rotation through Euler angles (α, β, γ) is

$$\left[D^{(1/2)}_{m'm}(\alpha,\beta,\gamma)\right] = \begin{bmatrix} e^{-i(\alpha+\gamma)/2}\cos(\beta/2) & -e^{-i(\alpha-\gamma)/2}\sin(\beta/2) \\ e^{i(\alpha-\gamma)/2}\sin(\beta/2) & e^{i(\alpha+\gamma)/2}\cos(\beta/2) \end{bmatrix} \tag{7.285}$$

for the case $j = 1/2$. The point of this is, of course, that *any* rotation specified by a rotation vector $\boldsymbol{\zeta}$ can be specified in terms of the Euler angles.

Conversely, suppose that someone gives you a rotation in terms of the Euler angles (α, β, γ). Using the above form of the $j = 1/2$ rotation matrix, what is the equivalent rotation vector $\boldsymbol{\zeta}$ (i.e., the angle and axis of the equivalent, *single* rotation)? (The identity in Problem 9.1 will be useful here.)

(b) In the case of $j = 1$, the Wigner matrix is

$$\left[D^{(1)}_{m'm}(\alpha,\beta,\gamma)\right] = \begin{bmatrix} e^{-i\alpha}\dfrac{1+\cos\beta}{2}e^{-i\gamma} & -e^{-i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{-i\alpha}\dfrac{1-\cos\beta}{2}e^{i\gamma} \\ \dfrac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & -\dfrac{\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\dfrac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\dfrac{1+\cos\beta}{2}e^{i\gamma} \end{bmatrix}. \tag{7.286}$$

Does the same equivalent single rotation still hold here? Prove your answer either way.

Problem 7.12

(a) Show that

$$R(-\epsilon^2\hat{z}) = R(-\epsilon\hat{y})R(-\epsilon\hat{x})R(\epsilon\hat{y})R(\epsilon\hat{x}) + O(\epsilon^3) \tag{7.287}$$

(that is, that the rotation on the left and the composite rotation on the right are equivalent up to second order in ϵ).

Note the physical content of this mathematical statement: a small rotation about $\hat{x}$ followed by a small rotation about $\hat{y}$ is *not quite* the same as the net rotation in the reversed order, the difference being $O(\epsilon^2)$. Here we see this by applying the two rotations, and then seeing if we can undo the rotations by applying the opposing rotations in the wrong order (if the rotations commuted, we would see unity on the left-hand side).

(b) An alternate approach to defining angular momentum to the method we used in Section 7.1.1 is as follows. Note that in classical mechanics, Eq. (7.287) holds, and J_z is the generator of rotations about the z axis (to pick an arbitrary direction). In quantum mechanics, we can assume that Eq. (7.287) holds, and J_z is still the generator of rotations (which from Problem 1.17 means, for example, that $R(\epsilon\hat{z}) = 1 - i\epsilon J_z/\hbar$). Show that these two assumptions imply that J_x, J_y, and J_z are the angular momentum components in the sense we defined them.

Problem 7.13

(a) Starting with the eigenstate $|j\ m\rangle = |1\ 0\rangle$, find the state after a $\pi/2$ rotation about the y-axis, using

$$R(\hat{y}\pi/2)\,|1\ 0\rangle = \sum_m |1\ m\rangle\langle 1\ m|R(\hat{y}\pi/2)\,|1\ 0\rangle = \sum_m |1\ m\rangle\, d^{(1)}_{m0}(\hat{y}\pi/2) \tag{7.288}$$

and the explicit form of the rotation matrix (7.159). Note that this rotation transforms the z axis into the x axis; so your answer is also the eigenstate $|j\ m_x\rangle = |1\ 0\rangle$ (where m_x is the quantum number for the eigenstates of J_x), expressed as a superposition of states $|j\ m_z\rangle$ the normal basis.

(b) Do the same thing, but for a $-\pi/2$ rotation about the x-axis. This rotation transforms the z axis into the y axis; so your answer is also the eigenstate $|j\ m_y\rangle = |1\ 0\rangle$ (where m_y is the quantum number for the eigenstates of J_y), expressed in the normal basis $|j\ m_z\rangle$.

Problem 7.14

For an eigenstate $|j\ m\rangle$ of J^2 and J_z, compute $\langle J_x\rangle$, $\langle J_x^2\rangle$, σ_{J_x}, and $\sigma_{J_x}\sigma_{J_y}$. Demonstrate explicitly that the last quantity is compatible with the uncertainty principle.

Problem 7.15

A particle of spin $S = 1$ with $m = 1$ splits into two particles each with $S = 2$. If you make a measurement of S_z on one of the particles, compute the probability of observing the value $m = 0$ for that particle. (Assume the particles to be distinguishable.)

Problem 7.16

Consider a particle of angular-momentum quantum number j that decays into two other particles of angular-momentum numbers j and 1, respectively. Show that if the parent particle has $m = 0$, then it is impossible for both of the child particles to also have $m = 0$.

Note that this is an important result in atom–photon interactions, because one of the ''child'' particles could be a photon, which has an angular-momentum quantum number of 1 for electric-dipole emission. This means that if an atom emits a photon with $m = 0$ (linear polarization), then either the atomic j or m quantum number (or both) must change as a result of the emission.

In your solution, you should start by writing down the class of Clebsch–Gordan coefficients that should vanish. Note that it shouldn't necessarily be obvious that it vanishes—it should satisfy the usual triangularity constraints required for Clebsch–Gordan coefficients to make sense. Then to begin your argument that the coefficient indeed vanishes (i.e., don't just ask Prof. *Mathematica*), skim through Section 7.3.5 to find a symmetry relation that would make for a handy starting point. (And make sure you see why the argument *doesn't* carry through if the child particle *isn't* in the $|j\ 0\rangle$ state.)

Problem 7.17

Compute numerical values for the following (squared) Clebsch–Gordan coefficients. Remember the notation convention for the coefficients is $\langle j_1\, m_1; j_2\, m_2 | j_3\, m_3\rangle$, where $\mathbf{J}_3 = \mathbf{J}_1 + \mathbf{J}_2$. (Keep in mind: your reasoning is at least as important as your numerical result.)

(a) $|\langle 1\,1; 1\,0 | 3\,1\rangle|^2$

(b) $|\langle 1\,1; 1\,0 | 1\,(-1)\rangle|^2$

(c) $|\langle 0\,0; 1\,0 | 1\,0\rangle|^2$

(d) $|\langle 0\,0; 1\,0 | 0\,0\rangle|^2$

(e) $|\langle 1\,0; 1\,0 | 0\,0\rangle|^2$

Problem 7.18

(a) Show that the magnitude of $\langle j\ m; j\ -m | 0\ 0\rangle$ is independent of m.

(b) Prove that

$$\sum_{jm} (-1)^m \langle j\ m; j\ -m | j\ 0\rangle = 1. \tag{7.289}$$

Hint: in both parts, use $\langle j\ m;0\ 0|j\ m\rangle = 1$.

Problem 7.19

(a) Consider a "stretched" angular-momentum eigenstate $|j\ m{=}j\rangle$. Compute the probability of a measurement of J_z to still find $m = j$ after a rotation about the x axis by a small angle α. (Use the rotation *operator*, not the rotation *matrix*, and compute your result up to order α^2.)

(b) Do the same for a "centered" angular-momentum eigenstate $|j\ m{=}0\rangle$, finding the probability of a measurement of J_z to still find $m = 0$ after a rotation about the x axis by a small angle α.

Problem 7.20

(a) Show that any rotation can be written as the product of two 180° rotations [considering rotations in coordinate space, where a 180° rotation is an involution, $R^2(\pi\hat{\zeta}) = 1$].

Hint: Consider a 180°-rotation about the x-axis, $R(\pi\hat{x})$. Now consider a second rotation of 180° about a second axis, say $\hat{\xi}$, which lies somewhere in the x–y plane. The second rotation is the same as the first one except for its orientation (i.e., equivalent up to a rotation). Write down this last statement mathematically, and then compose the two rotations to find the net result. You may even want to sketch the effect of the two rotations in some simple case to get a feel for the expected result.

(b) Give the explicit decomposition of a 90° rotation about the x axis in terms of two 180° rotations.

Problem 7.21

The Wigner rotation matrix for a rotation of a state through Euler angles (α, β, γ) is

$$\left[D^{(1)}_{m'm}(\alpha,\beta,\gamma)\right] = \begin{bmatrix} e^{-i\alpha}\dfrac{1+\cos\beta}{2}e^{-i\gamma} & -e^{-i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{-i\alpha}\dfrac{1-\cos\beta}{2}e^{i\gamma} \\ \dfrac{\sin\beta}{\sqrt{2}}e^{-i\gamma} & \cos\beta & -\dfrac{\sin\beta}{\sqrt{2}}e^{i\gamma} \\ e^{i\alpha}\dfrac{1-\cos\beta}{2}e^{-i\gamma} & e^{i\alpha}\dfrac{\sin\beta}{\sqrt{2}} & e^{i\alpha}\dfrac{1+\cos\beta}{2}e^{i\gamma} \end{bmatrix}. \tag{7.290}$$

Recall that the Wigner matrix is defined to transform basis states in a *passive* rotation via [Eq. (7.133)]

$$R|j\ m\rangle = \sum_{m'} |j\ m'\rangle\, D^{(j)}_{m'm}, \tag{7.291}$$

but remember that it more literally represents an *active* rotation of a state $|\psi\rangle$ through angles (α, β, γ) in the representation of $|j\ m\rangle$ states; that is, it acts on the vector with components $\langle j\ m|\psi\rangle$, producing an active rotation of the state.

The Cartesian-rotation-matrix counterparts for a rotation through angle θ about the y and z axes are, respectively, z axis is

$$R_y(\theta) = \begin{bmatrix} \cos\theta & 0 & \sin\theta \\ 0 & 1 & 0 \\ -\sin\theta & 0 & \cos\theta \end{bmatrix}, \qquad R_z(\theta) = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{7.292}$$

The Cartesian matrix is defined to rotate components of the position vector by

$$\tilde{r}_\mu = \sum_{\mu'} R_{\mu\mu'} r_{\mu'} \tag{7.293}$$

(greek indices will refer to Cartesian components, latin indices to spherical-basis components, so that for example $r_\mu := \hat{x}_\mu \cdot \mathbf{r}$ is a Cartesian component and $r_m := \hat{\mathrm{e}}_m \cdot \mathbf{r}$ is a spherical component). A

Cartesian rotation thus represents a rotation of the Cartesian *axes*, and is therefore a *passive* rotation. Then the composite Cartesian rotation that most closely corresponds to the Wigner-matrix rotations is

$$R_{\mu\mu'}(-\alpha,-\beta,-\gamma) := \Big(R_z(-\gamma)R_y(-\beta)R_z(-\alpha)\Big)_{\mu\mu'}. \tag{7.294}$$

The signs of the angles are reversed to make an active rotation, and the rotations are applied in the order α first, γ last, because each successive rotation occurs with respect to the new rotated frame.

Now we need to more specifically relate the Cartesian matrix $R_{\mu\mu'}$ to the Wigner matrix $D_{m'm}$, because they are in different representations of vectors in three-dimensional space. In the standard quantum-mechanical notation, in the case of $j = 1$ and in the position representation, we are working with the $\ell = 1$ spherical harmonics,

$$Y_1^m(\theta,\phi) := \langle\theta,\phi|1\ m\rangle, \tag{7.295}$$

in terms of which the transformation rule is

$$\tilde{Y}_1^m = \sum_{m'} Y_1^{m'} D^{(1)}_{m'm}, \tag{7.296}$$

where $\tilde{Y}_1^m(\theta,\phi) := \langle\theta,\phi|R|1\ m\rangle$ is the rotated spherical harmonic. Let's transform the Cartesian matrix so that it matches this rotation formula.

Let the operator U represent the (unitary) transformation matrix going from the Cartesian basis to the spherical basis, so that $r_m = \sum_\mu U_{m\mu} r_\mu$ is in the spherical basis. Then

$$\begin{aligned}
\tilde{r}_m = \sum_\mu U_{m\mu}\tilde{r}_\mu &= \sum_{\mu\mu'} U_{m\mu} R_{\mu\mu'} r_{\mu'} \\
&= \sum_{\mu\mu'\mu''m'} U_{m\mu} R_{\mu\mu'} U^*_{\mu'm'} U_{m'\mu''} r_{\mu''} \\
&= \sum_{\mu\mu'm'} U_{m\mu} R_{\mu\mu'} U^*_{\mu'm'} r_{m'} \\
&= \sum_{m'} C_{mm'} r_{m'},
\end{aligned} \tag{7.297}$$

where we used the unitarity of U and then defined the spherical vector

$$r_{m'} := \sum_{\mu''} U_{m'\mu''} r_{\mu''} \tag{7.298}$$

and the spherical-basis rotation operator

$$C_{mm'} := \sum_{\mu\mu'} U_{m\mu} R_{\mu\mu'} U_{\mu'm'} = (URU^\dagger)_{mm'}. \tag{7.299}$$

Now remembering that the spherical harmonics of $\ell = 1$ form a representation of the position vector,

$$\hat{\mathrm{e}}_q \cdot \mathbf{r} = r_q = r\sqrt{\frac{4\pi}{3}}\, Y_1^q(\theta,\phi), \tag{7.300}$$

we have shown that

$$\tilde{Y}_1^m = \sum_{m'} C_{mm'} Y_1^{m'}. \tag{7.301}$$

Comparing to the direct spherical rotation (7.296), we finally see that

$$D^{(1)}_{m'm}(\alpha,\beta,\gamma) = C_{mm'}(-\alpha,-\beta,-\gamma). \tag{7.302}$$

That is, taking the composite Cartesian rotation (with reversed angles) and transforming it to the spherical basis gives the *transpose* of the Wigner form.

(a) Now to convert the Cartesian rotations into the Wigner matrix, start by writing down the matrix representation of U, which is defined by $a_m = \sum_m U_{m\mu} a_\mu$ for a general vector $\mathbf{a}$, or to fix the order convention of the components,

$$\begin{bmatrix} a_1 \\ a_0 \\ a_{-1} \end{bmatrix} = [U] \begin{bmatrix} a_x \\ a_y \\ a_z \end{bmatrix}. \tag{7.303}$$

(b) Transform the individual Cartesian passive rotation matrices using your matrix $[U]$ into the spherical basis (so you can see what the simpler transformed matrices look like), and then compose the matrices to compute the transformed Cartesian matrix $[C]$, via the matrix form of the operator product

$$[C(-\alpha,-\beta,-\gamma)] = [URU^\dagger] = [UR_z(-\gamma)U^\dagger]\,[UR_y(-\beta)U^\dagger]\,[UR_z(-\alpha)U^\dagger] =: [C(-\gamma)][C(-\beta)][C(-\alpha)]. \tag{7.304}$$

Note: the entire value of this problem is in the setup, and of course in seeing that everything comes out correctly. At this point in your life, grinding through the matrix multiplications probably won't make you a better person. A computer algebra system is your friend.

(c) Finally, transpose your result and verify that you recover Eq. (7.290) for the composite Wigner matrix.

Problem 7.22

Since irreducible tensor operators transform as spherical tensors, the way to form an irreducible product of two tensors is

$$T^{(k)}_q = \sum_{\substack{q_1 q_2 \\ (q_1+q_2=q)}} T^{(k_1)}_{q_1}\, T^{(k_2)}_{q_2}\, \langle k_1\, q_1; k_2\, q_2 | k\, q\rangle, \tag{7.305}$$

in analogy to the combination rule for spherical harmonics

$$Y^m_\ell(\theta,\phi) = \sum_{\substack{m_1 m_2 \\ (m_1+m_2=m)}} Y^{m_1}_{\ell_1}(\theta,\phi)\, Y^{m_2}_{\ell_2}(\theta,\phi)\, \langle \ell_1\, m_1; \ell_2\, m_2 | \ell\, m\rangle. \tag{7.306}$$

The rank-1 combination of two vectors $\mathbf{A}$ and $\mathbf{B}$ is thus

$$T^{(1)}_q = \sum_{q'=-1}^{1} A_{q'} B_{q-q'}\, \langle 1\, q'; 1\, q-q' | 1\, q\rangle. \tag{7.307}$$

Evaluate the Clebsch–Gordan coefficients and write out the explicit components

$$T^{(1)}_q = \frac{i}{\sqrt{2}} (\mathbf{A}\times\mathbf{B})_q \tag{7.308}$$

in the spherical basis.

Problem 7.23

Suppose $T^{(2)}_q$ and $U^{(2)}_q$ are the components of two rank-2 irreducible tensor operators.

(a) Show how to combine them to form a scalar (rank-0 irreducible tensor) operator.

(b) The two operators can also be combined to form other rank-k irreducible tensor operators. What is the range of possible k?

Problem 7.24

Recall that an irreducible tensor operator $T_q^{(k)}$ was defined such that its components rotate in the same way as the angular momentum states $|k\ q\rangle$. Given this similarity, it shouldn't be surprising that there are other analogous expressions for $T_q^{(k)}$ vs. $|k\ q\rangle$.

(a) Show, in analogy to $J_z|j\ m\rangle = \hbar m|j\ m\rangle$, that

$$[J_z, T_q^{(k)}] = \hbar q T_q^{(k)}. \tag{7.309}$$

(*Hint*: consider an *infinitesimal* rotation.)

(b) Similarly, show that

$$[J_\pm, T_q^{(k)}] = T_{q\pm1}^{(k)} \hbar \sqrt{k(k+1) - q(q\pm1)}, \tag{7.310}$$

in analogy to the expressions for $J_\pm|j\ m\rangle$.

(c) Finally, in analogy to $J^2|j\ m\rangle = \hbar^2 j(j+1)|j\ m\rangle$, show that

$$\sum_\alpha [J_\alpha, [J_\alpha, T_q^{(k)}]] = \hbar^2 k(k+1) T_q^{(k)}. \tag{7.311}$$

Problem 7.25

Let $\mathbf{V}$ be an operator whose (Cartesian) components satisfy the commutation relation $[J_\alpha, V_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}V_\gamma$. Such an operator is called a **vector operator**; this definition is the (equivalent) Cartesian counterpart to the definition of a vector operator as a rank-1 irreducible tensor operator.

(a) Obviously $\mathbf{J}$ satisfies the definition of a vector operator, and remember that one property of $\mathbf{J}$ is that different components don't commute. Is this true of every vector operator? (Give a proof or counterexample, as appropriate.)

(b) Show that $\mathbf{V}\cdot\mathbf{J} = \mathbf{J}\cdot\mathbf{V}$.

(c) Show that $\mathbf{J}$ commutes with $\mathbf{V}\cdot\mathbf{J}$.

(d) Show that

$$[J^2, [J^2, \mathbf{V}]] = 2\hbar^2[J^2, \mathbf{V}]_+ - 4\hbar^2(\mathbf{V}\cdot\mathbf{J})\mathbf{J}. \tag{7.312}$$

Problem 7.26

The quadrupole tensor operator (of an electron, proton, etc.) is a rank-2 irreducible operator defined by the component

$$Q_0^{(2)} = 3z^2 - r^2. \tag{7.313}$$

Defining the quadrupole moment as

$$Q = \langle j\ j|Q_0^{(2)}|j\ j\rangle, \tag{7.314}$$

write an expression for the matrix element

$$\langle j\ m|Q_0^{(2)}|j\ m\rangle \tag{7.315}$$

in terms of (only) Q, j, and m (use *Mathematica* or a table to evaluate any Clebsch–Gordan coefficients).

Problem 7.27

Given the derivative operators

$$\partial_\pm := \frac{\partial}{\partial\chi_\pm}, \tag{7.316}$$

defined in terms of independent variables χ_+ and χ_-, we can define the components

$$J_1 = -\frac{\hbar}{\sqrt{2}}\chi_+\partial_-, \qquad J_{-1} = \frac{\hbar}{\sqrt{2}}\chi_-\partial_+ \tag{7.317}$$

of a vector $\mathbf{J}$ in the spherical basis. Derive an expression for the remaining component J_0 in terms of $\chi_\pm$ and $\partial_\pm$ so that $\mathbf{J}$ is an angular-momentum operator, and prove that it is indeed an angular-momentum operator.

Be careful not to conflate the vector components $J_{\pm1}$ with the ladder operators $J_\pm$; also try working exclusively in the spherical basis.

Chapter 8

Particle in Three Dimensions

With the apparatus of orbital angular momentum in hand, we can tackle particles in three-dimensional potentials. Only certain, highly symmetric problems are amenable to solution in closed form, and those are the type we'll consider here—their solution amounts to three independent, one-dimensional solutions.

8.1 Free Particle and the Helmholtz Equation

The simplest potential in three dimensions is, of course, no potential at all—the free particle. In this case $H = p^2/2m_\mathrm{p}$ in three dimensions (with m_p the "particle mass," to keep it distinct from the quantum number m that we'll introduce later), and so we can write the time-independent Schrödinger equation in the position representation as

$$-\frac{\hbar^2}{2m_\mathrm{p}}\nabla^2\psi = E\psi. \tag{8.1}$$

Rearranging this a bit, we can rewrite this as the important equation

$$(\nabla^2 + k^2)\psi = 0, \tag{8.2}$$
(Helmholtz equation)

which is the **Helmholtz equation**, where we have defined the wave number

$$k = \frac{\sqrt{2m_\mathrm{p}E}}{\hbar} \tag{8.3}$$

as usual in terms of the energy $E > 0$.

8.1.1 Cartesian Coordinates

In three dimensions, we have some latitude for choosing a coordinate system for the solution. This could be dictated by boundary conditions, though we won't consider anything explicit here (except outgoing boundaries at infinity). The simplest choice is ordinary Cartesian coordinates, where the Laplacian has the specific form

$$\nabla^2 = \partial_x^2 + \partial_y^2 + \partial_z^2. \tag{8.4}$$

The key to solving this problem is to make the separation **ansatz** that the wave function may be written as the product

$$\psi(\mathbf{r}) = X(x)Y(y)Z(z) \tag{8.5}$$

Putting this form into the Helmholtz equation (8.2) with the Laplacian (8.4) gives

$$\frac{X''}{X} + \frac{Y''}{Y} + \frac{Z''}{Z} + k^2 = 0 \tag{8.6}$$

after dividing through by ψ. Now notice that the first three terms are separately functions only of x, y, or z; for the equality to hold, each term must separately be a constant (i.e. varying x can't change X''/X because the rest of the equation doesn't change). Introducing constants $k_{x,y,z}$ we can thus write

$$\frac{X''}{X} = -k_x^2, \qquad \frac{Y''}{Y} = -k_y^2, \qquad \frac{Z''}{Z} = -k_z^2, \tag{8.7}$$

so that the Helmholtz equation becomes simply

$$k^2 = k_x^2 + k_y^2 + k_z^2, \tag{8.8}$$

which is just a resolution of the wave vector into components. Note that we are anticipating the form of the final solution in setting up the constants in Eqs. (8.7), but we aren't losing any generality because the $k_{x,y,z}$ could be real or imaginary numbers. In free space these will naturally be real, but they could be imaginary under some boundary conditions (see Problem 8.3).

Now to solve Eqs. (8.7); the x component of the solution integrates readily to

$$X(x) = X(0)e^{\pm ik_x x}. \tag{8.9}$$

For consistency with the one-dimensional free particle, where we took the momentum eigenstates (1.157) to be the energy eigenstates, we can choose $X(0) = 1/\sqrt{2\pi\hbar}$, though it's worth reiterating that the wave functions are not normalizable. The solutions in y and z follow in the same way and the resulting eigenfunctions are

$$\psi(\mathbf{r}) = \frac{1}{(2\pi\hbar)^{3/2}} e^{ik_x x} e^{ik_y y} e^{ik_z z} = \frac{1}{(2\pi\hbar)^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{8.10}$$
(free-particle eigenfunctions)

making for straightforward generalizations of the one-dimensional case.

8.1.2 Spherical Coordinates

The next obvious choice for a coordinate system for the free particle is cylindrical coordinates. But since this will be similar to the spherical-coordinate case, we'll leave this as an exercise (see Problem 8.3).

Moving on to the case of spherical coordinates, the Laplacian in the Helmholtz equation (8.2) takes the form

$$\begin{aligned} \nabla^2 &= \frac{1}{r^2}\partial_r r^2 \partial_r + \frac{1}{r^2 \sin\theta}\partial_\theta \sin\theta\, \partial_\theta + \frac{1}{r^2 \sin^2\theta}\partial_\phi^2 \\ &= \frac{1}{r}\partial_r^2 r + \frac{1}{r^2 \sin\theta}\partial_\theta \sin\theta\, \partial_\theta + \frac{1}{r^2 \sin^2\theta}\partial_\phi^2, \end{aligned} \tag{8.11}$$

where the derivative operators are understood to operate on everything to the right, including an arbitrary test function. In this case we can separate the Helmholtz equation by taking the separation *ansatz* $\psi(\mathbf{r}) = R(r)\Theta(\theta)\Phi(\phi)$. Given our development of the angular eigenstates of orbital angular momentum in Section 7.2.3, we can anticipate that the solution of the angular part $\Theta(\theta)\Phi(\phi)$ will be given by the spherical harmonics $Y_\ell^m(\theta,\phi)$. However, let's pretend that we don't already know this, and sketch the idea for how these will arrive anyway.

8.1.2.1 Separation

Substitution of the separation *ansatz* into the Helmholtz equation (8.2) yields

$$\frac{1}{rR}(rR)'' + \frac{1}{r^2 \sin\theta\,\Theta}(\sin\theta\,\Theta')' + \frac{1}{r^2\sin^2\theta\,\Phi}\Phi'' + k^2 = 0, \tag{8.12}$$

after dividing through by ψ. The separation of variables here is slightly trickier than in the Cartesian case. Let's first take

$$\frac{\Phi''}{\Phi} = -c_2^2 \tag{8.13}$$

for an undetermined constant c_2, which we can do by isolating this term (multiplying through by $r^2 \sin^2\theta$) and requiring it to be constant. What remains of Eq. (8.12) is

$$\frac{r}{R}(rR)'' + \frac{1}{\sin\theta\,\Theta}(\sin\theta\,\Theta')' - \frac{c_2^2}{\sin^2\theta\,\Phi}\Phi'' + k^2r^2 = 0, \tag{8.14}$$

after multiplying through by r^2. The middle two terms represent the only dependence on θ, so we can set it equal to another undetermined constant $-c_1^2$. To summarize, now we have the triplet of separated equations

$$\begin{aligned} r^2\partial_r^2 R + 2r\partial_r R + (k^2r^2 - c_1^2)R &= 0 \\ \frac{1}{\sin\theta}\partial_\theta\left(\sin\theta\,\partial_\theta\Theta\right) + \left(c_1^2 - \frac{c_2^2}{\sin^2\theta}\right)\Theta &= 0 \\ \partial_\phi^2\Phi + c_2^2\Phi &= 0, \end{aligned} \tag{8.15}$$

where c_1 and c_2 are the separation constants.

8.1.2.2 Angular Solution

The last of Eqs. (8.15) is easiest to solve, giving

$$\Phi(\phi) = e^{\pm ic_2\phi}. \tag{8.16}$$

Since $\Phi(\phi)$ must be 2π periodic, clearly, c_2 must be an integer, $c_2 = m$, so that

$$\Phi_m(\phi) = e^{im\phi}, \tag{8.17}$$

where m can be positive or negative (or zero). The second separation equation thus becomes, letting $x = \cos\theta$ and regarding Θ to be function of x,

$$\left(1-x^2\right)\partial_x^2\Theta - 2x\partial_x\Theta + \left(c_1^2 - \frac{m^2}{1-x^2}\right)\Theta = 0. \tag{8.18}$$

Taking $c_1^2 = \ell(\ell+1)$, this equation becomes the **general Legendre equation**,

$$\left(1-x^2\right)\partial_x^2\Theta - 2x\partial_x\Theta + \left(\ell(\ell+1) - \frac{m^2}{1-x^2}\right)\Theta = 0, \tag{8.19}$$

which has nondivergent solutions on the domain $[-1,1]$ if and only if ℓ is a nonnegative integer and $|m| \le \ell$. These solutions are the **associated Legendre functions**, denoted by $P_\ell^m(x)$. They are given explicitly by

$$\begin{aligned} P_\ell^m(x) &= \frac{(-1)^m}{2^\ell \ell!}(1-x^2)^{m/2}\partial_x^{\ell+m}(x^2-1)^\ell \qquad (m \ge 0) \\ P_\ell^m(x) &= (-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m(x). \end{aligned} \tag{8.20}$$

Clearly, $P_\ell^m(x)$ is a polynomial if m is even, and $P_\ell^0(x)$ is an ordinary Legendre polynomial. The $P_\ell^m(x)$ obey the orthogonality condition

$$\int_{-1}^{\ell} P_\ell^m(x)\,P_{\ell'}^m(x)\,dx = \frac{2(\ell+m)!}{(2\ell+1)(\ell-m)!}\delta_{\ell\ell'} \qquad (m \ge 0). \tag{8.21}$$

The full solution to the Helmholtz equation is also orthogonal for different values of m, due to the form of $\Phi(\phi)$ above.

The angular solutions are generally combined, and thus the solution $\Theta(\theta)\Phi(\phi)$ is given by the **spherical harmonics**

$$Y_\ell^m(\theta,\phi) := \sqrt{\frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!}}\, P_\ell^m(\cos\theta)\, e^{im\phi}, \tag{8.22}$$
(spherical harmonic)

which are more conveniently normalized such that

$$\begin{aligned} Y_\ell^{m*}(\theta,\phi) &= (-1)^m Y_\ell^{-m}(\theta,\phi) \\ \int d\Omega\, Y_\ell^m(\theta,\phi)\, Y_{\ell'}^{m'}(\theta,\phi) &= \delta_{\ell\ell'}\delta_{mm'}. \end{aligned} \tag{8.23}$$
(orthonormality relations)

(See also Section 7.4.1.5 for a more quantum-mechanical introduction.) They also obey the sum rule

$$\sum_{m=-\ell}^{\ell} |Y_\ell^m(\theta,\phi)|^2 = \frac{2\ell+1}{4\pi}, \tag{8.24}$$
(sum rule)

showing that the m quantum number determines the orientation of the modes; summing over it results in an isotropic angular distribution. Some examples of the lowest few (monopole and dipole) spherical harmonics are

$$Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}, \quad Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_1^{\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\phi}, \tag{8.25}$$

The spherical harmonics form a complete set for the angular dependence of the scalar-field solutions.

8.1.2.3 Radial Solution

As for the radial equation for $R(r)$ in Eqs. (8.15), we now have

$$r^2\partial_r^2 R + 2r\partial_r R + [k^2r^2 - \ell(\ell+1)]R = 0. \tag{8.26}$$

Changing variables by setting $\chi(r) := \sqrt{kr}\, R(r)$ leads to

$$r^2\partial_r^2\chi + r\partial_r\chi + \left[k^2r^2 - \left(\ell+\frac{1}{2}\right)^2\right]\chi = 0. \tag{8.27}$$

This is **Bessel's equation** (with independent variable kr), and the solutions are ordinary (cylindrical) Bessel functions of the first kind, $J_{\ell+1/2}(kr)$, of order $\ell+1/2$, as well as the ordinary (cylindrical) Bessel functions of the second kind, $Y_{\ell+1/2}(kr)$, of the same order. The solutions $R(r)$ are thus generally written as **spherical Bessel functions** of the first and second kind, defined by

$$\begin{aligned} j_\ell(r) &:= \sqrt{\frac{\pi}{2r}}\, J_{\ell+1/2}(r) \\ y_\ell(r) &:= \sqrt{\frac{\pi}{2r}}\, Y_{\ell+1/2}(r), \end{aligned} \tag{8.28}$$
(spherical Bessel functions)

respectively. These represent the direct solutions in terms of $R(r)$ (i.e., without the variable change). In lieu of the variable-change technique, an alternate approach is to define the spherical Bessel functions directly in terms of the integral representation

$$j_\ell(z) = \frac{1}{2i^\ell}\int_{-1}^{1} d\mu\, e^{iz\mu}\, P_\ell(\mu), \tag{8.29}$$
(spherical Bessel functions, integral representation)

and then show directly that these satisfy the radial equation (8.26) (see Problem 8.2).

Near the origin, these functions have the small-r asymptotic forms[1]

$$\begin{aligned} j_\ell(r) &\approx \frac{r^\ell}{(2\ell+1)!!} \\ y_\ell(r) &\approx -\frac{(2\ell-1)!!}{r^{\ell+1}}, \end{aligned} \tag{8.30}$$

where $n!! = 1 \cdot 3 \cdot 5 \cdots n$. The $y_\ell(r)$ thus correspond to singular modes, and we can henceforth dump them. Technically, the $y_l(r)$ are not even square-integrable (normalizable over a finite radius) for $l > 0$, but $y_0(r)$ technically doesn't have a divergence in the normalization integral. Nevertheless, it has no place in representing a general but bounded quantum state. In any case, our desired radial solutions are $R(r) = j_\ell(kr)$. That these functions form a complete set, as follows for example from the partial-wave representation that we have already seen in Eqs. (7.233)

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}} j_\ell(kr) Y_\ell^0(\theta, 0) = \sum_{\ell=0}^{\infty} i^\ell (2\ell+1) j_\ell(kr) P_\ell(\cos\theta), \tag{8.31}$$

where $P_\ell(x) = P_\ell^0(x)$ is a Legendre polynomial, and θ is the angle between $\mathbf{k}$ and $\mathbf{r}$. Since an arbitrary plane wave may be decomposed into spherical Bessel functions of the first kind, and plane waves are complete, so are the $j_\ell(r)$.

To summarize, then, in spherical coordinates we have the solutions

$$\psi_{\ell m}(\mathbf{r}) = j_\ell(kr) Y_\ell^m(\theta, \phi). \tag{8.32}$$

(free-particle eigenfunctions)

These solutions are also not normalizable [the spherical Bessel functions decaying like $(kr)^{-1/2}$ for large r] as was the case in Cartesian coordinates. Recall that in Cartesian coordinates we had a continuous set of basis functions (8.10). In spherical coordinates, the angular quantum numbers are discrete, owing to the finite (mathematically, compact) angular domain. The continuous nature of the spectrum is only evident here in the k quantum number, which is continuous in the absence of other boundary conditions (other than outgoing at infinity).

8.2 Orbital Angular Momentum, Revisited

We discussed orbital angular momentum,

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}, \tag{8.33}$$

quite extensively before in Section 7.2; now it's time to make more use of those results. What we really want to work with is the square of the angular-momentum operator:

$$L^2 = (\mathbf{r} \times \mathbf{p}) \cdot (\mathbf{r} \times \mathbf{p}). \tag{8.34}$$

To work with this, let's switch to index notation, since it will be easier to keep the operator orderings straight. Writing out the cross products in terms of the Levi-Civita symbol, we have

$$L^2 = \epsilon_{\alpha\beta\gamma} r_\beta p_\gamma \epsilon_{\alpha\mu\nu} r_\mu p_\nu, \tag{8.35}$$

with an implied summation of the repeated α. Then using the identity (Problem 7.6)

$$\epsilon_{\alpha\beta\gamma}\epsilon_{\alpha\mu\nu} = \delta_{\beta\mu}\delta_{\gamma\nu} - \delta_{\beta\nu}\delta_{\gamma\mu}, \tag{8.36}$$

[1] For this and other properties see Milton Abramowitz and Irene A. Stegun, *Handbook of Mathematical Functions* (Dover, 1965), pp. 437-41 (ISBN: 0486612724).

we find

$$L^2 = r_\beta p_\gamma r_\beta p_\gamma - r_\beta p_\gamma r_\gamma p_\beta. \tag{8.37}$$

The first term here then simplifies to

$$\begin{aligned} r_\beta p_\gamma r_\beta p_\gamma &= r_\beta r_\beta p_\gamma p_\gamma - i\hbar r_\beta p_\beta \\ &= r^2 p^2 - i\hbar \mathbf{r}\cdot\mathbf{p} \end{aligned} \tag{8.38}$$

after using $[r_\beta, p_\gamma] = i\hbar\delta_{\beta\gamma}$, while the second term becomes

$$\begin{aligned} r_\beta p_\gamma r_\gamma p_\beta &= r_\beta p_\gamma p_\beta r_\gamma + i\hbar r_\beta p_\beta \\ &= r_\beta p_\beta p_\gamma r_\gamma + i\hbar r_\beta p_\beta \\ &= r_\beta p_\beta r_\gamma p_\gamma - 2i\hbar r_\beta p_\beta \\ &= (\mathbf{r}\cdot\mathbf{p})^2 - 2i\hbar \mathbf{r}\cdot\mathbf{p}. \end{aligned} \tag{8.39}$$

Putting these results into Eq. (8.37) then gives

$$L^2 = r^2 p^2 - (\mathbf{r}\cdot\mathbf{p})^2 + i\hbar \mathbf{r}\cdot\mathbf{p}. \tag{8.40}$$

Ultimately, we will want to write the kinetic energy in terms of L^2; thus, solving for p^2 gives

$$p^2 = \frac{1}{r^2}(\mathbf{r}\cdot\mathbf{p})^2 - \frac{i\hbar}{r^2}\mathbf{r}\cdot\mathbf{p} + \frac{1}{r^2}L^2. \tag{8.41}$$

Now what remains is to rewrite the factors of $\mathbf{r}\cdot\mathbf{p}$.

8.2.1 Radial Momentum and Orbital Angular Momentum

To transform into spherical coordinates, we will want to work with the radial momentum

$$p_r = \frac{1}{2}\big(\hat{r}\cdot\mathbf{p} + \mathbf{p}\cdot\hat{r}\big) = \frac{1}{2r}\mathbf{r}\cdot\mathbf{p} + \mathbf{p}\cdot\mathbf{r}\frac{1}{2r}, \tag{8.42}$$

keeping in mind that $\hat{r} = \mathbf{r}/r$ is an operator. Note that p_r is symmetrized, and thus Hermitian (the classical guess $\hat{r}\cdot\mathbf{p}$ doesn't have this property). To show that this is really the correct radial momentum, we should show that

$$[r, p_r] = i\hbar, \tag{8.43}$$

which is indeed the case (see Problem 8.1).

Now to write the expression (8.42) for p_r in terms of a single ordering, we can say that

$$p_r = \hat{r}\cdot\mathbf{p} + \frac{1}{2}[p_\alpha, \hat{r}_\alpha]. \tag{8.44}$$

Evaluating this commutator, we find

$$\begin{aligned} [p_\alpha, \hat{r}_\alpha] &= -\frac{i\hbar}{2}\left(\partial_\alpha \frac{r_\alpha}{r}\right) \\ &= -\frac{i\hbar}{2}\left(\frac{3}{r} + r_\alpha \partial_\alpha \frac{1}{r}\right) \\ &= -\frac{i\hbar}{2}\left(\frac{3}{r} - r_\alpha \frac{r_\alpha}{r^3}\right) \\ &= -\frac{i\hbar}{2}\left(\frac{2}{r}\right) \\ &= -\frac{i\hbar}{r}, \end{aligned} \tag{8.45}$$

so that

$$p_r = \hat{r} \cdot \mathbf{p} - \frac{i\hbar}{r}. \tag{8.46}$$

Multiplying by r and solving for $\mathbf{r} \cdot \mathbf{p}$, we find

$$\mathbf{r} \cdot \mathbf{p} = r p_r + i\hbar. \tag{8.47}$$

Putting this expression into Eq. (8.41) gives

$$\begin{aligned} p^2 &= \frac{1}{r^2}(r p_r + i\hbar)^2 - \frac{i\hbar}{r^2}(r p_r + i\hbar) + \frac{1}{r^2}L^2 \\ &= \frac{1}{r} p_r (r p_r + i\hbar) + \frac{1}{r^2}L^2 \\ &= \frac{1}{r} p_r r p_r + \frac{i\hbar}{r} p_r + \frac{1}{r^2}L^2. \end{aligned} \tag{8.48}$$

Now using the commutator (8.43) in the first term, we find

$$p^2 = p_r^2 + \frac{1}{r^2}L^2. \tag{8.49}$$

(momentum as radial and angular momentum)

Similarly, the kinetic-energy operator becomes

$$T = \frac{p^2}{2m} = \frac{p_r^2}{2m} + \frac{1}{2mr^2}L^2. \tag{8.50}$$

(kinetic-energy operator)

Note that we've been careful throughout when dividing by r to preserve proper ordering.

8.3 Free Particle, Revisited

With the above formalism in hand, let's redo the free-particle problem, but in the operator language. We will pick simultaneous eigenstates of p^2, L^2, and L_z to determine a full set of quantum numbers. We need to know that these are all commuting operators. We already know that $[L^2, L_z] = 0$ because it is an angular momentum. We also established before that p^2 commutes with any component L_α of orbital angular momentum (Section 7.2.2), and thus it commutes with L^2 as well.

8.3.1 Radial Momentum and Spherical Laplacian

Note that we will also get "for free" simultaneous eigenstates also of p_r^2, as a consequence of Eq. (8.49). To work out the form of this operator, starting from Eq. (8.46) we have

$$p_r = \frac{\hbar}{i}\left(\hat{r} \cdot \nabla + \frac{1}{r}\right). \tag{8.51}$$

We can use the form (7.49) for the gradient operator in spherical coordinates,

$$\nabla = \hat{r}\partial_r + \frac{\hat{\theta}}{r}\partial_\theta + \frac{\hat{\phi}}{r\sin\theta}\partial_\phi, \tag{8.52}$$

so that

$$p_r = \frac{\hbar}{i}\left(\partial_r + \frac{1}{r}\right). \tag{8.53}$$

Finally we can rewrite the radial momentum as

$$p_r = \frac{\hbar}{i}\frac{1}{r}\partial_r r, \tag{8.54}$$

where the derivative operator also acts on anything to the right of the rightmost r. In this form it is easy to square the operator to find

$$p_r^2 = -\hbar^2 \frac{1}{r} \partial_r^2 r. \tag{8.55}$$

Note that this operator has the form of the first term in the Laplacian (8.11) in spherical coordinates. Together with the form (7.56) of L^2 in spherical coordinates and Eq. (8.49) with $p^2 = -\hbar^2 \nabla^2$, this acts as a derivation of the Laplacian form (8.11).

8.3.2 Simultaneous Eigenstates

Now we can choose the simultaneous eigenstates

$$\begin{aligned} p^2 |\ell\ m\rangle &= \hbar^2 k^2 |\ell\ m\rangle \\ L^2 |\ell\ m\rangle &= \hbar^2 \ell(\ell+1) |\ell\ m\rangle \\ L_z |\ell\ m\rangle &= \hbar m |\ell\ m\rangle, \end{aligned} \tag{8.56}$$

which are labeled as the usual eigenstates of orbital angular momentum. The first eigenvalue equation is just the Helmholtz equation (8.2), while the other two are familiar as the angular-momentum eigenvalue equations.

As we already noted, we can also obtain eigenvalues of p_r^2. Using Eq. (8.49), we find

$$p_r^2 |\ell\ m\rangle = \left(p^2 - \frac{1}{r^2} L^2 \right) |\ell\ m\rangle = \hbar^2 \left(k^2 - \frac{\ell(\ell+1)}{r^2} \right) |\ell\ m\rangle. \tag{8.57}$$

Multiplying on the left by $r^2/\hbar^2$, we then have

$$\frac{r^2 p_r^2}{\hbar^2} |\ell\ m\rangle = \Big(k^2 r^2 - \ell(\ell+1) \Big) |\ell\ m\rangle. \tag{8.58}$$

Now using Eq. (8.55) for p_r^2 and projecting into the position representation with $\langle r, \theta, \phi|$, this equation leads to the radial equation (8.26) as before, with spherical Bessel functions as solutions.

8.4 Hydrogen Atom

And now for one of the classic problems of quantum mechanics: the hydrogen atom. A hydrogen atom consists of an electron, a nucleus, and a Coulomb binding potential:

$$H = \frac{p_\mathrm{e}^2}{2m_\mathrm{e}} + \frac{p_\mathrm{n}^2}{2m_\mathrm{n}} - \frac{e^2}{4\pi\epsilon_0 r}. \tag{8.59}$$

(hydrogen-atom Hamiltonian)

Here $\mathbf{r} = \mathbf{r}_\mathrm{e} - \mathbf{r}_\mathrm{n}$ is the electron coordinate $\mathbf{r}_\mathrm{e}$ relative to the nuclear position $\mathbf{r}_\mathrm{n}$, $r = |\mathbf{r}|$ as usual, and the nuclear and electron charges are $+e$ and $-e$, respectively.

8.4.1 Center-of-Mass Coordinates

The first order of business is to simplify the Hamiltonian. Introducing the total momentum $\mathbf{P}$ and total mass M,

$$\begin{aligned} \mathbf{P} &:= \mathbf{p}_\mathrm{e} + \mathbf{p}_\mathrm{n} \\ M &:= m_\mathrm{e} + m_\mathrm{n}, \end{aligned} \tag{8.60}$$

(total momentum and mass)

along with the weighted relative momentum $\mathbf{p}$ and **reduced mass** μ

$$\begin{aligned}\mathbf{p} &:= \frac{m_\mathrm{n}\mathbf{p}_\mathrm{e} - m_\mathrm{e}\mathbf{p}_\mathrm{n}}{M} \\ \mu &:= \frac{m_\mathrm{e}m_\mathrm{n}}{m_\mathrm{e}+m_\mathrm{n}} = \frac{m_\mathrm{e}m_\mathrm{n}}{M},\end{aligned} \qquad \begin{matrix}(8.61)\\ \text{(relative momentum and reduced mass)}\end{matrix}$$

we can see that in the limit $m_\mathrm{n} \gg m_\mathrm{e}$, then $M \approx m_\mathrm{n}$ and $\mu \approx m_\mathrm{e}$. Then let's compute

$$\frac{P^2}{2M} + \frac{p^2}{2\mu} = \left(\frac{p_\mathrm{e}^2}{2M} + \frac{p_\mathrm{n}^2}{2M} + \frac{\mathbf{p}_\mathrm{e}\cdot\mathbf{p}_\mathrm{n}}{M}\right) + \left(\frac{m_\mathrm{n}p_\mathrm{e}^2}{2m_\mathrm{e}M} + \frac{m_\mathrm{e}p_\mathrm{n}^2}{2m_\mathrm{n}M} - \frac{\mathbf{p}_\mathrm{e}\cdot\mathbf{p}_\mathrm{n}}{M}\right). \tag{8.62}$$

The cross terms cancel and the remaining terms combine to give

$$\frac{P^2}{2M} + \frac{p^2}{2\mu} = \frac{p_\mathrm{e}^2}{2m_\mathrm{e}} + \frac{p_\mathrm{n}^2}{2m_\mathrm{n}}. \tag{8.63}$$

Thus, the Hamiltonian (8.59) becomes

$$H = \frac{P^2}{2M} + \frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r}. \tag{8.64}$$

in these coordinates. Now, the first kinetic term refers only to the total motion (of the center of mass), and is thus not so interesting for us; classically, we would just transform into the co-moving frame where its value is zero. Here, we can note that the first term $P^2/2M$ commutes with the rest of the Hamiltonian. That $[\mathbf{P},\mathbf{p}] = 0$ is clear from the definitions (8.60) and (8.61) and that $\mathbf{p}_\mathrm{e}$ commutes with $\mathbf{p}_\mathrm{n}$. That $[\mathbf{P}, r^2] = [\mathbf{p}_\mathrm{e}+\mathbf{p}_\mathrm{n}, (\mathbf{r}_\mathrm{e}-\mathbf{r}_\mathrm{n})^2] = 0$ follows from working through the derivatives, nothing that there will be two contributions of opposing sign. Thus, we can solve the center-of-mass and relative parts separately, and so we will take

$$H = \frac{p^2}{2\mu} - \frac{e^2}{4\pi\epsilon_0 r} \qquad \begin{matrix}(8.65)\\ \text{(reduced hydrogen-atom Hamiltonian)}\end{matrix}$$

as the Hamiltonian to solve, or alternately

$$H = \frac{p^2}{2\mu} - \frac{\hbar c\alpha}{r}, \qquad \begin{matrix}(8.66)\\ \text{(reduced hydrogen-atom Hamiltonian)}\end{matrix}$$

where we have introduced the fine-structure constant

$$\alpha := \frac{e^2}{4\pi\epsilon_0\hbar c}. \qquad \begin{matrix}(8.67)\\ \text{(fine-structure constant)}\end{matrix}$$

This is a vast improvement over the original Hamiltonian, as we now have a single particle in three dimensions, as opposed to a pair of coupled particles in three dimensions.

8.4.2 Central-Potential Eigenstates

Now for a particle in a central potential of the form

$$H = \frac{p^2}{2\mu} + V(r), \tag{8.68}$$

as we have for the reduced hydrogen atom (8.66), according to Eq. (8.50), this becomes

$$H = \frac{p_r^2}{2\mu} + \frac{1}{2\mu r^2}L^2 + V(r) \tag{8.69}$$

after switching to spherical coordinates. If we take simultaneous eigenstates of H, L^2, and L_z (we already know that L_z and L^2 commute with r and thus $V(r)$ from Section 7.2.2, so we know we can do this). Calling these eigenstates $|E\ \ell\ m\rangle$, the eigenvalue equation

$$H|E\ \ell\ m\rangle = E|E\ \ell\ m\rangle \tag{8.70}$$

becomes

$$\left(\frac{p_r^2}{2\mu} + \frac{\hbar^2\ell(\ell+1)}{2\mu r^2} + V(r)\right)|E\ \ell\ m\rangle = E|E\ \ell\ m\rangle. \tag{8.71}$$

Thus, there is an extra, repulsive effective potential

$$V_{\text{CB}}(r) := \frac{\hbar^2\ell(\ell+1)}{2\mu r^2}, \tag{8.72}$$
(centrifugal-barrier potential)

in addition to the regular central potential $V(r)$. This can be thought of as giving rise to a noninertial force, because staying at constant r (which a rough way to think about what eigenstates "do") corresponds, classically, to being in a noninertial frame. The radial solution will then be that of a (one-dimensional) particle in a potential $V_{\text{CB}}(r) + V(r)$. For there to be bound states, $V(r)$ must be attractive and stronger at large r than $V_{\text{CB}}(r)$.

8.4.3 Factorization Method

There is a nice method for finding analytic solutions of particles in potentials, and it works as a generalization of the method that we used in Chapter 5 for generating the harmonic-oscillator eigenstates using ladder operators. However, the harmonic oscillator is very special in that the energy levels are spaced uniformly. In general, we won't have this, and the consequence is that we will effectively need to have a different raising and lowering operator for each neighboring pair of energy levels. Doing so, however, the method, called the **factorization method**,[2] is quite general.

8.4.3.1 Recursion Relations

The factorization method is based on relations that generalize the operator relations from the harmonic oscillator. Recall that, for the harmonic oscillator, the Hamiltonian is

$$H = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \tag{8.73}$$

in terms of the ladder operators. That is, the Hamiltonian is a scaled number operator plus a little excess, corresponding to the zero-point energy. We'll now change notation a little and write the ground state energy as $E_1 = \hbar\omega/2$, that is, we'll start counting energy levels from 1 instead of 0. Now in general, suppose that we define an analogous annihilation operator b_1 so that

$$H = b_1^\dagger b_1 + E_1, \tag{8.74}$$
(factorization method: initialization)

where note that we have absorbed the overall $\hbar\omega$ into the definition of the ladder operators.

[2] See Hans C. O'hanian, *Principles of Quantum Mechanics* (Prentice-Hall, 1990) (ISBN: 0137127952), Chapter 6. This method dates back to E. Schrödinger, "A Method of Determining Quantum-Mechanical Eigenvalues and Eigenfunctions," *Proceedings of the Royal Irish Academy. Section A: Mathematical and Physical Sciences* **46**, 9 (1940) https://www.jstor.org/stable/20490744; E. Schrödinger, "Further Studies on Solving Eigenvalue Problems by Factorization," *Proceedings of the Royal Irish Academy. Section A: Mathematical and Physical Sciences* **46**, 183 (1941) https://www.jstor.org/stable/20490756; E. Schrödinger, "The Factorization of the Hypergeometric Equation," *Proceedings of the Royal Irish Academy. Section A: Mathematical and Physical Sciences* **47**, 53 (1941) https://www.jstor.org/stable/20488434. The method was developed further by L. Infeld and T. E. Hull, "The Factorization Method," *Reviews of Modern Physics* **23**, 21 (1951) (doi: 10.1103/RevModPhys.23.21).

For the remaining relations, we can look to the commutation relation

$$[a, a^\dagger] = 1 \tag{8.75}$$

for the harmonic oscillator. Multiplying by $\hbar\omega$ gives

$$\hbar\omega a a^\dagger = \hbar\omega a^\dagger a + \hbar\omega. \tag{8.76}$$

Then recognizing the constant term as the energy difference $\hbar\omega = E_2 - E_1$, we can rewrite this as

$$\hbar\omega a a^\dagger + E_2 = \hbar\omega a^\dagger a + E_1. \tag{8.77}$$

Now to write an analogous relation in terms of generalized ladder operators, we can say

$$b_2^\dagger b_2 + E_2 = b_1 b_1^\dagger + E_1. \tag{8.78}$$

Notice the difference in operators: The combination $b_2^\dagger b_2$ lowers level 2 to level 1 and then raises back to level 2. On the other hand, $b_1 b_1^\dagger$ raises level 1 to 2 and then lowers back to 1. In any case this relation is a sensible generalization in *only* referring to the pair of levels. More generally, we can write

$$b_{k+1}^\dagger b_{k+1} + E_{k+1} = b_k b_k^\dagger + E_k \tag{8.79}$$
(factorization method: recursion)

for $k \geq 1$. This equation acts as a recursion relation, starting with Eq. (8.74), for the b_k's and E_k's. In general, this won't define a unique set of energies and operators; however, it is sufficient to require that, at each step of the recursion, we choose the *maximum possible* energy. Note that this procedure generates a countable set of energies by definition; it thus works for a discrete family of bound states, but not for continuum states (such as the ionized states of hydrogen).

8.4.3.2 Construction of the Eigenvectors

Now the next step in defining the factorization method is to show that the above recursions in fact generate the proper eigenenergies. We'll start by defining

$$H_k := b_k^\dagger b_k + E_k. \tag{8.80}$$

That is, $H_1 = H$ is the "real" Hamiltonian, and the other H_k for $k > 1$ are just analogous shorthands for useful quantities. Then the recursion relation (8.79) implies that

$$H_{k+1} = b_k b_k^\dagger + E_k. \tag{8.81}$$

Now we can derive two simple "commutation" rules for this family of operators:

$$\begin{aligned} H_{k+1} b_k &= \Big(b_k b_k^\dagger + E_k\Big) b_k = b_k \Big(b_k^\dagger b_k + E_k\Big) = b_k H_k \\ H_k b_k^\dagger &= \Big(b_k^\dagger b_k + E_k\Big) b_k^\dagger = b_k^\dagger \Big(b_k b_k^\dagger + E_k\Big) = b_k^\dagger H_{k+1}. \end{aligned} \tag{8.82}$$

Now to use the operators to construct eigenvectors of H. Consider the (unnormalized) state

$$|k\rangle = b_1^\dagger b_2^\dagger \cdots b_{k-1}^\dagger |0_k\rangle, \tag{8.83}$$
(factorization-method eigenstate)

in terms of some state $|0_k\rangle$ yet to be determined. Then the second of Eqs. (8.82) allows us to shift the H_1 operator to the right through all the raising operators:

$$\begin{aligned} H|k\rangle &= H_1 b_1^\dagger b_2^\dagger \cdots b_{k-1}^\dagger |0_k\rangle \\ &= b_1^\dagger H_2 b_2^\dagger \cdots b_{k-1}^\dagger |0_k\rangle \\ &= b_1^\dagger b_2^\dagger \cdots b_{k-1}^\dagger H_k |0_k\rangle. \end{aligned} \tag{8.84}$$

In the last expression, because of Eq. (8.80), we have $H_k = E_k$ provided

$$b_k|0_k\rangle = 0. \tag{8.85}$$
(null-eigenvector condition)

That is, the state (8.83) is an eigenstate provided $|0_k\rangle$ is a null eigenvector of b_k.

8.4.3.3 Ordering of Eigenvalues

Now what remains is to show that the E_k are in ascending order, and that we didn't skip over any eigenvalues. Consider two adjacent eigenvalues E_k and E_{k+1}. Then assuming the null eigenvectors to be normalized, we can write

$$\begin{aligned} E_{k+1} - E_k &= \langle 0_{k+1}|\Big(E_{k+1} - E_k\Big)|0_{k+1}\rangle \\ &= \langle 0_{k+1}|\Big(b_k b_k^\dagger - b_{k+1}^\dagger b_{k+1}\Big)|0_{k+1}\rangle \\ &= \langle 0_{k+1}|b_k b_k^\dagger|0_{k+1}\rangle \\ &\geq 0, \end{aligned} \tag{8.86}$$

after applying the recursion (8.79) and using that $b_{k+1}|0_{k+1}\rangle = 0$. The inequality comes from noting that the last expression is the squared modulus of the vector $b_k^\dagger|0_{k+1}\rangle$. This shows that the E_k are properly ordered.

8.4.3.4 Completeness of the Eigenvalues Search

To prove that we haven't missed any eigenvalues, assume that there is some eigenvalue E between E_k and E_{k+1}. Then consider the quantity

$$\langle E|b_1^\dagger b_2^\dagger \cdots b_{k+1}^\dagger b_{k+1} \cdots b_2 b_1|E\rangle \geq 0. \tag{8.87}$$

Then using the definition (8.80) and iterating using the first of Eqs. (8.82), we find

$$\begin{aligned} \langle E|b_1^\dagger b_2^\dagger \cdots b_{k+1}^\dagger b_{k+1} \cdots b_2 b_1|E\rangle &= \langle E|b_1^\dagger b_2^\dagger \cdots b_k^\dagger\Big(H_{k+1} - E_{k+1}\Big)b_k \cdots b_2 b_1|E\rangle \\ &= \langle E|b_1^\dagger b_2^\dagger \cdots b_k^\dagger b_k\Big(H_k - E_{k+1}\Big)b_{k-1} \cdots b_2 b_1|E\rangle \\ &\vdots \\ &= \langle E|b_1^\dagger b_2^\dagger \cdots b_k^\dagger b_k \cdots b_2 b_1\Big(H_1 - E_{k+1}\Big)|E\rangle \\ &= \langle E|b_1^\dagger b_2^\dagger \cdots b_k^\dagger b_k \cdots b_2 b_1\Big(H - E_{k+1}\Big)|E\rangle \\ &= \Big(E - E_{k+1}\Big)\langle E|b_1^\dagger b_2^\dagger \cdots b_k^\dagger b_k \cdots b_2 b_1|E\rangle. \end{aligned} \tag{8.88}$$

Now because of inequality (8.87), this last quantity is nonnegative. The last expectation value is likewise nonnegative. If it is strictly positive, then we can conclude

$$E \geq E_{k+1}, \tag{8.89}$$

which contradicts the assumption that E is between E_k and E_{k+1}. If the last expectation value vanishes, then we can iterate the procedure in Eqs. (8.88) to obtain

$$\langle E|b_1^\dagger b_2^\dagger \cdots b_{k+1}^\dagger b_{k+1} \cdots b_2 b_1|E\rangle = \Big(E - E_{k+1}\Big)\Big(E - E_k\Big) \cdots \Big(E - E_1\Big), \tag{8.90}$$

which now vanishes by assumption. This means that E is equal to one of the E_k, which again violates our assumption. Thus, we haven't missed any eigenvalues.

8.4.3.5 Uniqueness of Maximal Eigenvalues

Let's return for a second to the previous comment that the recursion relations (8.74) and (8.79) of the factorization method don't give unique solutions, but the ambiguity can be resolved by the maximum choice of the energies at each stage. Returning to the recursion Eq. (8.79),

$$b_{k+1}^\dagger b_{k+1} + E_{k+1} = b_k b_k^\dagger + E_k, \tag{8.91}$$

consider small changes δE_{k+1} and δb_{k+1} in E_{k+1} and b_{k+1}, respectively, while holding E_k and b_k fixed. To linear order in the changes, the result is

$$\delta E_{k+1} = -\delta b_{k+1}^\dagger b_{k+1} - b_{k+1}^\dagger \delta b_{k+1} \tag{8.92}$$

In an expectation value with respect to $|0_{k+1}\rangle$, the right-hand side vanishes because $b_{k+1}|0_{k+1}\rangle = 0$ and $\langle 0_{k+1}|b_{k+1}^\dagger = 0$. Thus, $\delta E_{k+1} = 0$, and thus maximization (or at least stationarity, but maximization is sensible since the idea is to construct an ascending ladder of states) with respect to choice of the b_k is a direct consequence of the null-eigenvector condition (8.85).

8.4.3.6 Construction of the Ladder Operators

What we need next is to set up the ladder operators, so we can go about constructing the eigenenergies and eigenvectors. Recall that, for the harmonic oscillator, we had the annihilation operator (5.24):

$$a = i\frac{p}{\sqrt{2m\hbar\omega}} + \sqrt{\frac{m\omega}{2\hbar}}\, x. \tag{8.93}$$

In the factorization method, we are comparing the generalized annihilation operators b_k with $\sqrt{\hbar\omega}\, a$, in which case we would identify

$$b_k = i\frac{p}{\sqrt{2m}} + \sqrt{\frac{m\omega^2}{2}}\, x. \tag{8.94}$$

Changing this operator by an overall phase (which is arbitrary since only $b_k^\dagger b_k$ appears in the recursions), we choose instead to work with

$$b_k = \frac{p}{\sqrt{2m}} - i\sqrt{\frac{m\omega^2}{2}}\, x = \frac{1}{\sqrt{2m}}\big(p - im\omega x\big). \tag{8.95}$$

Roughly speaking, the first term is the root of the kinetic energy, and the second is the root of the potential energy. In the general case, this operator won't have the same form, so, we will make the *ansatz*

$$b_k = \frac{1}{\sqrt{2m}}\big[p + i f_k(x)\big], \tag{8.96}$$

(generalized annihilation *ansatz*)

for some functions $f_k(x)$ to be determined (which will still be something like the square root of the potential).

To proceed, we can start by computing the product

$$\begin{aligned} b_k^\dagger b_k &= \frac{1}{2m}\Big(p^2 + f_k^2 + i[p, f_k]\Big) \\ &= \frac{1}{2m}\Big(p^2 + f_k^2 + \hbar f_k'\Big), \end{aligned} \tag{8.97}$$

after using the general commutator $[p, f(x)] = -i\hbar f'$. Similarly,

$$b_k b_k^\dagger = \frac{1}{2m}\Big(p^2 + f_k^2 - \hbar f_k'\Big). \tag{8.98}$$

Then the method continues by using the relation (8.74),

$$H = b_1^\dagger b_1 + E_1, \tag{8.99}$$

to deduce $f_1(x)$. As an illustration of the method, let's try this out for the harmonic oscillator, where this condition becomes

$$\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 = \frac{1}{2m}\Big(p^2 + f_1^2 + \hbar f_1'\Big) + E_1. \tag{8.100}$$

Simplifying a little, we find

$$f_1^2 + \hbar f_1' = (m\omega x)^2 - 2mE_1. \tag{8.101}$$

As an aside, this ordinary differential equation is a type of **Riccati equation**, being first order but quadratic in the function. It is reasonably easy to see that we can generate a solution by picking

$$f_1(x) = \pm m\omega x, \tag{8.102}$$

in which case substitution back into the Riccati equation gives

$$E_1 = \mp\frac{\hbar\omega}{2}. \tag{8.103}$$

The solution is clearly not unique, but we choose $E_1 = +\hbar\omega/2$ to maximize E_1, in which case

$$f_1(x) = -m\omega x. \tag{8.104}$$

This procedure correctly recovers the annihilation operator a in Eq. (8.93) after dividing by $\sqrt{\hbar\omega}$, and it gets the zero-point energy correct.

To continue, the recursion (8.79), in the form

$$b_2^\dagger b_2 + E_2 = b_1 b_1^\dagger + E_1 \tag{8.105}$$

will allow us to deduce the next energy E_2 and $f_2(x)$. With Eqs. (8.97) and (8.98), this becomes

$$\frac{1}{2m}\Big(f_2^2 + \hbar f_2'\Big) + E_2 = \frac{1}{2m}\Big(f_1^2 - \hbar f_1'\Big) + E_1. \tag{8.106}$$

Again, let's use the harmonic oscillator to illustrate. Putting in the forms of f_1 and E_1, we have

$$\frac{1}{2m}\Big(f_2^2 + \hbar f_2'\Big) + E_2 = \frac{m\omega^2 x^2}{2} + \hbar\omega. \tag{8.107}$$

Rearranging, we have a similar Riccati equation to the initial step:

$$f_2^2 + \hbar f_2' = (m\omega x)^2 + 2m\big(\hbar\omega - E_2\big). \tag{8.108}$$

Again, we can choose

$$f_2(x) = \pm m\omega x, \tag{8.109}$$

and we should again choose the minus sign to maximize the energy. Putting the solution into the Riccati equation again, we obtain

$$E_2 = \frac{3}{2}\hbar\omega. \tag{8.110}$$

Iterating the procedure leads to

$$f_k(x) = -m\omega x, \tag{8.111}$$

and

$$E_k = \left(k - \frac{1}{2}\right)\hbar\omega, \tag{8.112}$$

correctly reproducing the harmonic-oscillator eigenstates.

8.4.3.7 Construction of the Eigenvectors: Harmonic Oscillator

To complete the harmonic-oscillator example, let's return to the construction (8.83) for the eigenstates, which for the harmonic oscillator becomes

$$|k\rangle \propto b_1^\dagger b_2^\dagger \cdots b_{k-1}^\dagger |0_k\rangle \propto \big(p + im\omega x\big)^{k-1} |0\rangle, \tag{8.113}$$

where the common null eigenvector satisfies

$$\big(p - im\omega x\big)|0\rangle = 0. \tag{8.114}$$

In the position representation, this last condition amounts to an ordinary differential equation for the ground state $|0\rangle$ (see Section 5.3.1), which we should be calling $|1\rangle$ in our present notation. Then the states generated by Eq. (8.113) amounts to the same ladder-operator procedure that we used before in Section 5.3.2.

8.4.4 Energy Eigenvalues: Hydrogen Atom

With the factorization method in hand, we can finally return to the solution of the hydrogen atom, specifically the diagonalization of the radial part of the Hamiltonian in Eq. (8.71),

$$H_r = \frac{p_r^2}{2\mu} + \frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{\hbar c \alpha}{r}, \tag{8.115}$$

adapted for the hydrogen-atom reduced Hamiltonian (8.66). Returning to Eq. (8.74), we will start with

$$H_r = b_1^\dagger b_1 + E_1, \tag{8.116}$$

we can now take the *ansatz* of the form (8.96), specifically the parameterized form

$$b_k = \frac{1}{\sqrt{2\mu}} \left[p_r + i \left(\beta_k + \frac{\gamma_k}{r} \right) \right], \tag{8.117}$$

again trying to mimic a square root of the potential, which here involves terms with r^{-1} and r^{-2}. Here, β_k and γ_k are undetermined constants, which also depend on ℓ via the Hamiltonian. Now using Eqs. (8.97) and (8.98), we can compute the needed combinations

$$\begin{aligned} b_k^\dagger b_k &= \frac{1}{2\mu} \left(p_r^2 + \beta_k^2 + \frac{2\beta_k \gamma_k}{r} + \frac{\gamma_k}{r^2}(\gamma_k - \hbar) \right) \\ b_k b_k^\dagger &= \frac{1}{2\mu} \left(p_r^2 + \beta_k^2 + \frac{2\beta_k \gamma_k}{r} + \frac{\gamma_k}{r^2}(\gamma_k + \hbar) \right). \end{aligned} \tag{8.118}$$

Then in Eq. (8.116), we have

$$\frac{\hbar^2 \ell(\ell+1)}{2\mu r^2} - \frac{\hbar c \alpha}{r} = \frac{1}{2\mu} \left(\beta_1^2 + \frac{2\beta_1 \gamma_1}{r} + \frac{\gamma_1}{r^2}(\gamma_1 - \hbar) \right) + E_1. \tag{8.119}$$

Matching powers of r gives the three relations

$$\begin{aligned} E_1 &= -\frac{\beta_1^2}{2\mu} \\ \frac{\beta_1 \gamma_1}{\mu} &= -\hbar c \alpha \\ \gamma_1(\gamma_1 - \hbar) &= \hbar^2 \ell(\ell+1). \end{aligned} \tag{8.120}$$

The last equation here has two solutions; the first is

$$\gamma_1 = \hbar(\ell+1), \tag{8.121}$$

which will be the solution that we want, although $\gamma_1 = -\hbar\ell$ is also a solution. Now the second of Eqs. (8.120) gives

$$\beta_1 = -\frac{\alpha\mu c}{\gamma_1} = -\frac{\alpha\mu c}{\ell+1} \tag{8.122}$$

(with an alternate value of γ_1 giving $\beta_1 = c\alpha\mu/\ell$). Finally, the first of Eqs. (8.120) gives

$$E_1 = -\frac{\alpha^2\mu c^2}{2(\ell+1)^2}.$$

(radial ground-state energy, hydrogen atom) (8.123)

The alternate value of γ_1 gives $E_1 = -c^2\alpha^2\mu/2\ell^2$, which is the lower-energy option, so that the correct (maximum) energy is given by Eq. (8.123).

Now to determine the remaining energies, we can return to the recursion relation (8.79)

$$b_{k+1}^\dagger b_{k+1} + E_{k+1} = b_k b_k^\dagger + E_k. \tag{8.124}$$

Now using Eqs. (8.118), this recursion becomes

$$\frac{1}{2\mu}\left(\beta_{k+1}^2 + \frac{2\beta_{k+1}\gamma_{k+1}}{r} + \frac{\gamma_{k+1}}{r^2}(\gamma_{k+1}-\hbar)\right) + E_{k+1} = \frac{1}{2\mu}\left(\beta_k^2 + \frac{2\beta_k\gamma_k}{r} + \frac{\gamma_k}{r^2}(\gamma_k+\hbar)\right) + E_k. \tag{8.125}$$

Again matching powers of r gives the three relations

$$\begin{aligned} E_{k+1} + \frac{\beta_{k+1}^2}{2\mu} &= E_k + \frac{\beta_k^2}{2\mu} \\ \beta_{k+1}\gamma_{k+1} &= \beta_k\gamma_k \\ \gamma_{k+1}(\gamma_{k+1}-\hbar) &= \gamma_k(\gamma_k+\hbar). \end{aligned} \tag{8.126}$$

Again, the last equation here has two solutions; the first is

$$\gamma_{k+1} = \gamma_k + \hbar, \tag{8.127}$$

which will be the solution that we want, but $\gamma_{k+1} = -\gamma_k$ is also possible, though we'll rule it out shortly. With the initial condition (8.121), this recursion has the solution

$$\gamma_k = \hbar(\ell+k). \tag{8.128}$$

The second of Eqs. (8.126) gives

$$\beta_{k+1} = \beta_k\frac{\gamma_k}{\gamma_{k+1}} = \beta_k\frac{(\ell+k)}{(\ell+k+1)}, \tag{8.129}$$

and with the initial condition (8.122), we have the solution

$$\beta_k = -\frac{\alpha\mu c}{\ell+k}. \tag{8.130}$$

Finally, the first of Eqs. (8.126) can be rewritten

$$E_{k+1} + \frac{\beta_{k+1}^2}{2\mu} = E_k + \frac{\beta_k^2}{2\mu} = E_1 + \frac{\beta_1^2}{2\mu} = 0, \tag{8.131}$$

where the last equality follows from the first of Eqs. (8.120). This then gives the energies

$$E_k = -\frac{\beta_k^2}{2\mu}, \tag{8.132}$$

or

$$E_k = -\frac{\alpha^2\mu c^2}{2(\ell+k)^2}. \tag{8.133}$$

(radial energies, hydrogen atom)

Now let's trace through the effect of the alternate solution $\gamma_{k+1} = -\gamma_k$. In Eqs. (8.122), this does not reduce the magnitude of the successive β_k, which leads to constant energies E_k. Thus, the solutions (8.133) are the maximum, and hence correct, choices.

8.4.5 Radial Eigenfunctions: Hydrogen Atom

Now to construct the radial components of the hydrogen-atom eigenfucntions. In the factorization method, recall that this first requires that we find the null eigenvectors $|0_k\rangle$ of the annihilation operators b_k, as in Eq. (8.85):

$$b_k|0_k\rangle = 0. \tag{8.134}$$

Using Eqs. (8.128) and (8.130), we can write the annihilation operator b_k from Eq. (8.117) as

$$b_k = \frac{1}{\sqrt{2\mu}}\left(p_r - \frac{i\alpha\mu c}{\ell+k} + \frac{i\hbar(\ell+k)}{r}\right). \tag{8.135}$$

Then in the position representation, Eq. (8.134) becomes the differential equation

$$\left(\partial_r + \frac{1}{r} + \frac{\alpha\mu c}{\hbar(\ell+k)} - \frac{\ell+k}{r}\right)\zeta_k(r) = 0, \tag{8.136}$$

where $\zeta_k(r) := \langle r|0_k\rangle$ is the radial wave function, and we used Eq. (8.53) to write p_r as a radial derivative,

$$p_r = \frac{\hbar}{i}\left(\partial_r + \frac{1}{r}\right). \tag{8.137}$$

Introducing the **Bohr radius**[3]

$$a_0 := \frac{\hbar}{\alpha\mu c} = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}, \tag{8.138}$$
(Bohr radius)

this lumps together all the parameters in the condition (8.136) into a single parameter, so that we need to solve

$$\left(a_0\partial_r + \frac{1}{\ell+k} - \frac{\ell+k-1}{r/a_0}\right)\zeta_k(r) = 0, \tag{8.139}$$

after multiplying through by a_0. This differential equation is a function of the dimensionless radius r/a_0, and it has

$$\zeta_k(r) = \left(\frac{r}{a_0}\right)^{\ell+k-1} e^{-r/a_0(\ell+k)} \tag{8.140}$$

as the (unnormalized) solution.

Now that we have the null eigenvalue, according to Eq. (8.83) we can construct the (unnormalized) eigenstates by applying creation operators,

$$|k\rangle = b_1^\dagger b_2^\dagger \cdots b_{k-1}^\dagger |0_k\rangle, \tag{8.141}$$

where the creation operators are

$$b_k^\dagger = \frac{\hbar}{ia_0\sqrt{2\mu}}\left(a_0\partial_r - \frac{1}{\ell+k} + \frac{\ell+k+1}{r/a_0}\right).$$
(creation operators for eigenfunction construction) (8.142)

Strictly speaking, we should be more careful to track the dependence on the ℓ (angular-momentum) quantum number. In the position representation, the eigenstate construction (8.141) then reads

$$\psi_{k\ell}(r) \propto b_{1\ell}^\dagger b_{2\ell}^\dagger \cdots b_{(k-1)\ell}^\dagger \zeta_{k\ell}(r), \tag{8.143}$$

where $\zeta_{k\ell}(r)$ is as in Eq. (8.141), and the creation operators $b_{k\ell}^\dagger$ are the same as in Eq. (8.142).

[3]The Bohr radius is conventionally defined in terms of m_e instead of μ; see the discussion in Section 8.4.5.5.

8.4.5.1 Unnormalized Examples

Let's work out a few example wave functions using Eq. (8.143). The simplest case is for $k = 1$ and $\ell = 0$; in this case there are no raising operators to apply, and we just have

$$\psi_{10}(r) \propto \zeta_{10}(r) = e^{-r/a_0} \tag{8.144}$$

after using Eq. (8.140) for $\zeta_{k\ell}(r)$. Again, this is unnormalized, something we'll take care of shortly.

A slightly more complicated case is $k = 2$ and $\ell = 0$, which involves one raising operator:

$$\begin{aligned}\psi_{20}(r) &\propto b_{10}^\dagger \zeta_{20}(r) \\ &\propto \left(a_0\partial_r - 1 + \frac{2}{r/a_0}\right)\left(\frac{r}{a_0}\right) e^{-r/2a_0} \\ &= 3\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}.\end{aligned} \tag{8.145}$$

Note that in the calculation, we omitted the factor $\hbar/ia_0\sqrt{2\mu}$ from $b_{10}^\dagger$, since this is not needed in view of the coming normalization; however, we kept the other factors that will be essential in the normalization procedure to come.

As one more example, but with $\ell \neq 0$, let's try $k = 2$, $\ell = 1$. In this case we again have a single raising operator:

$$\begin{aligned}\psi_{21}(r) &\propto b_{11}^\dagger \zeta_{21}(r) \\ &\propto \left(a_0\partial_r - \frac{1}{2} + \frac{3}{r/a_0}\right)\left(\frac{r}{a_0}\right)^2 e^{-r/3a_0} \\ &= \frac{5r}{a_0}\left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}.\end{aligned} \tag{8.146}$$

Again, we omitted the factor $\hbar/ia_0\sqrt{2\mu}$ from $b_{11}^\dagger$, but kept other numerical factors.

8.4.5.2 Normalization

As the final step in constructing the radial eigenfunctions, let's take care of the normalization. Rewriting Eq. (8.141) with a normalization factor η_k (to be determined), we have

$$|k\rangle = \eta_k b_1^\dagger b_2^\dagger \cdots b_{k-1}^\dagger |0_k\rangle. \tag{8.147}$$

Let's proceed under the assumption that $|0_k\rangle$ is normalized. We haven't enforced this yet, but we will in a bit. Then for this state to be normalized, we require

$$\left|\eta_k\right|^{-2} = \langle 0_k | b_{k-1} \cdots b_1 b_1^\dagger \cdots b_{k-1}^\dagger |0_k\rangle. \tag{8.148}$$

From Eq. (8.81), we can identify the operator product in the middle as

$$b_1 b_1^\dagger = H_2 - E_1. \tag{8.149}$$

Just to the right of this product is $b_2^\dagger$, and we can commute $H_2 - E_1$ with $b_2^\dagger$ using the second of Eqs. (8.82), which gives

$$(H_2 - E_1) b_2^\dagger = b_2^\dagger (H_3 - E_1). \tag{8.150}$$

We can continue commuting the operator to the right through $b_3^\dagger$ through $b_{k-1}^\dagger$, and by the end the operator becomes $(H_k - E_1)$:

$$\left|\eta_k\right|^{-2} = \langle 0_k | b_{k-1} \cdots b_2 b_2^\dagger \cdots b_{k-1}^\dagger (H_k - E_1) |0_k\rangle. \tag{8.151}$$

But from Eqs. (8.84) and (8.85), the condition that $|0_k\rangle$ is a null eigenvalue is the same as the requirement $H_k|0_k\rangle = E_k|0_k\rangle$, and so

$$\left|\eta_k\right|^{-2} = (E_k - E_1)\langle 0_k|b_{k-1}\cdots b_2 b_2^\dagger \cdots b_{k-1}^\dagger|0_k\rangle. \tag{8.152}$$

Now we can iterate this process, starting with $b_2 b_2^\dagger$ and ending with $b_{k-1}b_{k-1}^\dagger$. The result is

$$\left|\eta_k\right|^{-2} = (E_k - E_1)(E_k - E_2)\cdots(E_k - E_{k-1}), \tag{8.153}$$

or solving for the normalization factor (and restoring the explicit ℓ-dependence),

$$\eta_{k\ell} = \Big[(E_{k\ell} - E_{1\ell})(E_{k\ell} - E_{2\ell})\cdots(E_{k\ell} - E_{(k-1)\ell})\Big]^{-1/2}. \tag{8.154}$$

(normalization factor)

It's a little odd that the eigenenergies determine the normalization factor. But recall the hydrogen eigenenergies (8.133)

$$E_{k\ell} = -\frac{\alpha^2\mu c^2}{2(\ell+k)^2} = -\frac{\hbar^2}{2\mu a_0^2(\ell+k)^2}, \tag{8.155}$$

where in the second expression we eliminated the fine-structure constant α in favor of the Bohr radius (8.138). Here the energies have factors $\hbar^2/2\mu a_0^2$, and normalization involves dividing by the square root of these factors. These factors exactly cancel (up to an arbitrary phase) the factors $\hbar/ia_0\sqrt{2\mu}$ in the $b_k^\dagger$ from Eq. (8.142), which we dropped in constructing the example eigenfunctions in the previous section. Thus we can construct the eigenfunctions by omitting factors of this form in both the creation operators and the normalization factors.

The last step is to normalize the null eigenvector (8.140). The resulting normalized form is

$$\zeta_{k\ell}(r) = \frac{2^{k+\ell}}{(k+\ell)^{k+\ell+1}a_0^{3/2}\sqrt{[2(k+\ell)-1]!}}\left(\frac{r}{a_0}\right)^{\ell+k-1} e^{-r/a_0(\ell+k)}.$$

(normalized null eigenvector) (8.156)

This comes from requiring the normalization condition

$$\int_0^\infty dr\, r^2\,|\zeta_{k\ell}(r)|^2 = 1, \tag{8.157}$$

as appropriate for the radial dependence in spherical coordinates (the angular parts having already been accounted for in the normalization of the spherical harmonics).

8.4.5.3 Normalized Examples

Now let's rewrite the example eigenfunctions from Section 8.4.5.1 in normalized form. In doing so, we will switch to a more conventional notation for the radial functions, which will amount to the notation change

$$\psi_{k\ell}(r) \longrightarrow R_{n\ell}(r), \tag{8.158}$$

where

$$n := k + \ell. \tag{8.159}$$

In terms of this new index, the hydrogen-atom energies simplify to

$$E_n = -\frac{\alpha^2\mu c^2}{2n^2}. \tag{8.160}$$

(energy eigenvalues, hydrogen atom)

Now starting with $\psi_{10}(r)$ in Eq. (8.144), corresponding to $R_{10}(r)$. In this case, there were no creation operators involved, so there is no extra normalization beyond the normalization factor in the null eigenvector (8.140). Putting in $k = 1$ and $\ell = 0$ into this normalization factor, we find

$$R_{10}(r) = \zeta_{10}(r) = \frac{2}{a_0^{3/2}}\, e^{-r/a_0}. \tag{8.161}$$

In Eq. (8.145), we had $\psi_{20}(r)$, which corresponds to $R_{20}(r)$. There is one creation operator, so in addition to the normalization factor in the null eigenvector (8.140), we need the normalization factor (8.154), which amounts to the factor $(1 - 1/4)^{-1/2}$:

$$\begin{aligned} R_{20}(r) &= \eta_{20} b_{10}^\dagger \zeta_{20}(r) \\ &= (1 - 1/4)^{-1/2} \frac{1}{\sqrt{24}\, a_0^{3/2}} 3\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \\ &= \frac{2}{(2a_0)^{3/2}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}. \end{aligned} \tag{8.162}$$

Finally, in Eq. (8.146), we had $\psi_{21}(r)$, which corresponds to $R_{31}(r)$. Again, there is one creation operator involved, which requires a normalization factor factor $(1/4 - 1/9)^{-1/2}$:

$$\begin{aligned} R_{31}(r) &= \eta_{21} b_{11}^\dagger \zeta_{21}(r) \\ &= (1/4 - 1/9)^{-1/2} \frac{2}{81}\sqrt{\frac{2}{15}} \frac{1}{a_0^{3/2}} \frac{5r}{a_0}\left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0} \\ &= \frac{1}{(3a_0)^{3/2}} \frac{4\sqrt{2}}{3} \frac{r}{3a_0}\left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}. \end{aligned} \tag{8.163}$$

Construction of any other eigenfunction proceeds in the same way. To summarize the eigenfunctions that we derived, as well as a few more:

$$\begin{aligned} R_{10}(r) &= \frac{2}{a_0^{3/2}} e^{-r/a_0} \\ R_{20}(r) &= \frac{2}{(2a_0)^{3/2}}\left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0} \\ R_{21}(r) &= \frac{1}{(2a_0)^{3/2}} \frac{2}{\sqrt{3}} \frac{r}{2a_0} e^{-r/2a_0} \\ R_{30}(r) &= \frac{2}{(3a_0)^{3/2}}\left(1 - \frac{2r}{3a_0} + \frac{2r^2}{3(3a_0)^2}\right) e^{-r/3a_0} \\ R_{31}(r) &= \frac{1}{(3a_0)^{3/2}} \frac{4\sqrt{2}}{3} \frac{r}{3a_0}\left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0} \\ R_{32}(r) &= \frac{1}{(3a_0)^{3/2}} \frac{2\sqrt{2}}{3\sqrt{5}} \frac{r^2}{(3a_0)^2} e^{-r/3a_0}. \end{aligned}$$

(example radial eigenfunctions) (8.164)

The derivations of $R_{21}(r)$, $R_{31}(r)$, and $R_{32}(r)$ via the same method are left as exercises.

A couple of patterns are already evident in the above radial functions. For a given quantum number n, the length scale for the wave function is na_0. In the cases of minimum k (i.e., $n = \ell + 1$), where no creation operator is involved in the construction of the eigenstate, there are no nodes for $r > 0$ (and only a node at $r = 0$ for $n > 1$). As k is fixed and ℓ increases, additional nodes appear for $r > 0$, one for each increase in ℓ.

8.4.5.4 Summary: Hydrogen-Atom Eigenstates

Now to summarize where we're at with the energy eigenstates of the hydrogen atom. We started back in Section 8.4.2, seeking eigenstates of the form $|E\ \ell\ m\rangle$. From Eq. (8.160), the energy eigenvalues depend only on the $n = k + \ell$ quantum number, so we can label the eigenstates by n instead of E. Thus, we have states labeled $|n\ \ell\ m\rangle$. Projecting into the position representation in spherical coordinates, we have

$$\psi_{n\ell m}(r, \theta, \phi) = \langle r, \theta, \phi | n\ \ell\ m\rangle = R_{n\ell}(r)\, Y_\ell^m(\theta, \phi).$$

(full hydrogen-atom eigenstates) (8.165)

We have seen that $R_{n\ell}(r)$ and the spherical harmonics $Y_\ell^m(\theta,\phi)$ are normalized separately, and so the eigenstates satisfy the normalization condition

$$\int dr \int d\Omega\, r^2\, |\psi_{n\ell m}(r,\theta,\phi)|^2 = 1 \tag{8.166}$$

when putting everything together, where $d\Omega = \sin\theta\, d\theta\, d\phi$ as usual.

We already discussed the calculation of spherical harmonics in depth before [see Eq. (7.88) and the surrounding discussion]. For the radial functions, we can take write the eigenfunction in parts as

$$\begin{aligned}
R_{n\ell}(r) &= \frac{b_{1\ell}^\dagger}{\sqrt{E_{k\ell} - E_{1\ell}}} \cdots \frac{b_{(k-1)\ell}^\dagger}{\sqrt{E_{k\ell} - E_{(k-1)\ell}}}\, \zeta_n(r) \\
k &= n - \ell \\
\frac{b_{k'\ell}^\dagger}{\sqrt{E_{k\ell} - E_{k'\ell}}} &= \frac{1}{\sqrt{1/(k'+\ell)^2 - 1/(k+\ell)^2}} \left(a_0 \partial_r - \frac{1}{\ell + k'} + \frac{\ell + k' + 1}{r/a_0} \right) \\
\zeta_n(r) &= \frac{2^n}{n^{n+1} a_0^{3/2} \sqrt{(2n-1)!}} \left(\frac{r}{a_0} \right)^{n-1} e^{-r/na_0},
\end{aligned}$$

(radial eigenfunctions) (8.167)

after gathering Eqs. (8.142), (8.143), (8.153), and (8.140) in one spot. These radial functions can be further refined into the conventional form

$$R_{n\ell}(r) = \sqrt{\frac{2}{n^3 r a_0^2}}\, \Lambda_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{na_0} \right), \tag{8.168}$$

(radial eigenfunction)

where the **Laguerre functions** are defined by

$$\Lambda_k^j(z) := \left[\Gamma(1+j) \binom{k+j}{k} \right]^{-1/2} z^{j/2}\, L_k^j(z)\, e^{-z/2} \tag{8.169}$$

(Laguerre functions)

and normalized such that

$$\int_0^\infty dz\, \Lambda_k^\alpha(z)\, \Lambda_{k'}^\alpha(z) = \delta_{kk'}. \tag{8.170}$$

The Laguerre functions involve the **associated Laguerre polynomials**

$$L_k^j(z) := \frac{z^{-j} e^z}{k!} \partial_z^k \left(z^{k+j} e^{-z} \right). \tag{8.171}$$

(associated Laguerre polynomial)

In the case of $j = 0$, the polynomials are called **Laguerre polynomials**.

8.4.5.5 Reduced-Mass Convention

There is one important oddity in the notation for the hydrogen-atom wave functions, which is that constants like the Bohr radius (8.138) that appears in the radial eigenfunction (8.168) are conventionally defined in terms of the electron mass m_e instead of the more appropriate reduced mass μ. These are approximately the same, but of course the distinction is important for high-accuracy calculations. The reason for this is that it is far easier to define the fundamental constants in terms of m_e instead of μ, particularly in setting their best-known values and propagating their errors. From the viewpoint of hydrogen-atom calculations, the idea is to just do the calculation assuming $\mu = m_\mathrm{e}$ (i.e., in the limit of a large nuclear mass). At the last minute, just before plugging in numbers, the correcting replacement $m_\mathrm{e} \longrightarrow \mu$ can be done to get the proper results. It is a little strange, but the convention is so standard that it's hard to avoid. For this reason we will be a bit fluid in the notation for the electron mass, but ultimately it is always the reduced mass μ that should enter in the final solution in place of m_e.

8.4.6 Degeneracy, Symmetries, Generators, and Conserved Quantities

Going back to the form (8.155) for the hydrogen-atom energy levels,

$$E_{k\ell} = -\frac{\alpha^2 \mu c^2}{2(\ell + k)^2}, \tag{8.172}$$

it is useful to discuss the **degeneracies** of the levels—the occurrence of multiple states with the same energy. There are two apparent kinds of degeneracy here. First, the energies are independent of the m quantum number, which means that for a given k and ℓ, there are $2\ell + 1$ states of different m with the same energy. The other degeneracy to observe is that various combinations of k and ℓ can produce the same energies.

Generally speaking, such degeneracies reflect underlying symmetries of the system. The first degeneracy (m-independence of energy) is the more obvious one—it reflects the spherical symmetry of the hydrogen-atom problem. To explore this in a bit more depth, recall that the operator for a rotation about the z-axis by angle θ may be written

$$R(\theta) = e^{-i\theta L_z/\hbar}. \tag{8.173}$$

That the system is invariant under rotations means that the Hamiltonian is invariant under a transformation by this rotation operator [recall the transformation rule (1.133) for the Hamiltonian]:

$$R(\theta) H R^\dagger(\theta) = H. \tag{8.174}$$

Multiplying on the right by $R(\theta)$ and collecting the terms on the left-hand side, this condition is equivalent to

$$[R(\theta), H] = 0, \tag{8.175}$$

that the rotation operator commutes with the Hamiltonian. Since the rotation operator involves all powers of L_z, this condition also implies that

$$[L_z, H] = 0. \tag{8.176}$$

This in turn implies that L_z is a "constant of the motion" as in classical mechanics, in the sense that the time derivative of this operator vanishes in the Heisenberg picture.

More formally, since the rotation operator is an exponentiated form of L_z, L_z is called the **generator** of rotations about the z-axis. The generator also corresponds to the operator for an infinitesimal rotation, in the sense that a rotation through a small angle ϵ has the form $1 - i\epsilon L_z/\hbar$. Other analogous generators occur for similar transformations. For example, the unitary time-evolution operator is

$$U(t, 0) = e^{-iHt/\hbar} \tag{8.177}$$

for a time-independent Hamiltonian, in which case H is the generator for time translations. Invariance under time translations implies (constant) energy eigenvalues. Also, we have seen that the operator for space translation is [recall Eq. (5.115)]

$$e^{-ip\chi/\hbar}\psi(x) = \psi(x - \chi), \tag{8.178}$$

and thus the momentum operator generates space translations. Invariance under space translations implies constant momentum.

So the first degeneracy is related to momentum invariance. What explains the other degeneracy? This is much less obvious, and it is called an "accidental degeneracy" because it does not correspond to an invariance under a coordinate transformation. However, it turns out that this degeneracy is related to the **Runge–Lenz vector**

$$\mathbf{C} := \frac{1}{2}\Big(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}\Big) - \mu\hbar c\hat{r}. \tag{8.179}$$

(Runge–Lenz vector)

In classical mechanics (where the symmetrization of $\mathbf{p} \times \mathbf{L}$ is unnecessary), the conservation of the Runge–Lenz vector leads to closed orbits in the $1/r$ potential (Problem 8.6). In quantum mechanics, the analogous manifestation is this degeneracy of the energy levels (8.7).

8.5 Exercises

Problem 8.1

(a) Show that

$$[r, \mathbf{p}] = i\hbar\hat{r} = i\hbar\frac{\mathbf{r}}{r}. \tag{8.180}$$

(b) Use the result from (a) to show

$$[r, p_r] = i\hbar. \tag{8.181}$$

Problem 8.2

Show, using the integral representation of the spherical Bessel function

$$j_\ell(z) = \frac{1}{2i^\ell}\int_{-1}^{1} d\mu\, e^{iz\mu}\, P_\ell(\mu) \tag{8.182}$$

that $R(r) = j_\ell(kr)$ solves the radial part of the Schrödinger equation

$$r^2\partial_r^2 R + 2r\partial_r R + [k^2r^2 - \ell(\ell+1)]R = 0. \tag{8.183}$$

Problem 8.3

(a) Starting with the Laplacian in cylindrical coordinates

$$\begin{aligned}\nabla^2 &= \frac{1}{r}\partial_r r\partial_r + \frac{1}{r^2}\partial_\phi^2 + \partial_z^2 \\ &= \partial_r^2 + \frac{1}{r}\partial_r + \frac{1}{r^2}\partial_\phi^2 + \partial_z^2,\end{aligned} \tag{8.184}$$

show, using the *ansatz* $\psi(\mathbf{r}) = R(r)\Phi(\phi)Z(z)$, that the Helmholtz equation $(\nabla^2 + k^2)\psi = 0$ may be separated into the equations

$$\begin{aligned} r^2\partial_r^2 R + r\partial_r R + \left(k_{\text{T}}^2 r^2 - m^2\right)R &= 0 \\ \partial_\phi^2\Phi + m^2\Phi &= 0 \\ \partial_z^2 Z + k_z^2 Z &= 0,\end{aligned} \tag{8.185}$$

where k_z, k_{T}, and m are constants, and

$$k^2 = k_z^2 + k_{\text{T}}^2. \tag{8.186}$$

(b) Integrate the above equations to find the solution

$$\psi(r, \phi, z) = \Big[c_j J_m(k_{\text{T}}r) + c_y Y_m(k_{\text{T}}r)\Big]e^{im\phi}e^{ik_z z}, \tag{8.187}$$

where m is an integer, and $J_m(x)$ and $Y_m(x)$ are the cylindrical Bessel functions (of integer order) of the first and second kind, respectively. The constants c_j and c_y must still be determined by normalization. Look up the small-argument and large-argument asymptotic expressions for the Bessel functions (Abramowitz and Stegun is always a good place to start). Which of the possible eigenfunctions can we throw out because they're unnormalizable? Singular? (Note that this is something of a trick question; part of the problem is to figure out what the trick is, and to make sense of the eigenfunctions.)

(c) Suppose that the wave function is confined to a cylindrical "pipe" wave guide that that applies a Dirichlet boundary at radius $r = a$. Consider only the $m = 0$ eigenstate, with the smallest possible value of k_{T} (that is, the first zero z_{01} of $J_0(z)$ coincides with the boundary). For fixed energy E, write down an expression for the wavelength of the eigenfunction along the pipe in terms of m_{p} (the particle mass), E, a, and z_{01}. At fixed energy, what is the critical value of a where the eigenfunction changes between propagating and localized? For a larger than this critical value, does the wavelength increase or decrease with a?[4]

Problem 8.4

Recall that the free-particle wave function in three dimensions has the form

$$\psi(\mathbf{r}) = c_j j_0(kr) + c_y y_0(kr) \tag{8.188}$$

under the condition of spherical symmetry ($\ell = 0$ angular momentum), before requiring any regularity of the eigenfunction. You may use the explicit expressions

$$j_0(r) = \frac{\sin r}{r}, \qquad y_0(r) = -\frac{\cos r}{r} \tag{8.189}$$

for the spherical Bessel functions in this problem.

(a) Now suppose you have a particle in a finite, spherical potential well, with $V(r) = -V_0 < 0$ for $r < a$ and $V(r) = 0$ for $r > a$. Derive an equation that determines the wave number $k_<$ (and thus the energy) for a bound state inside the well, assuming a regular wave function for the bound state.

(b) Show that there is no bound state below some critical value of V_0; what is this value?

Problem 8.5

Use the factorization method to derive the following normalized eigenfunctions:

(a)

$$R_{21}(r) = \frac{1}{(2a_0)^{3/2}} \frac{2}{\sqrt{3}} \frac{r}{2a_0} e^{-r/2a_0}. \tag{8.190}$$

(b)

$$R_{31}(r) = \frac{1}{(3a_0)^{3/2}} \frac{4\sqrt{2}}{3} \frac{r}{3a_0} \left(1 - \frac{r}{6a_0}\right) e^{-r/3a_0}. \tag{8.191}$$

(c)

$$R_{32}(r) = \frac{1}{(3a_0)^{3/2}} \frac{2\sqrt{2}}{3\sqrt{5}} \frac{r^2}{(3a_0)^2} e^{-r/3a_0}. \tag{8.192}$$

Problem 8.6

In the *classical* Kepler problem, we can write the Hamiltonian

$$H = \frac{(\hat{r} \cdot \mathbf{p})^2}{2m} + \frac{(\hat{\theta} \cdot \mathbf{p})^2}{2m} - \frac{k}{r} \tag{8.193}$$

in spherical coordinates, assuming motion confined to the $\phi = 0$ plane. Note that, if we denote p_θ as the canonically conjugate momentum to θ, that $p_\theta \neq \hat{\theta} \cdot \mathbf{p}$.

(a) Show explicitly that the angular momentum $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ is a constant of the motion.

[4] There is a similar effect of wavelength variation of organ pipes (of finite length), but the reason for that is quite different (and much more complicated). See Harold Levine and Julian Schwinger, "On the Radiation of Sound from an Unflanged Circular Pipe," *Physical Review* **73**, 383 (1948) (doi: 10.1103/PhysRev.73.383).

(b) Show explicitly that the Runge–Lenz vector

$$\mathbf{C} := \mathbf{p} \times \mathbf{L} - mk\hat{r} \tag{8.194}$$

is a constant of the motion.

(c) That the Runge–Lenz vector is conserved implies that orbits close in the Kepler problem. Show this by first showing that

$$\mathbf{C} \cdot \mathbf{r} = L^2 - mkr, \tag{8.195}$$

and then that this equation implies that the orbits are conic sections.

Problem 8.7

Now let's treat the *quantum* Kepler problem (i.e., the hydrogen atom) in terms of the Hamiltonian

$$H = \frac{p^2}{2m} - \frac{k}{r}. \tag{8.196}$$

In the quantum case, the Runge–Lenz vector must be symmetrized to read

$$\mathbf{C} := \frac{1}{2}\Big(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}\Big) - mk\hat{r}. \tag{8.197}$$

Now let's see why the conservation of this vector in quantum mechanics implies the ''accidental degeneracy'' among the energy levels.

(a) Show that $\mathbf{C} \cdot \mathbf{L} = \mathbf{L} \cdot \mathbf{C} = 0$.

(b) Show explicitly that $[\mathbf{C}, H] = 0$.

(c) Show that

$$[C_\alpha, C_\beta] = -2i\hbar m \epsilon_{\alpha\beta\gamma} H L_\gamma. \tag{8.198}$$

(d) Show that

$$C^2 = 2mH\big(L^2 + \hbar^2\big) + m^2k^2. \tag{8.199}$$

Now we can finally get to the point of all this. The Runge–Lenz commutator motivates the definition of the scaled operator

$$\mathbf{A} := \frac{1}{\sqrt{-2mE}}\,\mathbf{C}, \tag{8.200}$$

if we consider this operator to only operate on bound states where $E < 0$. Then this operator has the commutator

$$[A_\alpha, A_\beta] = i\hbar \epsilon_{\alpha\beta\gamma} L_\gamma, \tag{8.201}$$

and Eq. (8.199) can be rewritten

$$A^2 + L^2 + \hbar^2 = -\frac{mk^2}{2E}. \tag{8.202}$$

In terms of this scaled Runge–Lenz vector we can now define two new angular-momentum operators

$$\mathbf{J}_\pm := \frac{\mathbf{L} \pm \mathbf{A}}{2} \tag{8.203}$$

(i.e., these are not the raising/lowering operators; the sign here just keeps track of the sign in the linear combination).

(e) Show that $\mathbf{J}_+$ and $\mathbf{J}_-$ behave as angular-momentum operators. Also show that $[\mathbf{J}_+, \mathbf{J}_-] = 0$, and that $J_+^2 = J_-^2$.

At this point, we're basically done. Since $\mathbf{J}_\pm$ are angular-momentum operators, eigenstates of L^2 are also eigenstates of $J_+^2 = J_-^2$, with eigenvalues of the form $\hbar^2 j(j+1)$, for j an integer or half-integer. Equation (8.202) then says that

$$2\big(J_+^2 + J_-^2\big) + \hbar^2 = -\frac{mk^2}{2E}, \tag{8.204}$$

and putting in the eigenvalues and solving for E,

$$E = -\frac{mk^2}{2\hbar^2(2j+1)^2}, \tag{8.205}$$

which is the usual expression for the hydrogen-atom eigenstates if we identify $(2j+1)$ as the n quantum number, and $k = \hbar c\alpha$.

Chapter 9

Spin

9.1 Spin Angular Momentum

We already discussed orbital angular momentum in Section 7.2, where we saw that the ℓ quantum number must be an integer. Nevertheless, half-integer angular momenta are a possibility given the definition of angular momenta in terms of the operator commutation relations. These exist as **spin angular momentum**. (Spin angular momentum can occur with integer quantum numbers as well.) They are not, however predicted by the combination of the Schrödinger equation and the canonical quantization procedure from Section 1.6.1. Spin angular momentum is only predicted directly from a proper, relativistic version of quantum mechanics, which we won't get into here. Instead, we will ''patch'' spin onto the Schrödinger equation.

The landmark experiment that confirmed the existence of spin was the Stern–Gerlach experiment.[1] The idea is that an electron (say, in an atom) has an orbital angular momentum $\mathbf{L}$; this generates a magnetic moment, which can be written

$$\boldsymbol{\mu}_{\mathrm{L}} = -\frac{\mu_{\mathrm{B}}}{\hbar}\mathbf{L}, \tag{9.1}$$

where

$$\mu_{\mathrm{B}} := \frac{e\hbar}{2m_{\mathrm{e}}} \approx 9.27 \times 10^{-24}\,\mathrm{J/T} \tag{9.2}$$

is called the *Bohr magneton*, with e the magnitude of the electron charge and m_{e} the electron mass. (This expression for the magnetic moment isn't quite correct, because it ignores the finite nuclear mass, but it is conventional.) By analogy, the spin magnetic moment, with angular-momentum operator $\mathbf{S}$, produces a magnetic moment

$$\boldsymbol{\mu}_{\mathrm{S}} = -g_S\frac{\mu_{\mathrm{B}}}{\hbar}\mathbf{S}, \tag{9.3}$$

where g_S is the **gyromagnetic ratio** of the electron, which appears as a ''fudge factor'' for the proportionality of the magnetic moment and the spin. The gyromagnetic ratio has the value $g_S \approx 2.002$, and it is known (through heroic efforts in both theory and experiment) to around 12 digits. The point of this is that the magnetic dipole moment of the spin is observable through its interaction with the field. The energy of the dipole–field interaction is

$$V_{\mathrm{dip}} = -\boldsymbol{\mu}_{\mathrm{S}} \cdot \mathbf{B}, \tag{9.4}$$

and this corresponds to a magnetic dipole force

$$\mathbf{F}_{\mathrm{dip}} = -\nabla V_{\mathrm{dip}} = \nabla(\boldsymbol{\mu}_{\mathrm{S}} \cdot \mathbf{B}). \tag{9.5}$$

Using the vector identity $\nabla(\mathbf{A}\cdot\mathbf{B}) = (\mathbf{A}\cdot\nabla)\mathbf{B} + (\mathbf{B}\cdot\nabla)\mathbf{A} + \mathbf{A}\times(\nabla\times\mathbf{B}) + \mathbf{B}\times(\nabla\times\mathbf{A})$, this becomes

$$\mathbf{F}_{\mathrm{dip}} = (\boldsymbol{\mu}_{\mathrm{S}} \cdot \nabla)\mathbf{B} + \boldsymbol{\mu}_{\mathrm{S}} \times (\nabla \times \mathbf{B}), \tag{9.6}$$

[1] Walther Gerlach and Otto Stern, ''Der experimentelle Nachweis der Richtungsquantelung im Magnetfeld,'' *Zeitschrift für Physik* **9**, 349 (1922) (doi: 10.1007/BF01326983).

and in the absence of currents or a time-dependent electric field, $\nabla \times \mathbf{B} = 0$, so the magnetic dipole force is

$$\mathbf{F}_{\text{dip}} = (\boldsymbol{\mu}_{\text{S}} \cdot \nabla)\mathbf{B}. \tag{9.7}$$

Thus, the magnetic dipole experiences a force that depends on the **gradient** of the magnetic field. Furthermore, since S_z has the eigenvalues $\pm\hbar/2$, this force is *state-dependent*, with two different values. In the Stern–Gerlach experiment, this state-dependent force was manifest as a splitting in a beam of silver atoms after passing through a nonuniform magnetic field.[2,3]

9.2 Spin-½

The case of $S = 1/2$ (i.e., the eigenvalue of S^2 is $\hbar^2(1/2)(1/2+1) = 3\hbar^2/4$) is especially important, so we'll now spend some time developing it. There are only two states, so we'll switch to an abbreviated notation

$$|S{=}1/2,\ m_{\text{S}}{=}\pm 1/2\rangle \longrightarrow |\pm\rangle. \tag{9.8}$$

(Note that this differs from the notation in Section 3.3, where the same state labels referred to symmetric and antisymmetric superpositions of the one-well states.) Since the eigenvalues of S_z are $\pm\hbar/2$, we can express S_z in terms of projectors for the eigenstates as

$$S_z = \frac{\hbar}{2}\Big(|+\rangle\langle+| - |-\rangle\langle-|\Big). \tag{9.9}$$
(S_z in Dirac notation)

Since the Hilbert space is so small, it is also conventional to work in standard matrix notation. In the case of S_z, it is conventional to define the **Pauli matrix**[4]

$$(\sigma_z) := \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{9.10}$$
(z Pauli matrix)

in which case the spin operator is

$$S_z = \frac{\hbar}{2}\sigma_z. \tag{9.11}$$

Note the ordering here: the upper-left matrix slot corresponds to $|+\rangle\langle+|$ in Dirac notation, while the lower-right slot corresponds to $|-\rangle\langle-|$. Happily, this is consistent with the convention that we used for rotation matrices in Section 7.4.1.4, where m and m' decrease downward and to the right. These matrices operate on states that are written as two-component vectors in this same representation; these vectors are often called **spinors**.

To construct the other two Pauli operators, we can go back to the general angular-momentum formalism, where we have already made choices that fix their form. In particular, we already have constructed the ladder operators [Eqs. (7.8) and (7.31)]; for spin-1/2, these read

$$S_\pm = S_x \pm iS_y, \qquad S_+|-\rangle = \hbar|+\rangle, \qquad S_-|+\rangle = \hbar|-\rangle, \tag{9.12}$$

with of course $S_\pm|\pm\rangle = 0$. These relations imply

$$S_x = \frac{S_+ + S_-}{2}, \qquad S_y = \frac{S_+ - S_-}{2i}, \tag{9.13}$$

[2]For a nice history and details of the experiment, along with stories of vexation over spectral lines and an experiment saved by cheap cigar breath, see Bretislav Friedrich and Dudley Herschbach, "Stern and Gerlach: How a Bad Cigar Helped Reorient Atomic Physics," *Physics Today* **56**, 53 (2003) (doi: 10.1063/1.1650229).

[3]For a more modern realization with laser-cooled atoms splitting into nine different groups in a magnetic-field gradient according to their m state, see G. Klose, G. Smith, and P. S. Jessen, "Measuring the Quantum State of a Large Angular Momentum," *Physical Review Letters* **86**, 4721 (2001) (doi: 10.1103/PhysRevLett.86.4721).

[4]A reminder of the notation here [see Eq. (1.70)]: σ_z is an abstract operator on the Hilbert space of vectors spanned by $|\pm\rangle$, while (σ_z) indicates the operator σ_z, but expressed in a particular representation, here, in terms of its eigenstates $|\pm\rangle$. Strictly speaking, we shouldn't write something like $\sigma_z =$ (matrix), although informally it's common to do this without causing confusion, particularly for the Pauli operators.

or defining the lowering Pauli operator[5]

$$\sigma_- := |-\rangle\langle +|, \qquad (\sigma_-) = \begin{bmatrix} 0 & 0 \\ 1 & 0 \end{bmatrix}, \qquad S_- = \hbar\sigma_-, \qquad S_+ = \hbar\sigma_+, \tag{9.14}$$

the spin operators become

$$S_x = \frac{\hbar}{2}(\sigma_- + \sigma_+), \qquad S_y = \frac{i\hbar}{2}(\sigma_- - \sigma_+). \tag{9.15}$$

These relations are sufficient to fix the conventional operators

$$\sigma_x := |+\rangle\langle -| + |-\rangle\langle +| \qquad \sigma_y := i|-\rangle\langle +| - i|+\rangle\langle -| \tag{9.16}$$
(other Pauli operators)

or matrices

$$(\sigma_x) = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \qquad (\sigma_y) = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \tag{9.17}$$
(other Pauli matrices)

where of course now the spin operators satisfy the commutation relation

$$[S_\alpha, S_\beta] = i\hbar\epsilon_{\alpha\beta\gamma}S_\gamma. \tag{9.18}$$

The same commutator in terms of the Pauli matrices is

$$[\sigma_\alpha, \sigma_\beta] = 2i\epsilon_{\alpha\beta\gamma}\sigma_\gamma. \tag{9.19}$$
(Pauli matrix commutator)

It's also not hard to show that the Pauli matrices satisfy the anticommutation relation

$$[\sigma_\alpha, \sigma_\beta]_+ = 2\delta_{\alpha\beta}, \tag{9.20}$$
(Pauli matrix anticommutator)

where the identity operator is understood to be on the right-hand side (i.e, in spinor notation the 2×2 identity matrix $\mathcal{I}_2$ would appear). This simple anticommutator is unique to the spin $1/2$ case. More formally, this is because the set of infinitesimal rotations forms a **Lie algebra**, which is defined only in terms of an antisymmetric bracket (here, the anticommutator).

The Pauli operators are generally fairly special: they have eigenvalues ± 1, and they are Hermitian and unitary, so that $\sigma_\alpha^2 = 1$. Since we know all the eigenvalues, the operators are also all traceless and have determinant -1.

To finish up the list of handy results, it is useful to write the other spin operators in Dirac notation as

$$\begin{aligned} S_x &= \frac{\hbar}{2}\sigma_x = \frac{\hbar}{2}\Big(|+\rangle\langle -| + |-\rangle\langle +|\Big) \\ S_y &= \frac{\hbar}{2}\sigma_y = \frac{i\hbar}{2}\Big(|-\rangle\langle +| - |+\rangle\langle -|\Big), \end{aligned} \tag{9.21}$$
(spin-$1/2$ operators)

keeping in mind that the ket in each ket/bra combination indexes the matrix row, while the bra indexes the matrix column. Also, note that the ket/bra combinations in these two operators are not projection operators, but rather raising ($|+\rangle\langle -| = \sigma^\dagger$) and lowering ($|-\rangle\langle +| = \sigma$) operators.

9.2.1 Coupling of Spin-½ to a Magnetic Field

On its own, a spin doesn't do very much; it merely "is." That is, until it interacts with something. As noted before, the primary interaction of a spin is to a magnetic field via its magnetic dipole moment. Thus, let's consider the evolution of the spin-$1/2$ system under the Hamiltonian

$$H = -\boldsymbol{\mu}_{\text{S}} \cdot \mathbf{B}. \tag{9.22}$$

Let's break this interaction up into cases.

[5] Another common notation is σ for σ_- and $\sigma^\dagger$ for σ_+.

1. $\mathbf{B} = B_z\hat{z}$: The simplest case is a magnetic field aligned with the quantization axis (z). In this case, the Hamiltonian becomes
$$H = \frac{g_S\mu_B B_z}{\hbar} S_z, \tag{9.23}$$
and thus the Hamiltonian is diagonal in the $|\pm\rangle$ basis, with corresponding eigenvalues $\pm g_S\mu_B B_z/2$. Thus, we can write the Hamiltonian in this case as
$$(H) = \begin{bmatrix} \hbar\Delta/2 & 0 \\ 0 & -\hbar\Delta/2 \end{bmatrix}, \tag{9.24}$$
where we have defined the energy splitting
$$\hbar\Delta := g_S\mu_B B_z. \tag{9.25}$$
Again, the states are uncoupled for this field orientation.

2. $\mathbf{B} = B_x\hat{x}$: In the next case, the magnetic field is orthogonal to the quantization axis, and we have a Hamiltonian of the form
$$H = \frac{g_S\mu_B B_x}{\hbar} S_x. \tag{9.26}$$
This is of the form
$$(H) = \begin{bmatrix} 0 & \hbar\Omega/2 \\ \hbar\Omega/2 & 0 \end{bmatrix}, \tag{9.27}$$
where we have defined the coupling energy
$$\hbar\Omega := g_S\mu_B B_x. \tag{9.28}$$
Note that this has the form of the tunneling Hamiltonian for two symmetric potential wells (Section 3.3), and thus we expect Rabi oscillations between the $|\pm\rangle$ states with angular frequency Ω.

3. General $\mathbf{B}$: The case of $\mathbf{B} = B_y\hat{y}$ is basically the same as $\mathbf{B} = B_x\hat{x}$, except that the Rabi frequency will be imaginary. So let's handle all the components of $\mathbf{B}$ at once, in which case the Hamiltonian (9.22) has the matrix representation
$$(H) = \frac{\hbar}{2}\begin{bmatrix} \Delta & \Omega \\ \Omega^* & -\Delta \end{bmatrix},$$
(magnetic dipole interaction Hamiltonian) (9.29)
where
$$\hbar\Delta := g_S\mu_B B_z, \qquad \hbar\Omega := g_S\mu_B(B_x - iB_y),$$
(coupling parameters) (9.30)
where the minus sign of B_y makes the upper-right matrix element of the Hamiltonian be Ω instead of Ω^* (which is just a common convention, nothing essential). This Hamiltonian now has the form of the tunneling Hamiltonian for an *asymmetric* pair of potential wells [Eq. (3.78)], except that the Rabi frequency is now complex. It turns out this doesn't really change anything; for example, the off-resonant Rabi oscillations here occur at a generalized Rabi frequency
$$\tilde{\Omega} := \sqrt{|\Omega|^2 + \Delta^2}, \tag{9.31}$$
whereas in the case of real Ω, the solution from before had the same form but with $|\Omega|^2$ written as Ω^2. We will derive this generalized Rabi frequency using a nice representation below, and this form of the generalized Rabi frequency also follows directly from Problem 1.23.

9.2.2 Bloch Sphere

A general state of a single spin-$^1/_2$ system has the form

$$|\psi\rangle = c_+|+\rangle + c_-|-\rangle. \tag{9.32}$$

Since there are two complex coefficients, there are in principle four (real-valued) degrees of freedom here. However, the normalization requirement eliminates one of these, and if we discard the global phase as one of these (something we'll undo later!), there are only two real-valued degrees of freedom. Thus, it should be possible to represent the state of a spin-$^1/_2$ system (or, importantly, *any* two-level system, like a two-level atom or a qubit), on a two-dimensional manifold, and that's what we aim to do here.

The idea is to represent $|\psi\rangle$ via the **three** expectation values $\langle\sigma_x\rangle$, $\langle\sigma_y\rangle$, and $\langle\sigma_z\rangle$. In terms of the coefficients $c_\pm$, using the representations

$$\begin{aligned}\sigma_x &= |+\rangle\langle -| + |-\rangle\langle +| \\ \sigma_y &= i|-\rangle\langle +| - i|+\rangle\langle -| \\ \sigma_z &= |+\rangle\langle +| - |-\rangle\langle -|,\end{aligned} \tag{9.33}$$

it isn't hard to take expectation values with respect to the state (9.32), with the results

$$\begin{aligned}\langle\sigma_x\rangle &= c_+^* c_- + \text{c.c.} \\ \langle\sigma_y\rangle &= -ic_+^* c_- + \text{c.c.} \\ \langle\sigma_z\rangle &= |c_+|^2 - |c_-|^2.\end{aligned} \tag{9.34}$$

Now let's consider the dynamical evolution of the state in these variables. The Schrödinger equation $|\dot\psi\rangle = -(i/\hbar)H|\psi\rangle$ gives

$$\frac{d}{dt}\begin{bmatrix} c_+ \\ c_- \end{bmatrix} = -\frac{i}{2}\begin{bmatrix} \Delta & \Omega \\ \Omega^* & -\Delta \end{bmatrix}\begin{bmatrix} c_+ \\ c_- \end{bmatrix}, \tag{9.35}$$

which yields the coupled equations

$$\begin{aligned}\dot c_+ &= -\frac{i}{2}\big(\Delta c_+ + \Omega c_-\big) \\ \dot c_- &= -\frac{i}{2}\big(\Omega^* c_+ - \Delta c_-\big).\end{aligned} \tag{9.36}$$

Then, for example,

$$\begin{aligned}\frac{d}{dt}\langle\sigma_z\rangle &= c_+^*\dot c_+ - c_-^*\dot c_- + \text{c.c.} \\ &= -\frac{i}{2}\Big(\Delta|c_+|^2 + \Omega c_+^* c_- - \Omega^* c_-^* c_+ - \Delta|c_-|^2\Big) + \text{c.c.} \\ &= \text{Re}[\Omega]\langle\sigma_y\rangle + \text{Im}[\Omega]\langle\sigma_x\rangle\,.\end{aligned} \tag{9.37}$$

The other two components follow in the same way (Problem 9.3), with results

$$\begin{aligned}\frac{d}{dt}\langle\sigma_x\rangle &= -\Delta\langle\sigma_y\rangle - \text{Im}[\Omega]\langle\sigma_z\rangle \\ \frac{d}{dt}\langle\sigma_y\rangle &= \Delta\langle\sigma_x\rangle - \text{Re}[\Omega]\langle\sigma_z\rangle\,.\end{aligned} \tag{9.38}$$

These three evolution equations can be combined into a single equation in terms of a "precession vector" $\boldsymbol{\wp}$ as[6]

$$\partial_t\langle\boldsymbol{\sigma}\rangle = \boldsymbol{\wp}\times\langle\boldsymbol{\sigma}\rangle\,, \tag{9.39}$$

(Bloch-vector equation of motion)

[6]The symbol $\wp$ is pronounced "squiggle."

where

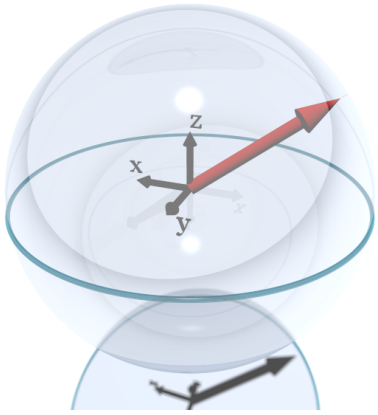
$$\boldsymbol{\wp} := \mathrm{Re}[\Omega]\hat{x} - \mathrm{Im}[\Omega]\hat{y} + \Delta\hat{z}, \tag{9.40}$$
(precession vector)

in analogy with $\boldsymbol{\tau} = \partial_t \mathbf{L} = \boldsymbol{\Omega} \times \mathbf{L}$, with $\mathbf{L}$ the angular momentum, $\boldsymbol{\tau}$ the torque, and $\boldsymbol{\Omega}$ the angular frequency vector for the precession (or the magnetic field vector in the case of **Larmor precession** of a magnetic moment).[7] This picture of the two-level atom in terms of a precessing spin is known as the **Feynman–Vernon–Hellwarth representation**.[8]

One property that follows immediately from this representation is that the length of the **Bloch vector**

$$\langle \boldsymbol{\sigma} \rangle := \langle \sigma_x \rangle \, \hat{x} + \langle \sigma_y \rangle \, \hat{y} + \langle \sigma_z \rangle \, \hat{z} \tag{9.41}$$
(Bloch vector)

is a constant of the motion. That's because the change in $\langle \boldsymbol{\sigma} \rangle$ is always normal to it. Furthermore, for the state (9.32), it turns out that the Bloch vector has unit length (Problem 9.2). Thus, the Bloch vector lives on a sphere, the **Bloch sphere**. What we have shown is that *any* evolution of the two-state system according to the Hamiltonian (9.29)—which is, of course, about as general as it gets—is a simple rotation of the Bloch sphere (at constant angular velocity, if the Hamiltonian is time-independent). This is a powerful and general representation for two-state systems, in addition to the spin-1/2 model; plus it's a good way to visualize the state of such systems.

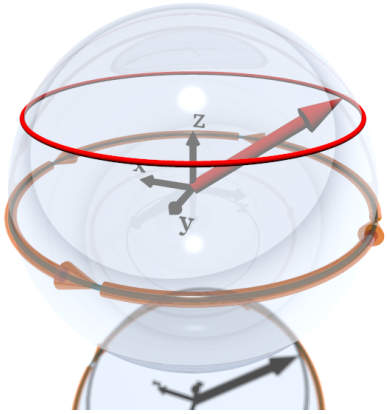


Now for some interpretation.

First, note that a spin in $|+\rangle$ corresponds to a Bloch vector pointing straight up (i.e., the "north pole" of the Bloch sphere is $|+\rangle$), while the $|-\rangle$ state is straight down. The equatorial states are equal superpositions of $|\pm\rangle$, so for example the $|+\rangle_x$ state (the $|+\rangle$ state, but with x the quantization axis) points along the $+x$ direction, and so on. When the magnetic field is purely in the z direction (i.e., $\Omega = 0$, $\Delta \neq 0$), the precession vector is $\boldsymbol{\wp} = \Delta\hat{z}$, and thus the resulting phase evolution is just rotation about the z axis.

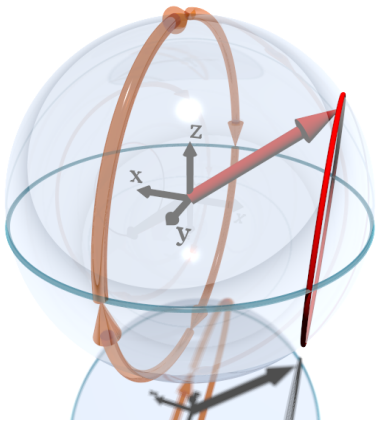
[7] See Richard Feynman, Robert B. Leighton, and Matthew L. Sands, *The Feynman Lectures in Physics* (Addison–Wesley, 1963), Chapter 20.

[8] Richard P. Feynman, Frank L. Vernon, and Robert W. Hellwarth, "Geometrical Representation of the Schrödinger Equation for Solving Maser Problems," *Journal of Applied Physics* **28**, 49 (1957) (doi: 10.1063/1.1722572).



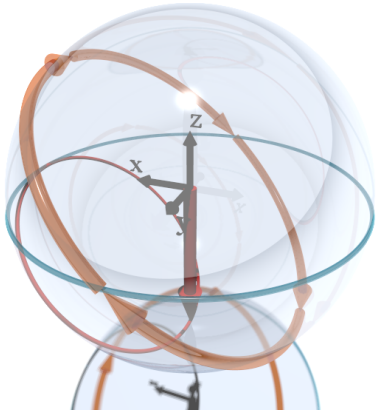
Thus, the Bloch sphere simply spins about the z-axis, causing azimuthal rotation of the trajectories. This evolution represents the relative phase precession of the $|\pm\rangle$ states. The relative phase of $|\pm\rangle$ is thus encoded in this azimuthal angle.

In the case where the magnetic field is purely in the x direction (i.e., a resonant interaction where $\Delta = 0$ and $\Omega \in \mathbb{R}$), the precession vector is $\boldsymbol{\wp} = \Omega\hat{x}$, which rotates the sphere as shown below (note the unusual orientation of the x axis).



If the atom is initially in $|-\rangle$, for example, the trajectory follows the great circle given by the intersection of the Bloch sphere with the $x = 0$ plane. Thus, it passes through the $|+\rangle$ state, and it oscillates between the two states at the Rabi frequency—that is, Rabi oscillations just popped out of the FVH representation. Note that Rabi oscillations may be incomplete (or may not occur at all), depending on the initial orientation of the Bloch vector.

In the general case, we will have $\Delta \neq 0$ and $\Omega \neq 0$. In this case, the rotation axis is tilted, being a combination of the previous two rotations. If the atom starts in $|-\rangle$ state, the trajectory never quite makes it exactly to $|+\rangle$ state, and thus the Rabi oscillations are always incomplete. The example below is for $\Delta < 0$ and $\Omega \in \mathbb{R}$.



This a nice way to visualize how the off-resonant excitation ends up being incomplete. Furthermore, the angular frequency at which the Rabi oscillations occur is given by the magnitude

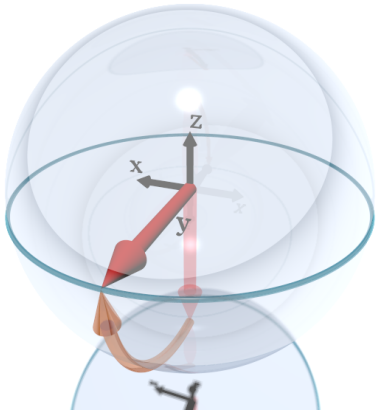
$$|\wp| = \sqrt{\mathrm{Re}[\Omega]^2 + \mathrm{Im}[\Omega]^2 + \Delta^2} = \sqrt{|\Omega|^2 + \Delta^2}. \tag{9.42}$$

(generalized Rabi frequency)

This is the generalized Rabi frequency, as we already mentioned.

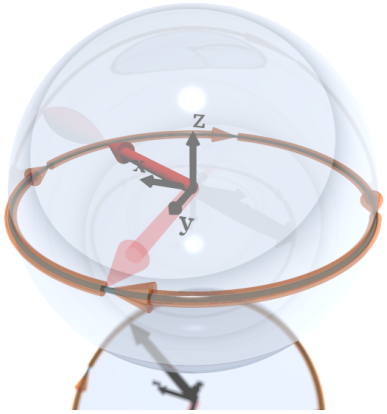
9.2.2.1 Ramsey Method

One nice application of the Bloch sphere is to understand the **Ramsey method**,[9] which forms the basis for atomic time and frequency standards. In a simplified version, first the spin starts in $|-\rangle$, and then it interacts with a field that puts it into an equal superposition of $|\pm\rangle$. This is called a "$\pi/2$-pulse," since the duration of the interaction must be controlled to put the spin in the desired superposition.

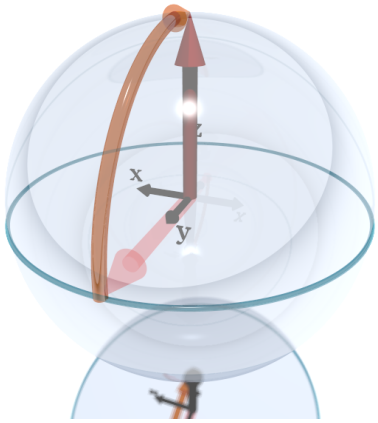


Then the interaction is turned off, and the atom undergoes free evolution—precession about the z-axis at rate Δ—for a time T. The accumulated phase is thus ΔT.

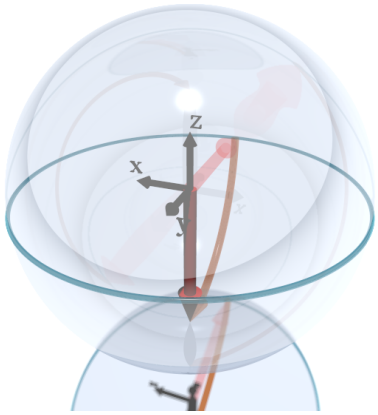
[9] Ramsey, a former student of Rabi, shared the 1989 Nobel prize for the method of separated, oscillatory fields. See Norman F. Ramsey, "A New Molecular Beam Resonance Method," *Physical Review* **76**, 996 (1949) (doi: 10.1103/PhysRev.76.996); Norman F. Ramsey, "A Molecular Beam Resonance Method with Separated Oscillating Fields," *Physical Review* **78**, 695 (1950) (doi: 10.1103/PhysRev.78.695); Norman F. Ramsey, *Molecular Beams* (Oxford, 1956).



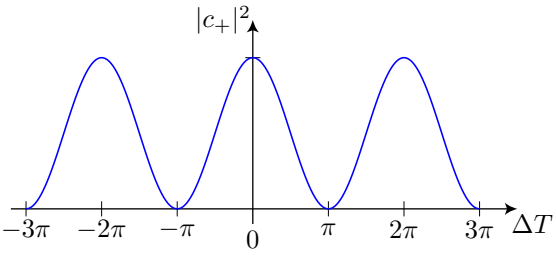
A final $\pi/2$-pulse again transforms the spin state, but its effect depends on the state after the precession stage. If the spin ends up with its initial phase after the precession, which happens if ΔT is an integer multiple of 2π, then the effect of the second $\pi/2$-pulse continues the evolution from before and promotes the atom to the $|+\rangle$ state.



On the other hand, if the atom ends up with the *opposite* phase after precession, as happens when ΔT is an odd-integer multiple of π, then the second $\pi/2$-pulse has the opposite effect: the atom returns to the $|-\rangle$ state.



For other final phases after the precession stage, the final probability of occupying $|+\rangle$ interpolates sinusoidally between these extreme values. We thus see that the output signal (the probability that a measurement finds the spin to be in $|+\rangle$) is sinusoidal in T with period $2\pi/\Delta$. Similarly the output signal is sinusoidal in Δ with period $2\pi/T$.



These oscillations are called **Ramsey fringes**.

In an atomic clock, the "spin" is represented by two states of an atom. The current standard for measuring time and frequency is the hyperfine-split ground state of ^{133}Cs, where the transition frequency is defined to be exactly 9.192 631 77 GHz (but future clocks will use optical transitions for better precision). A microwave field takes the place of the B_x field to cause Rabi oscillations. The measurement is somewhat more complicated than the above picture suggests, because generally the idea is to compare the *frequency* of the microwave source to the atomic transition, and thus it is necessary to account for off-resonant ($\Delta \neq 0$) interactions in deriving the final signal.

9.2.3 A Global Sign, or When is a Global Phase not a Global Phase?

Since the Bloch-vector representation is based only on expectation values, it lacks one thing: the global phase of the state. Remember that this is an oddity of rotations of spin-$^1/_2$ states. For example, the operator for rotation about the z-axis is [Eq. (7.132)]

$$R(\alpha\hat{z})|\pm\rangle = e^{-i\alpha S_z/\hbar}|\pm\rangle = e^{\mp i\alpha/2}|\pm\rangle. \tag{9.43}$$

In this case, a "full" rotation through angle 2π gives the original state back with a minus sign. It takes two full rotations, $\alpha = 4\pi$, to really get the original state back. The same can be seen in the form of the matrix for a rotation about the y axis [Eq. (7.158)],

$$\left[d^{(1/2)}_{m'm}(\beta\hat{y})\right] = \begin{bmatrix} \cos(\beta/2) & -\sin(\beta/2) \\ \sin(\beta/2) & \cos(\beta/2) \end{bmatrix}. \tag{9.44}$$

where $\beta = 2\pi$ gives a sign change but $\beta = 4\pi$ does not.

But perhaps this funny sign is an artifact of rotations, does it occur in the evolution of a spin interacting with a magnetic field? The answer is of course yes, but it's instructive to look for this sign in the time evolution that we have studied so far. In the Hamiltonian (9.24) for an interaction with a field $\mathbf{B} = B_z\hat{z}$,

$$(H) = \frac{\hbar\Delta}{2}\begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{9.45}$$

the evolution of the states $|\pm\rangle$ is of the form $e^{\mp i\Delta t/2}$. In this case the relative phase processes as $e^{\mp i\Delta t}$, and thus has period $2\pi/\Delta$. However, the *absolute* phase has period $2\pi/(\Delta/2) = 4\pi/\Delta$, since each state must return to the original phase. The relative phase is zero whenever the two counter-rotating phases line up, which can happen with either a + or a − sign. Similarly, for a field interaction of the form $\mathbf{B} = B_x\hat{x}$ the Hamiltonian (9.27) is

$$(H) = \frac{\hbar\Omega}{2}\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \tag{9.46}$$

and the time-dependent solution for a state of the form $|\psi\rangle = c_+|+\rangle + c_-|-\rangle$ is [see Problem 3.1 or Eq. (4.2)]

$$c_-(t) = \cos\left(\frac{\Omega t}{2}\right) \tag{9.47}$$

in the case where $c_+(0) = 0$. The corresponding time-dependent probability is

$$|c_-(t)|^2 = \cos^2\left(\frac{\Omega t}{2}\right) = \frac{1}{2} + \frac{1}{2}\cos\Omega t. \tag{9.48}$$

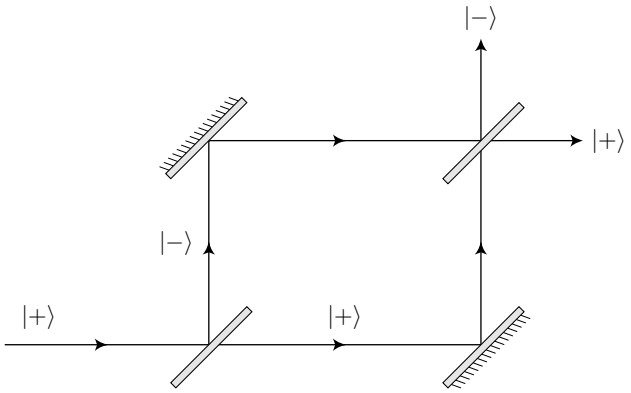
So while the period of the Rabi oscillations of the probability is $2\pi/\Omega$, the period of the *amplitude* is $2\pi/(\Omega/2) = 4\pi/\Omega$. This is because on each population oscillation, the amplitude alternates sign. So the same sign that shows up in the rotation operator also shows up in the dynamical evolution (which we already know from the FVH representation, since dynamical evolution is just a rotation).

So does this sign matter? After all, a global phase is just a global phase; we've already argued that it shouldn't matter. Unless, of course, it isn't a global phase...[10,11]

9.2.3.1 Interference Experiment

Before turning to the question of how to observe this 360°-rotation phase, let's review how you go about detecting a phase. The gold standard is an interference experiment. We've already seen this in the Ramsey method of Section 9.2.2.1, but this is such an important and general concept that we'll review it using more abstract language.

The prototype for an interference experiment is an optical interferometer, shown below; this works for classical light (i.e., a laser), but we will adapt it as a framework for the analysis of a general interference experiment with a quantum system. The idea is that light enters the interferometer, hits a beam splitter and divides into two beams, which are redirected by two mirrors, and then the beams are recombined on another beamsplitter; the two outputs of the second beam splitter provide the experimental signal. The diagram corresponds to a Mach–Zehnder optical interferometer, but the exact scheme isn't important.



Now let's analyze this in terms of a sequence of actions on a quantum state.

1. **Initial state.** Let's label the initial quantum state $|+\rangle$. This is a label for a two-state system, the two

[10] Of course, in what follows, we'll show that this phase is observable. But more deeply, this phase turns out to be a *topological phase*, which can be demonstrated via the "Dirac belt trick" or the "Feynman plate trick." See, for example, David Pengelley and Daniel Ramras, "How Efficiently Can One Untangle a Double-Twist? Waving is Believing!" *The Mathematical Intelligencer* **39**, 27 (2017) (doi: 10.1007/s00283-016-9690-x) (arXiv: 1610.04680). Yet more deeply, the exchange of two particles is equivalent to a rotation by 360°, which gives an intuitive explanation for the spin–statistics theorem that we will mention later in Section 10.4—this theorem says that half-integer-spin particles gain a minus sign under exchange and thus behave as fermions, whereas integer-spin particles don't gain the sign under exchange, thus behaving as bosons. See Richard P. Feynman and Steven Weinberg, *Elementary Particles and the Laws of Physics: The 1986 Dirac Memorial Lectures* (Lecture notes compiled by Richard MacKenzie and Paul Doust) (Cambridge University Press, 1987), pp. 56-9 (ISBN: 0521340004).

[11] Another comment: mathematically, one says that SU(2) is a double cover of SO(3), with SO(3) being the **special orthogonal** group of all orthogonal ($A^{\mathsf{T}} = A^{-1}$) 3×3 matrices of unit determinant (i.e., rotations of 3-vectors), and SU(2) being the **special unitary** group of all unitary ($A^{\dagger} = A^{-1}$) 2×2 matrices of unit determinant (i.e., rotations, but on spin-1/2 vectors). Note that the Bloch sphere, being a representation of states and not operators, is itself not a representation of SU(2). But the unit sphere is a representation of the so(3) and su(2) groups of *generators* (Problem 1.17) of SO(3) and SU(2), respectively, with the points on the sphere specifying the axis of an infinitesimal rotation on the respective vector space. The group SO(3) is kind of like the sphere in three dimensions plus its interior (3-ball), with the radius specifying the rotation angle in say $[0, 2\pi)$, and the angular orientation again specifying the rotation axis. However, pairs of points reflected through the origin in this 3-ball are redundant, because they correspond to the same rotation axis, and so SO(3) is really *half* of the 3-ball (technically, it is called the real projective space in 3 dimensions). Then because of this extra sign, SU(2) must amount to two copies of this SO(3) space. For an excellent discussion of this and the related Lie-group structure of quantum mechanics, see Michael Weiss, "Lie Groups and Quantum Mechanics" (2001), available at `https://www-zeuthen.desy.de/~kolanosk/eep06/skripte/lie.pdf` or `https://math.ucr.edu/home/baez/lie/lie.html`.

states being the two possible inputs to the first beam splitter. The initial state is the left-hand input; the bottom input (unlabeled) is the other state.

2. **First beam splitter.** The beam splitter maps the two input states to two output states. Assuming a lossless process, this map corresponds to a unitary operator. On a spin-$^1/_2$ Hilbert space (or the space for any two-level system), we have seen that a unitary evolution corresponds to a rotation, at least on the Bloch sphere. That gives us some guidance on the form of a general unitary operator on this space: it should correspond to a general rotation operator. We have already written most of this down; the rotation matrix for a general rotation in terms of Euler angles is, from Eq. (7.145),

$$d^{(j)}_{m'm}(\alpha,\beta,\gamma) = e^{-im'\alpha}\, d^{(j)}_{m'm}(\beta\hat{y})\, e^{-im\gamma}.$$

(rotation matrix, Euler angles) (9.49)

But note that we can simplify this a bit for the present case. As far as the beam splitter is concerned, the input state is given, but there is freedom in defining the output states, specifically the phases of the output states (both absolute and relative). Thus, we can absorb one of the phase factors in the rotation matrix into the phase of the output states, say the phase corresponding to α. Then using the β rotation matrix (7.158), including the α rotation, we have

$$\left[d^{(1/2)}_{m'm}(\beta,\gamma)\right] = \begin{bmatrix} \cos(\beta/2)\, e^{-i\gamma/2} & -\sin(\beta/2)\, e^{i\gamma/2} \\ \sin(\beta/2)\, e^{-i\gamma/2} & \cos(\beta/2)\, e^{i\gamma/2} \end{bmatrix}. \tag{9.50}$$

We can simplify this further by factoring out another global phase, and changing notation to $\theta = -\beta/2$ and $\phi = \gamma$, to give the general unitary operator

$$\left[U(\theta,\phi)\right] = \begin{bmatrix} \cos(\theta) & \sin(\theta)\, e^{i\phi} \\ -\sin(\theta) & \cos(\theta)\, e^{-i\phi} \end{bmatrix}.$$

(general unitary operator, two-state space) (9.51)

For the purposes of discussing interference, we can simplify to a more specific case corresponding to the maximum possible effect, which is $\theta = \pi/4$ and $\phi = 0$, for which the unitary operator is just

$$(U) = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & 1 \\ -1 & 1 \end{bmatrix}. \tag{9.52}$$

This amounts to the transformation

$$|\psi\rangle = |+\rangle \longrightarrow \frac{|+\rangle - |-\rangle}{\sqrt{2}} \tag{9.53}$$

of the initial state. Note that we are recycling the $|\pm\rangle$ notation for the arms of the interferometer; while we could use a different notation (e.g., $|\mathrm{L}\rangle$, $|\mathrm{R}\rangle$), this notation emphasizes that this treatment is much more general than a representation of the interferometer, and the redundant notation doesn't make this derivation too much harder to follow.

In the Ramsey experiment above, this corresponds to the $\pi/2$-pulse that set up the superposition between $|\pm\rangle$.

3. **Differential phase evolution.** In the arms of the interferometer, there should be some difference that leads to the accumulation of a relative phase between the $|\pm\rangle$ states. The *differential* aspect is critical—one arm acts as an effective phase *reference* for the other. In an optical interferometer, this could include different optical media or different path lengths; in interferometers with atomic waves, the difference could be differing heights, corresponding to different gravitational potentials (for sensitivity to the gravitational acceleration g). Without such a difference, the interferometer doesn't really do much. At this point, however, we won't specify the source of the phase, but simply note that the differential phase evolution will amount to a transformation of the form

$$|\psi\rangle \longrightarrow \frac{|+\rangle\, e^{-i\varphi_+} - |-\rangle\, e^{-i\varphi_-}}{\sqrt{2}} \tag{9.54}$$

on the state at the output of the first beam splitter.

4. **Second beam splitter.** The second beam splitter need not be identical to the first one, but the analysis is simpler if it is. Applying the same unitary transformation as for the first beam splitter, the phase is transformed according to

$$|\psi\rangle \longrightarrow \frac{1}{2}\Big[\big(|+\rangle - |-\rangle\big)\, e^{-i\varphi_+} - \big(|+\rangle + |-\rangle\big)\, e^{-i\varphi_-}\Big] = \frac{1}{2}\Big[|+\rangle\big(e^{-i\varphi_+} - e^{-i\varphi_-}\big) - |-\rangle\big(e^{-i\varphi_+} + e^{-i\varphi_-}\big)\Big]. \tag{9.55}$$

5. **Output signal.** The output signal is just the probability that the particle appears in one output or the other. The probability at the $|+\rangle$ output port is

$$P_+ = \frac{1}{4}\big|e^{-i\varphi_+} - e^{-i\varphi_-}\big|^2 = \frac{1}{2}\big[1 - \cos(\varphi_+ - \varphi_-)\big], \tag{9.56}$$

and correspondingly, the other output port is associated with the complementary probability:

$$P_- = \frac{1}{4}\big|e^{-i\varphi_+} + e^{-i\varphi_-}\big|^2 = \frac{1}{2}\big[1 + \cos(\varphi_+ - \varphi_-)\big]. \tag{9.57}$$

This sinusoidal dependence on the relative phase represents ''interference fringes'' in the output (from double-slit diffraction, where the double aperture acts as the first beam splitter, and the second beam splitter is replaced by a screen that shows the interference fringes in the intensity of the light).

Again, an interference experiment of this form is *the* way to sense relative phases. Returning to the problem of a 2π rotation of a spin-$^1/_2$ particle, the key is that such particles have other degrees of freedom besides spin—namely, position. So we can take advantage of the multiple degrees of freedom to set up an experiment to observe the phase. To set up the notation, let's take the initial state to be

$$|\psi\rangle = |+\rangle|+\rangle. \tag{9.58}$$

The first $|+\rangle$ refers to the input port of the interferometer, while the second $|+\rangle$ is the spin state of the particle. Now tracing the state through the interferometer, the first beam splitter only acts on the first ket, and maps the state as

$$|\psi\rangle \longrightarrow \frac{|+\rangle - |-\rangle}{\sqrt{2}}|+\rangle = \frac{|+\rangle|+\rangle - |-\rangle|+\rangle}{\sqrt{2}}. \tag{9.59}$$

Now for the relative-phase evolution. Suppose we arrange for there to be a magnetic field of the form $\mathbf{B} = B_z\hat{z}$ to cause a 2π spin rotation, but only in one arm of the interferometer (say, the ''$-$'' arm). Then the state transforms as

$$|\psi\rangle \longrightarrow \frac{|+\rangle|+\rangle + |-\rangle|+\rangle}{\sqrt{2}} = \frac{|+\rangle + |-\rangle}{\sqrt{2}}|+\rangle, \tag{9.60}$$

since only a component with $|-\rangle$ for the interferometer state picks up a minus sign—that is, in the second term, the $|+\rangle$ spin state picks up a minus sign, but only because it is associated with the $|-\rangle$ interferometer state. Note that in this state, we have explicitly factorized out the spin part in the second expression. At the second beam splitter, since the interferometer part of the state factorizes from the spin part, the treatment is just like before, but with a relative phase shifted by π. This amounts to swapping the probabilities $P_\pm$ at the interferometer output ports in the above interference discussion. Thus, turning the magnetic field on and off can have a large effect on the interference signal, and so this ''global'' phase (which can appear as a relative phase when there are multiple degrees of freedom) is observable in this interferometer. This effect was in fact demonstrated experimentally in neutron-interferometry experiments.[12]

[12] H. Rauch, A. Zeilinger, G. Badurek A. Wilfing W. Bauspiess and U.Bonse, *Physics Letters A* **54**, 425 (1975) (doi: 10.1016/0375-9601(75)90798-7); S. A. Werner, R. Colella, A. W. Overhauser, and C. F. Eagen, Physical Review Letters **35**, 1053 (1975) (doi: 10.1103/PhysRevLett.35.1053).

9.2.4 Interactions, Gates, and Entanglement

The interactions in the above interferometric sequence are important for quantum information, so let's take a minute to stop and smell the roses, as it were. In analogy to logic gates in (classical) digital logic, operations on qubits (two-state systems) can be represented in terms of quantum gates. For example, the transformation (9.60) in the above interferometer example can be viewed as a conditional-phase (CPHASE) gate. In this example, states $|+\rangle|\cdot\rangle$ were unchanged, $|-\rangle|+\rangle$ gets a phase of $e^{-i\alpha/2}$, and $|-\rangle|-\rangle$ gets a phase of $e^{+i\alpha/2}$ (so the phase shift is conditioned on the state of the first qubit). Actually, the more conventional CPHASE gate has a phase shift only for the $|-\rangle|-\rangle$; the interferometer example can be changed into this more conventional gate with a relative phase shift of only the first qubit.

In the interferometer example above, we assumed an interaction with a magnetic field of the form $\mathbf{B} = B_z\hat{z}$, which causes the conditional phase shift. What if we instead used a magnetic field of the form $\mathbf{B} = B_x\hat{x}$ in one interferometer arm? In this case, the transformation (9.60) is replaced by

$$|\psi\rangle = \frac{|+\rangle|+\rangle - |-\rangle|+\rangle}{\sqrt{2}} \longrightarrow \frac{|+\rangle|+\rangle - |-\rangle|-\rangle}{\sqrt{2}}. \tag{9.61}$$

Note that, unlike the transformed state (9.60), this state cannot be factored into a product of the form $|\psi_1\rangle|\psi_2\rangle$ for the different qubits (although it is a linear combination of terms of this form). Such a state is called an **entangled state**—an extremely important concept in quantum mechanics. The quantum gate implementing the transformation (9.61) is called a conditional-NOT (CNOT) gate, and this is an important example of an entangling gate (one that maps a not-entangled, or **separable**, state to an entangled state).

9.3 Exercises

Problem 9.1

Show that on a spin-1/2 Hilbert space, the rotation operator for a rotation angle α about axis $\hat{\alpha}$ can be written

$$e^{-i\boldsymbol{\alpha}\cdot\mathbf{S}/\hbar} = \cos\left(\frac{\alpha}{2}\right)\mathcal{I} - i\sin\left(\frac{\alpha}{2}\right)(\hat{\alpha}\cdot\boldsymbol{\sigma}), \tag{9.62}$$

where $\mathcal{I}$ is the identity operator (shown explicitly for clarity) and $\boldsymbol{\sigma}$ is the "vector" of Pauli matrices. (For the analogous expression in the case $j = 1$, see Problem 7.9.)

Problem 9.2

For a spin-1/2 state of the form

$$|\psi\rangle = c_+|+\rangle + c_-|-\rangle, \tag{9.63}$$

show, by using the expressions (9.34) for the Bloch-vector components $\langle\sigma_\alpha\rangle$ in terms of $c_\pm$, that the Bloch vector has unit length.

Note: this is a fairly straightforward algebra problem, so it's a good time to practice working *efficiently*. Can you get this problem to work out while avoiding multiplying out all the terms? Try to "look ahead" in the calculation and anticipate terms that will cancel.

Problem 9.3

Show, for the spin-1/2 state of Problem 9.2, that

$$\begin{aligned}
\frac{d}{dt}\langle\sigma_x\rangle &= -\Delta\langle\sigma_y\rangle - \mathrm{Im}[\Omega]\langle\sigma_z\rangle \\
\frac{d}{dt}\langle\sigma_y\rangle &= \Delta\langle\sigma_x\rangle - \mathrm{Re}[\Omega]\langle\sigma_z\rangle \\
\frac{d}{dt}\langle\sigma_z\rangle &= \mathrm{Re}[\Omega]\langle\sigma_y\rangle + \mathrm{Im}[\Omega]\langle\sigma_x\rangle
\end{aligned} \tag{9.64}$$

That is, finish the derivation of Eqs. (9.38).

Problem 9.4

The derivation from Section 9.2.2 class for the FVH representation of spin-1/2 dynamics is useful because it emphasizes that the representation is valid for *any* two-level system, without direct reference to the angular-momentum structure of the problem. However, it's also possible to take advantage of this substructure to yield an alternate derivation of the equation of motion.

Starting with the magnetic-dipole Hamiltonian, compute the equation of motion in the Heisenberg picture for the spin operator $\mathbf{S}$ in the case of spin-1/2, with the result

$$\dot{\mathbf{S}} = \boldsymbol{\mu}_{\mathrm{S}} \times \mathbf{B}. \tag{9.65}$$

Then show explicitly that this equation of motion implies the equation of motion $\partial_t\langle\boldsymbol{\sigma}\rangle = \boldsymbol{\wp}\times\langle\boldsymbol{\sigma}\rangle$ [Eq. (9.39)].

Problem 9.5

(a) Consider a spin-1/2 particle, initially in the $|+\rangle$ state. Show that, *when operating on this particular initial state*, the following rotations are equivalent:

$$R(\pi\hat{x})|+\rangle = R(\hat{x}\pi/2)R(-\pi\hat{y})R(\hat{x}\pi/2)|+\rangle. \tag{9.66}$$

(Equivalent, that is, modulo a global phase factor that we don't care about.)

(b) Now suppose that you have the same particle in part (a), on which you want to perform the same rotation $R(\pi\hat{x})$. Suppose also that it has been a while since your Rotate-O-Matic® has been calibrated, and nowadays it effects rotations with a small error ϵ. That is, if $\tilde{R}(\boldsymbol{\zeta})$ denotes the *actual* rotation while the correct, *desired* rotation is $R(\boldsymbol{\zeta})$, then

$$\tilde{R}(\boldsymbol{\zeta}) = R[(1+\epsilon)\boldsymbol{\zeta}]. \tag{9.67}$$

Now show that using your (slightly) haywire Rotate-O-Matic®, the $\tilde{R}(\hat{x}\pi/2)\tilde{R}(-\pi\hat{y})\tilde{R}(\hat{x}\pi/2)$ composite rotation is a better approximation to the desired rotation $R(\pi\hat{x})$ than is the simple attempt $\tilde{R}(\pi\hat{x})$.[13]

You need only work to first order in ϵ throughout the calculation, to show that the simple rotation's error is $O(\epsilon)$, while the composite rotation's error is $O(\epsilon^2)$.

[13]This kind of trick can be used to improve the quality of qubit manipulations in quantum computers, at the expense of speed and complexity of operations. For more details and a nice visualization of how the error cancels out in this example, see Lieven M.K. Vandersypen and Isaac L. Chuang, ''NMR Techniques for Quantum Control and Computation,'' *Reviews of Modern Physics* **76**, 1037 (2005) (doi: 10.1103/RevModPhys.76.1037) (arXiv: quant-ph/0404064), Fig. 24 for the visualization.

Chapter 10

Multiparticle Quantum States and Entanglement

10.1 EPR Paradox

With the formalism for spin and the concept of entanglement in hand, it's a good time to explore entanglement a bit more and how it represents some of the most counterintuitive aspects of quantum mechanics. Now introducing... the **EPR paradox** (for Einstein, Podolsky, Rosen).[1] Consider a spin-0 particle, decaying to two spin-$1/2$ particles. The Clebsch–Gordan coefficients for adding the two daughter particles to form the original particle are

$$\langle 1/2\ \pm 1/2;\ 1/2\ \mp 1/2|0\ 0\rangle = \pm\frac{1}{\sqrt{2}}, \tag{10.1}$$

and thus we can write the original particle in terms of the decayed states (again with the shorthand $|\pm\rangle$ for $|1/2\ \pm 1/2\rangle$) as

$$|0\ 0\rangle = \frac{|+\rangle|-\rangle - |-\rangle|+\rangle}{\sqrt{2}} = \frac{|+-\rangle - |-+\rangle}{\sqrt{2}}, \tag{10.2}$$

where the two spins are anticorrelated—if one is up, the other is definitely down, and vice versa. Note that the minus sign is consistent with fermionic behavior (which we'll come back to later, it isn't essential), but here it comes right out of the angular-momentum formalism. This state is essentially of the same form as in Eq. (9.61), and as we discussed before, this state cannot be factored into a product of states for the two systems, and thus this is an entangled state. (Colloquially, this is called a **Bell state**, and the pair of entangled particles in this state is an **EPR pair**.)

The basic idea behind the EPR thought experiment is to allow the two daughter particles to become widely separated, and then for two observers to perform measurements on the separated particles. Specifically, we will want to consider the spin component of the particles along some direction, say $\hat{\alpha}$. Denoting the corresponding spin operator by $S(\hat{\alpha})$ (which is S_z under a rotation that would take $\hat{z}$ to $\hat{\alpha}$), we can write

$$S(\hat{\alpha}) = \frac{\hbar}{2}\sigma(\hat{\alpha}), \tag{10.3}$$

where $\sigma(\hat{\alpha}) = \boldsymbol{\sigma}\cdot\hat{\alpha}$ is the similarly rotated version of the Pauli matrix σ_z. Considering the spin in terms of such σ matrices means that we can dispense with unnecessary factors of $\hbar/2$. Now we will want to consider joint measurements of the two daughter particles, but along different angles. An average (either an expectation value in theory or an average over many experimental measurements) is a correlation function,

[1] A. Einstein, B. Podolsky, and N. Rosen "Can Quantum-Mechanical Description of Physical Reality Be Considered Complete?" *Physical Review* **47**, 777 (1935) (doi: 10.1103/PhysRev.47.777). This spin-based version of the EPR paradox was first discussed by D. Bohm and Y. Aharonov, "Discussion of Experimental Proof for the Paradox of Einstein, Rosen, and Podolsky," *Physical Review* **108**, 1070 (1957) (doi: 10.1103/PhysRev.108.1070).

which we may write as

$$\Big\langle \sigma_1(\hat\alpha)\,\sigma_2(\hat\beta)\Big\rangle \in [-1,1]. \tag{10.4}$$

This means that particle 1 gets a measurement along $\hat\alpha$, while particle 2 gets a measurement along $\hat\beta$; the average is in the range $[-1,1]$ because this is an average over measurements with possible values ±1—that is, these are *normalized* correlation functions in terms of the $\sigma(\hat\alpha)$ matrices.

To analyze the correlation function, first note that the original state was spherically symmetric, and so we can rotate the coordinate system such that $\hat\alpha = \hat z$. Then writing out the correlation function in terms of the state (10.2), we have

$$\begin{aligned}\Big\langle \sigma_1(\hat\alpha)\,\sigma_2(\hat\beta)\Big\rangle = \frac{1}{2}\Big[&\langle+|\sigma_1(\hat z)|+\rangle\langle-|\sigma_2(\hat\beta)|-\rangle + \langle-|\sigma_1(\hat z)|-\rangle\langle+|\sigma_2(\hat\beta)|+\rangle \\ &- \langle+|\sigma_1(\hat z)|-\rangle\langle-|\sigma_2(\hat\beta)|+\rangle - \langle-|\sigma_1(\hat z)|+\rangle\langle+|\sigma_2(\hat\beta)|-\rangle\Big].\end{aligned} \tag{10.5}$$

Here, off-diagonal terms like $\langle+|\sigma_1(\hat z)|-\rangle$ vanish, while $\langle+|\sigma_1(\hat z)|+\rangle = 1$ and $\langle-|\sigma_1(\hat z)|-\rangle = -1$. Thus, the correlation function simplifies to

$$\Big\langle \sigma_1(\hat\alpha)\,\sigma_2(\hat\beta)\Big\rangle = \frac{1}{2}\Big[\langle-|\sigma_2(\hat\beta)|-\rangle - \langle+|\sigma_2(\hat\beta)|+\rangle\Big]. \tag{10.6}$$

To finish the calculation, we need to find an expression for $\sigma_2(\hat\beta)$, which as we said before is a rotated version of σ_z:

$$\sigma_2(\hat\beta) = R\sigma_z R^\dagger. \tag{10.7}$$

For the rotation matrix, we can use the expression (7.158),

$$(R) = \begin{bmatrix} \cos\beta/2 & -\sin\beta/2 \\ \sin\beta/2 & \cos\beta/2 \end{bmatrix}, \tag{10.8}$$

and multiplying out the transformation then gives

$$\big[\sigma_2(\hat\beta)\big] = \begin{bmatrix} \cos\beta & \sin\beta \\ \sin\beta & -\cos\beta \end{bmatrix}. \tag{10.9}$$

(A shortcut for obtaining this expression for $\sigma(\hat\beta)$ is to note that in our coordinate system $\hat\beta = \hat z\cos\beta + \hat x\sin\beta$; because the angular-momentum vector is a Cartesian vector, its components rotate in the expected way, so that $\sigma(\hat\beta) = \hat\beta\cdot\boldsymbol{\sigma} = \sigma_z\cos\beta + \sigma_x\sin\beta$.) Thus, Eq. (10.6) finally becomes

$$\Big\langle \sigma_1(\hat\alpha)\,\sigma_2(\hat\beta)\Big\rangle = -\cos\beta \tag{10.10}$$

in the simplified coordinates; in general, we can write

$$\Big\langle \sigma_1(\hat\alpha)\,\sigma_2(\hat\beta)\Big\rangle = -\cos\theta, \tag{10.11}$$

(quantum-mechanical prediction)

where θ is the angle between $\hat\alpha$ and $\hat\beta$. Note that if $\hat\alpha = \hat\beta$, the value of the correlation function is -1, reflecting the perfect anticorrelation that we expect from the state (10.2). For $\hat\alpha = -\hat\beta$ the correlation function is $+1$, because we expect perfect correlation among oppositely oriented detectors. For $\hat\alpha \perp \hat\beta$, the correlation function is 0, because there is no correlation among (say) an $\hat x$ oriented detector and a $\hat z$ oriented detector.

Equation (10.11) is the quantum-mechanical prediction for the spin-correlation function. We will discuss this in more detail below, but for the moment let's briefly go over EPR's discomfort with this aspect of quantum mechanics. In quantum mechanics, $|\psi\rangle$ [in the form (10.2)] represents the state of the system. Observables (here, the spins) are not necessarily determined until they are measured, and the outcomes are

possibly random, depending on the state. *That's* not yet the problematic part. The weirdness here is related to the (anti)correlation built into the state (10.2). These correlations persist even if the particles are widely separated. Intuitively, particles that are sufficiently far apart should behave independently (if you do an experiment in the lab, you'd like to think that whatever is happening on Jupiter isn't affecting your results; otherwise, life as an experimentalist is going to be one huge headache). Nevertheless, a measurement of one spin tells you that *if* another distant observer makes the same measurement of the other particle, you will know, with certainty, the outcome of that measurement. *That's* still not the weird part. First of all, these are just correlations, so they can't be used to send information instantaneously, for example. Also, correlations can exist classically. For example, imagine a pair of marbles, one green and one orange. Give one to each of a pair of astronauts, who go to opposite ends of the universe. Only at the end of the journey do they look at their marbles; when one astronaut sees a green marble, there is no doubt that the other astronaut will see the orange counterpart. The weirdness in the EPR thought experiment is more subtle: basically, what observer #1 *can know* about the distant particle #2 *depends on* what the observer measured on particle #1. Again, this is something of a subtle point, so we'll discuss it more carefully below.

For now, let's just say that this oddness motivates thinking about alternate versions of quantum mechanics, that may be more ''complete'' than standard quantum mechanics. In particular, let's think about theories that extend the quantum state schematically as

$$|\psi\rangle \longrightarrow |\psi;\lambda\rangle, \tag{10.12}$$

where the λ represents a set of **hidden variables**. These are (possibly many) extra degrees of freedom and things analogous to quantum numbers that determine the outcomes of measurements, but whose values observers can't know. This would attempt to explain the indeterminism of quantum mechanics with some sufficiently complicated set of hidden variables. Again, all observables, would be *well-defined* (i.e., no uncertainty) in terms of $|\psi;\lambda\rangle$. The different measurement results on repetitions of the experiment in the same quantum state $|\psi\rangle$ would correspond to different values of λ. The question now is, is such a theory possible?

10.1.1 Bell's Theorem

John Bell came up with an elegant way to settle the question of whether such hidden variables are possible.[2] More specifically and precisely, he addressed the question of whether or not a *local* hidden variable theory—one where, say, the spins of the separated particles are *individually* well-defined—is possible.[3]

To consider how to treat the EPR spin experiment in terms of hidden variables, let's define $\sigma_1(\hat{\alpha},\lambda)$ to be a *function* (i.e., *not* an operator), which is a well-defined quantity for particle #1 that is *independent* of particle #2. Again, λ is a possibly complicated set of hidden variables, which are unknown to observers but concocted to reproduce the predictions of quantum mechanics. Note that we are associating the hidden variables with the ''operators'' now instead of the ''state,'' in a kind of hidden-variable Heisenbergish-picture.

Now consider the hidden-variable analogue of the correlation function (10.11). The quantum-mechanical expectation value is replaced by a weighted average over the hidden variables, with density $f(\lambda)$:

$$C(\hat{\alpha},\hat{\beta}) := \Big\langle \sigma_1(\hat{\alpha},\lambda)\,\sigma_2(\hat{\beta},\lambda)\Big\rangle_\lambda := \int d\lambda\, f(\lambda)\,\sigma_1(\hat{\alpha},\lambda)\,\sigma_2(\hat{\beta},\lambda). \tag{10.13}$$

You can think of $f(\lambda)$ being something like a probability density for the hidden variables, given that we don't know their values; the important thing is that the correlation function is uniquely fixed in terms of the hidden variables and the quantum state. Additionally, to faithfully reproduce the results of quantum mechanics, each function $\sigma_1(\hat{\alpha},\lambda)$ and $\sigma_2(\hat{\beta},\lambda)$ can only take on the values ±1 in terms of the hidden variables.

The idea of course is to concoct hidden variables such that Eq. (10.13) reproduces the results predicted by Eq. (10.11). It turns out that there is, in fact, no problem setting up a hidden-variable theory to reproduce

[2] J. S. Bell, ''On the Einstein Podolsky Rosen Paradox,'' *Physics* **1**, 195 (1964); J. S. Bell, ''Introduction to the hidden-variable question,'' in *Proceedings of the International School of Physics 'Enrico Fermi', course IL: Foundations of Quantum Mechanics* (Academic, 1971) p. 171. These articles are reprinted in J. S. Bell, *Speakable and Unspeakable in Quantum Mechanics* (Cambridge, 1987) (ISBN: 0521334950).

[3] For an interesting discussion of Bell's theorem, see the series by Mateus Araújo, ''Understanding Bell's theorem,'' at `http://mateusaraujo.info/2016/07/15/understanding-bells-theorem-part-1-the-simple-version/`.

the expectation values for a *single* spin $\langle\sigma(\hat{\alpha})\rangle$ (see Problem 10.1). It's only at the level of two-particle correlations that problems show up (because it takes a two-particle correlation function to be sensitive to entanglement).

Now Bell's argument involves a *third* direction, which we'll call $\hat{\gamma}$. Let's compute the correlation difference

$$\begin{aligned} C(\hat{\alpha},\hat{\beta}) - C(\hat{\alpha},\hat{\gamma}) &= \Big\langle \sigma_1(\hat{\alpha},\lambda)\,\sigma_2(\hat{\beta},\lambda) - \sigma_1(\hat{\alpha},\lambda)\,\sigma_2(\hat{\gamma},\lambda)\Big\rangle_\lambda \\ &= -\Big\langle \sigma_1(\hat{\alpha},\lambda)\,\sigma_1(\hat{\beta},\lambda) - \sigma_1(\hat{\alpha},\lambda)\,\sigma_1(\hat{\gamma},\lambda)\Big\rangle_\lambda , \end{aligned} \tag{10.14}$$

where in the last step we used the perfect anticorrelation $\sigma_1(\hat{\alpha},\lambda) = -\sigma_2(\hat{\alpha},\lambda)$ in both terms. This change in both terms makes the correlation quantity explicitly local—that is, it is determined entirely in terms of the hidden-variable state of particle 1. Then we can rewrite (10.14) as

$$C(\hat{\alpha},\hat{\beta}) - C(\hat{\alpha},\hat{\gamma}) = -\Big\langle \sigma_1(\hat{\alpha},\lambda)\,\sigma_1(\hat{\beta},\lambda)\Big[1 - \sigma_1(\hat{\beta},\lambda)\,\sigma_1(\hat{\gamma},\lambda)\Big]\Big\rangle_\lambda , \tag{10.15}$$

by noting that $\sigma_1(\hat{\beta})\,\sigma_1(\hat{\beta}) = 1$ (this is true for *any* Pauli matrix, of course). Then any averaged quantity must satisfy

$$\big|\,\langle X\rangle_\lambda\,\big| \le \langle |X|\rangle_\lambda , \tag{10.16}$$

because the left-hand side averages possibly negative with positive quantities, whereas the right-hand side averages the moduli of the same quantities. Then applying the inequality (10.16) to the quantities in Eq. (10.15), we arrive at

$$\Big|C(\hat{\alpha},\hat{\beta}) - C(\hat{\alpha},\hat{\gamma})\Big| \le \Big\langle 1 - \sigma_1(\hat{\beta},\lambda)\,\sigma_1(\hat{\gamma},\lambda)\Big\rangle_\lambda , \tag{10.17}$$

where we have used $|\sigma_1(\hat{\alpha},\lambda)\,\sigma_1(\hat{\beta},\lambda)| = 1$ (because without the modulus operation, the values could only be ± 1). Again using $\sigma_1(\hat{\gamma},\lambda) = -\sigma_2(\hat{\gamma},\lambda)$, the product of σ's under the hidden-variable average is just $C(\hat{\beta},\hat{\gamma})$ after collecting all the signs. Thus, we have the result

$$\Big|C(\hat{\alpha},\hat{\beta}) - C(\hat{\alpha},\hat{\gamma})\Big| - C(\hat{\beta},\hat{\gamma}) \le 1, \tag{10.18}$$

(Bell's inequality)

which is Bell's theorem. (A famous alternative inequality, the CHSH inequality, is more general than the Bell inequality, and it can be used to derive it; see Problem 10.2.) This is an inequality that must be satisfied by any local hidden-variable theory. Note that this is independent of the details of the hidden variables, which is what makes this argument so powerful. Before going on, look through the above argument, which seems pretty simple. There is one point that pretty clearly assumes a local hidden variable theory (while other parts of the argument can be more or less justified as quantum-like); can you find it?[4]

10.1.2 Quantum Mechanics and the Bell Inequality

Now, does quantum mechanics violate the Bell inequality (10.18)? The answer is yes. To see this, we only need to find an example, so pick

$$\begin{aligned} \hat{\alpha} &= \hat{z} \\ \hat{\beta} &= \hat{z}\cos\theta + \hat{x}\sin\theta \\ \hat{\gamma} &= \hat{z}\cos 2\theta + \hat{x}\sin 2\theta, \end{aligned} \tag{10.19}$$

[4]The assumption $|\sigma_1(\hat{\alpha},\lambda)\,\sigma_1(\hat{\beta},\lambda)| = 1$ is unmistakably that of a local-hidden-variable theory, because there is a well-defined spin value along two different directions for a single particle. The perfect anticorrelations and $\sigma_1(\hat{\beta})\,\sigma_1(\hat{\beta}) = 1$ assumptions are reasonably faithful to quantum mechanics.

or that is, the three measurement-direction vectors are coplanar and uniformly fanned out. The quantum prediction (10.11) then gives the correlations

$$\begin{aligned} \big\langle \sigma_1(\hat{\alpha})\, \sigma_2(\hat{\beta}) \big\rangle &= -\cos\theta \\ \big\langle \sigma_1(\hat{\beta})\, \sigma_2(\hat{\gamma}) \big\rangle &= -\cos\theta \\ \big\langle \sigma_1(\hat{\alpha})\, \sigma_2(\hat{\gamma}) \big\rangle &= -\cos 2\theta, \end{aligned} \tag{10.20}$$

and so the Bell inequality (10.18) becomes

$$\Big| -\cos\theta + \cos 2\theta \Big| + \cos\theta \leq 1. \tag{10.21}$$

The function on the left-hand side has a maximum at $\theta = \pi/3$, where it takes the value $3/2$, and thus quantum mechanics violates Bell's inequality.

There have been a number of experimental verifications of the quantum violation of Bell's inequality in various forms, the first being by Freedman and Clauser,[5] and probably the most famous being a demonstration by Aspect, Dalibard, and Roger.[6,7] In both of these experiments, entangled photon pairs were produced by a double-emission cascade in atomic calcium, For a model of a similar method of generating a photon pair, see Problem 10.5. and the experiments analyzed the correlations in the photon polarizations. In the Aspect–Dalibard–Roger work, the measurement axes were effectively varied between the photon-pair creation and detection events via fast optical switches that sent the photons to one of a pair of orthogonally oriented polarizer/detector pairs. The advantage of the time-varying axes is to rule out any ''conspiracy'' among the detectors to agree with the predictions of quantum-mechanics, say by communication via some hidden signals. The rapid time dependence effectively ensures that the detectors have a spacelike separation during the creation and flight of a photon pair, to ensure that the detectors behave independently.

10.1.3 Interpretation

Now let's discuss the implications of this violation of Bell's inequality,[8] but with some care. To review in more detail the EPR paradox, EPR started by making some reasonable assumptions that should intuitively hold for any physical theory:

1. **Locality.** Doing something to one system shouldn't cause a change in another system if it is located sufficiently far away.

2. **Reality.** If you can predict some aspect of a physical system with certainty (i.e., probability 1) without interacting with it, ''then there exists an element of physical reality corresponding to this physical quantity.''

3. **Completeness.** A physical theory is complete if it accounts for every element of physical reality.

These assumptions do indeed seem reasonable. EPR then went on to argue (here adapted to the language of the spin-measurement experiment), that once an observer makes a measurement of the spin of particle

[5] Stuart J. Freedman and John F. Clauser, ''Experimental Test of Local Hidden-Variable Theories,'' *Physical Review Letters* **28**, 938 (1972) (doi: 10.1103/PhysRevLett.28.938).

[6] Alain Aspect, Jean Dalibard, and Gérard Roger, ''Experimental Test of Bell's Inequalities Using Time-Varying Analyzers,'' *Physical Review Letters* **49**, 1804 (1982) (doi: 10.1103/PhysRevLett.49.1804). For a broader experimental review, see also Alain Aspect, ''Bell's Theorem: The Naive View of an Experimentalist,'' (arXiv: quant-ph/0402001) (2004).

[7] The 2022 Nobel Prize in Physics was awarded to Alain Aspect, John Clauser, and Anton Zeilinger for these and other Bell-type experiments, leading to important applications in quantum information science. See `https://www.nobelprize.org/prizes/physics/2022/press-release/`.

[8] There are too many discussions of the interpretation of Bell's theorem to count, but for a start, see for example: Daniel M. Greenberger, Michael A. Horne, Abner Shimony, and Anton Zeilinger, ''Bell's theorem without inequalities,'' *American Journal of Physics* **58**, 1131 (1990) (doi: 10.1119/1.16243); Asher Peres, *Quantum Theory: Concepts and Methods* (Springer, 1995), Chapter 6 (ISBN: 9780306471209) (doi: 10.1007/0-306-47120-5).

#1, there should be no change in particle #2 (locality assumption). But now the observer can predict with certainty the corresponding spin of particle #2, at least in a particular direction. However, the argument carries through for any pair of spin measurements along the same axis, so *all* of the spin components of particle #2 correspond to elements of physical reality (reality assumption). But in quantum mechanics, not all of the spin components are simultaneously well-defined, and thus quantum mechanics is incomplete (completeness assumption). All together now: EPR is saying that if quantum mechanics is assumed to be both local and real, then it can't be complete (and this statement is in fact correct, so the ''paradox'' amounts to something wrong with the natural expectations about what quantum mechanics should do).

It thus seemed to EPR that some theory more complete than quantum mechanics should be possible (i.e., a local hidden-variable theory, where all the spin components of particle #2 are all well-defined, independent of particle #1). The violation of Bell's inequality says that such a local hidden-variable theory is *not* possible, so something must be wrong in the assumptions of EPR. But all of their assumptions seem fairly reasonable, so which is the faulty one? As is often the case when it comes to interpretations of how quantum mechanics works, there is not a unique answer to this question. Let's try to mention a couple of possible answers while trying to remain relatively nonpartisan.

3. **Completeness.** It is probably easiest to start with the completeness assumption, and of course the intent of EPR is that quantum mechanics must be incomplete. Remember that their argument refers to possible measurements on an entangled pair, involving noncommuting observables. EPR asserted that things can be set up such that an observation of one part of half of entangled pair leads to a prediction with certainty about the same observable in the other half of the pair, so that observable must be an element of reality. But because an experimenter *could have* performed the same procedure on a **complementary** (noncommuting) observable, that complementary observable also corresponds to an element of reality (the term **counterfactual** is commonly used in reference to this hypothetical alternative experiment). The problem according to EPR is that quantum mechanics can't account simultaneously for the complementary variables, so it must be incomplete.

   However, an incompleteness of quantum mechanics should have caused more serious problems by now, and it's hard to stick with completeness of quantum mechanics as being the problem. It is commonly said that Bell's theorem rules out ''local realism,'' which we will discuss in pieces as the two remaining assumptions of EPR.

1. **Locality.** First, let's get a couple of objective facts out of the way. Locality, in the sense of having local interactions, is a handy thing in physics, being vastly more intuitive than nonlocal interactions. For example, we saw in the Aharonov–Bohm effect (Section 4.4.5) that it is preferable in quantum mechanics to think of a charged particle interacting fundamentally with the vector potential than with the magnetic field, because only the former interaction is local. On the other hand, it is explicitly *possible* to give up locality in quantum mechanics. The most famous example of a nonlocal, deterministic (hidden-variable) theory that is equivalent to standard quantum mechanics is Bohmian mechanics.[9] Briefly, in this theory, for example the motion of a quantum wave packet is encoded in an ensemble of particles with well defined positions and trajectories (i.e., the hidden variables). There is still the quantum wave function, but it acts as a ''pilot wave'' that influences the otherwise classical motion of the Bohmian trajectories. But in the way that the wave function couples to the trajectories [which is via the quantum potential, Eq. (6.32), where the Laplacian of the amplitude is divided by the amplitude], the quantum ''force'' can be significant even when the amplitude of the wave function is small—the theory is thus explicitly nonlocal. However, it is nonlocal in a way that forbids faster-than-light communication—while the particles have definite values of observables, they must be treated as members of an ensemble to reproduce quantum mechanics, and not individually meaningful.

   It is also important to reaffirm that for a spin-entangled state (10.2) with distantly separated particles, there is *no way to think of each particle as having its own state vector independent of the other*. It *is*

[9] See, for example, Peter R. Holland, *The Quantum Theory of Motion: An Account of the de Broglie-Bohm Causal Interpretation of Quantum Mechanics* (Cambridge, 1993) (doi: 10.1017/CBO9780511622687); Detlef Dürr, Sheldon Goldstein, and Nino Zanghì, *Quantum Physics Without Quantum Philosophy* (Springer, 2013) (doi: 10.1007/978-3-642-30690-71); Detlef Dürr and Stefan Teufel, *Bohmian Mechanics: The Physics and Mathematics of Quantum Theory* (Springer, 2009) (doi: 10.1007/978-3-540-89344-8).

possible to think of *some* quantum state for each particle independent of the other, which amounts to throwing away information about the other particle; we will return to this point later, but this local state is not representable in the form of a state vector.

Whether we choose to demand or reject locality, we should be more precise about what we mean by locality, as the meaning is not unique, and the nonuniqueness is a substantial source of confusion.

(a) **Einstein locality.** A strong form of locality is the one we laid out in the assumptions of EPR. Although locality was not laid out exclusively in the EPR paper, Einstein later laid out this assumption in the form[10]

> But on one supposition we should, in my opinion, absolutely hold fast: the real factual situation of the system S_2 is independent of what is done with the system S_1, which is spatially separated from the former.

This clearly rules out nonlocal interactions (e.g., forces) of the kind that we would not particularly like anyway.

(b) **Locality of what is knowable.** A much *weaker* form of locality is in the form of what we mentioned above is the weird thing about the EPR setup: What is an observer *can know* about a distant system S_2 depends on what the observer measured on their own system S_1. This is not the same as a nonlocal force, and giving up this version is much more palatable (we will return to this below, as this is what is given up by ''orthodox'' quantum mechanics).

(c) **Bell locality.** The notion of locality associated with Bell's theorem can be written in a mathematically precise way, and because it is useful to think of locality in this way we will discuss this formulation in more depth.

Recall that in the setup for the proof of Bell's theorem, we defined the correlation function (10.13), repeated here:

$$C(\hat{\alpha},\hat{\beta}) := \Big\langle \sigma_1(\hat{\alpha},\lambda)\,\sigma_2(\hat{\beta},\lambda)\Big\rangle_\lambda := \int d\lambda\, f(\lambda)\,\sigma_1(\hat{\alpha},\lambda)\,\sigma_2(\hat{\beta},\lambda). \tag{10.22}$$

Again, for example, $\sigma_1(\hat{\alpha},\lambda)$ represents the outcome of the measurement of the spin of particle 1 of the entangled pair along axis $\hat{\alpha}$. We assumed this to have a definite value of $+1$ or -1 in terms of the hidden variables λ. But more generally, $\sigma_1(\hat{\alpha},\lambda)$ and $\sigma_2(\hat{\beta},\lambda)$ could have both deterministic and random components. In this case, we should think of σ_1 and σ_2 directly as random variables (still with outcomes ±1), and the correlation function should involve an expectation value with respect to these random variables as

$$C(\hat{\alpha},\hat{\beta}) := \int d\lambda\, f(\lambda) \int d\sigma_1\, d\sigma_2\, P(\sigma_1,\sigma_2|\hat{\alpha},\hat{\beta},\lambda)\,\sigma_1\,\sigma_2, \tag{10.23}$$

where $P(\sigma_1,\sigma_2|\hat{\alpha},\hat{\beta},\lambda)$ is a joint probability distribution for the two variables, given that the measurement axes and hidden variables have been fixed. Of course, the proof of Bell's theorem used the fact that σ_1 and σ_2 have definite values, and this assumption of **determinism** amounts to the assumption

$$P(\sigma_1,\sigma_2|\hat{\alpha},\hat{\beta},\lambda) \in \{0,1\}, \tag{10.24}$$
(determinism)

so that only one ''random'' outcome is really possible.

Now in terms of the above joint probability, one form of the assumption of locality can be written

$$P(\sigma_1,\sigma_2|\hat{\alpha},\hat{\beta},\lambda) = P(\sigma_1|\hat{\alpha},\lambda)\,P(\sigma_2|\hat{\beta},\lambda). \tag{10.25}$$
(strong locality)

[10] J. S. Bell (1964), *op. cit.*, quoting A. Einstein from *Albert Einstein, Philosopher Scientist*, P. A. Schilp, Ed., p. 85 (Library of Living Philosophers, 1949).

This formulation of locality is termed **strong locality**,[11] and this assumption, along with determinism, is clearly sufficient to establish the form (10.22) of the hidden-variable correlation function (note that weaker assumptions are also sufficient). The assumption of strong locality can be broken down further into two sub-assumptions, which are together equivalent to strong locality:[12]

(a) **Parameter independence** states that the outcome of one observation is independent of the parameter setting of the other measurement:

$$P(\sigma_1|\hat{\alpha},\hat{\beta},\lambda) = P(\sigma_1|\hat{\alpha},\lambda), \qquad P(\sigma_2|\hat{\alpha},\hat{\beta},\lambda) = P(\sigma_2|\hat{\beta},\lambda).$$

(parameter independence) (10.26)

This assumption is particularly important for causality, because if this assumption fails, one observer can send a superluminal signal to a distant observer by making a local parameter change, which influences the distant observer's measurement outcome. This definition (10.26) is also used as the definition of **locality** (as opposed to strong locality).[13]

(b) **Outcome independence** states that the outcome of one observation is independent of the outcome of the other:

$$P(\sigma_1|\sigma_2,\hat{\alpha},\hat{\beta},\lambda) = P(\sigma_1|\hat{\alpha},\hat{\beta},\lambda), \qquad P(\sigma_2|\sigma_1,\hat{\alpha},\hat{\beta},\lambda) = P(\sigma_2|\hat{\alpha},\hat{\beta},\lambda).$$

(outcome independence) (10.27)

Since the dependence is on the *output* to the observation as opposed to an *input*, a failure of this assumption doesn't allow for superluminal signaling.

Clearly, if you're willing to give up strong locality, then outcome independence what you really want to give up more specifically, not parameter independence. In doing so, whatever you give up about locality doesn't violate causality. Orthodox quantum mechanics satisfies parameter independence, but violates outcome independence, owing to the correlations intrinsic to the entangled state. So, in a sense, orthodox quantum mechanics is nonlocal.

However, there is a real sense in which the quantum correlations can be thought of as local, even in violating outcome independence. It's worth reiterating that the measurement correlations are not usable in the sense of faster-than-light communication. If there is no other (classical) communication for the observers to compare spin-measurement results, the measurement of only one spin appears to be completely random (i.e. there is nothing for it to be correlated with). Said another way, the correlations observed by distant observers are only really manifest if they *compare* their observations, which requires an effective local interaction (via one observer traveling to the location of the other, or indirectly via a signal sent between the observers).

2. **Reality.** EPR gave a more precise definition of what they meant by reality, in the sense that it should incorporate any property of a physical system with unit probability. Bell's version of this concept amounts to determinism, in the mathematical sense (10.24), such that the results of observations are well defined in terms of hidden variables λ, these variables ''hiding'' the true, underlying deterministic character of the physical world.

[11] Jon P. Jarrett, ''On the Physical Significance of the Locality Conditions in the Bell Arguments,'' *Noûs* **18**, 569 (1984) (JSTOR: 2214878).

[12] Jarrett, *op. cit.*; Abner Shimony, ''Controllable and uncontrollable non-locality,'' in *Foundations of Quantum Mechanics in the Light of New Technology: Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo, Japan, August 29-31, 1983*, Susumu Kamefuchi, Ed. (Physical Society of Japan, 1984), p. 225; Abner Shimony, ''Physical and Philosophical Issues in the Bohr-Einstein Debate,'' in *Niels Bohr: Physics and the World*, H. Feshbach, T. Matsui, and A. Oleson, Eds., (Harwood, 1988) (ISBN: 9781315779331) (doi: 10.4324/9781315779331). The two Shimony references are reprinted in Abner Shimony, *Search for a naturalistic world view, vol. II: Natural science and metaphysics* (Cambridge, 1993), p. 171 (ISBN: 0521373530). The terminology used here is that of Shimony, not Jarrett.

[13] H. M. Wiseman, ''The two Bells theorems of John Bell,'' *Journal of Physics A: Mathematical and Theoretical* **47** 424001 (2014) (doi: 10.1088/1751-8113/47/42/424001). This paper is an exhaustive and careful analysis of the various assumptions and terms underlying the interpretations of Bell's theorem, the subtle differences between Bell's two versions of the theorem, and why two main ''camps'' disagree mostly due to a difference in terminology.

In Bohr's famous response to EPR, he said (emphasis in original)[14]

> ...essentially the question of *an influence on the very conditions which define the possible types of predictions regarding the future behavior of the system.* Since these conditions constitute an inherent element of the description of any phenomenon to which the term ''physical reality'' can be properly attached, we see that the argumentation of the mentioned authors does not justify their conclusion that quantum-mechanical description is essentially incomplete.

That is, the experimenter's choice of which complementary variable to measure is a part of what we mean by the physical reality, so the unchosen variable is not something quantum mechanics should be expected to account for. This statement embodies the orthodox approach to quantum mechanics (i.e., the **Copenhagen interpretation**). The underlying principle of **complementarity**, where complementary (noncommuting) observables cannot be simultaneously well defined, means that it doesn't make sense to regard an observable as having a particular value until it is measured. Or, in other words, ''unperformed experiments have no results.''[15] This goes back to the locality of what is knowable, or outcome independence; orthodox quantum mechanics violates both of these. Although we discussed these in the context of locality, the violation of these principles can also be thought of as a violation of realism, because the observables don't have definite values until at least the first measurement happens.

To summarize, orthodox quantum mechanics violates both locality (in the form of strong locality, specifically violating outcome independence) *and* realism, in the form of predetermined outcomes; it doesn't make a choice in the sense of the question: which of EPR's assumptions is the one that fails?

Interestingly, it is possible to insist that both locality *and* realism are correct. In the subjective interpretation (quantum Bayesianism, described a bit more in Section 11.3.3, pushed to its limits), states and observations are relative to a particular observer. In the EPR setup, there are two separated observers, each with their own subjective knowledge of the experiment. Thus,[16]

> Quantum mechanics, in the QBist interpretation, cannot assign correlations, spooky or otherwise, to space-like separated events, since they cannot be experienced by any single agent. Quantum mechanics is thus explicitly local in the QBist interpretation.

The same view also rejects the EPR notion of reality, insisting that there is nothing special about ''unit probability,'' so it should not indicate an objective element of reality—everything is subjective, including reality, which is what saves it. The assumption they reject is not usually articulated as one of the EPR assumptions, **macroreality**, which is the assumption that ''In an individual experimental run, exactly one outcome A and exactly one outcome B really happen, and are not 'relative' to anything.''[17]

Adding to the confusion is that there are *two* variations on Bell's theorem.[18] The one we proved above is the earlier ''1964 theorem,''[19] but a later version, the ''1975 theorem,''[20] made subtly different assumptions that are important interpreting the consequences of the theorem. In the later paper Bell introduced the concept of **local causality** as an alternate assumption to locality and determinism, which in probability language may be written in terms of the necessary condition

$$P(\sigma_1|\sigma_2,\hat{\alpha},\hat{\beta},\lambda)=P(\sigma_1|\hat{\alpha},\lambda),\qquad P(\sigma_2|\sigma_1,\hat{\alpha},\hat{\beta},\lambda)=P(\sigma_2|\hat{\beta},\lambda), \tag{10.28}$$
(local causality)

[14] N. Bohr, ''Can Quantum-Mechanical Description of Physical Reality be Considered Complete?'' *Physical Review* **48**, 696 (1935) (doi: 10.1103/PhysRev.48.696). Note that this paper makes use of exactly the same title as the EPR paper to which it responds.

[15] Asher Peres, ''Unperformed experiments have no results,'' *American Journal of Physics* **46**, 745 (1978) (doi: 10.1119/1.11393).

[16] Christopher A. Fuchs, N. David Mermin, and Rudiger Schack, ''An introduction to QBism with an application to the locality of quantum mechanics,'' *American Journal of Physics* **82** 749 (2014) (doi: 10.1119/1.4874855).

[17] H. M. Wiseman, *op. cit.*

[18] H. M. Wiseman, *op. cit.*; the discussion here in terms of local causality vs. locality and determinism follows and is a cartoon version of the detailed analysis in this paper.

[19] J. S. Bell (1964), *op. cit.*

[20] J. S. Bell, ''The theory of local beables,'' TH-2053-CERN, 1975 July 28, presented at the sixth GIFT seminar, Jaca, 2-7 June 1975, and reproduced in *Epistemological Letters* (March 1976); reprinted in J. S. Bell, *Speakable and Unspeakable in Quantum Mechanics* (Cambridge, 1987) (ISBN: 0521334950).

which says for example that the outcome of σ_1 is independent of *both the outcome and parameter setting* of the remote event. He also gave an alternate proof of his inequality that did not rely on determinism (the measurement outcomes did not have to be well defined in terms of the hidden variables before the measurement). The local-causality condition (10.28) is logically equivalent to the strong-locality condition (10.25). Local causality is a weaker assumption than the conjuction of locality/parameter independence (10.26) and determinism, because it explicitly does not require determinism. However, it turns out that local causality is in a sense *equivalent* to the conjunction of locality/parameter independence (10.26) and determinism, because the sets of phenomena respecting each are equivalent.[21] Thus, Bell's theorem (in its later form) does not necessarily imply a choice of rejecting either locality or determinism; rather it says that quantum mechanics—even orthodox quantum mechanics—is not locally causal. It *does* say, though, that if you want a deterministic theory to mimic quantum mechanics, it must violate locality (parameter independence).

Because local causality is equivalent to strong locality, a violation of local causality can be regarded as a choice between parameter independence (10.26) and outcome independence (10.27). As we noted before, orthodox quantum mechanics respects parameter independence (''locality'') but violates outcome independence. In this sense it is not necessary to think of quantum mechanics as nonlocal (in the sense of violating locality/parameter independence). More precisely, it either violates local causality or outcome independence. In the literature, confounding local causality with locality has been the source of much dispute. This confusion may explain why many if not most physicists are quite happy to dump realism in favor of locality, while on the other hand it has been argued that the realism principle is ''analytic,'' in that it doesn't even make sense to argue against it.[22]

10.2 Density Operator

Previously, we discussed the entanglement of the Bell state and how it implied an inherent nonlocality of quantum mechanics—it isn't possible to think of associating a local state $|\psi\rangle$ to only one member of the entangled pair. In that case, what *can* we say about the local state? After all, it wouldn't be very practical to only deal with nonlocal states (particularly for an experiment on a quantum particle that could be entangled with anything it has ever bumped into since the beginning of time). To answer this, we will develop a more general formalism for handling the quantum state. In particular, we will represent the **density operator** as an alternate representation of the quantum state. The density operator represents the state of a quantum system in a more general way than the state vector, and equivalently represents an observer's *state of knowledge* of a system. It is particularly important to use the density operator in the quantum theory of *open* systems, where a quantum system interacts with an external system whose evolution is unknown, and in the quantum theory of measurement and information.

When a quantum state can be represented by a state vector $|\psi\rangle$, the **density operator** is defined as the product

$$\rho := |\psi\rangle\langle\psi|. \tag{10.29}$$
(density operator, pure state)

In this case, it is obvious that the information content of the density operator is equivalent to that of the state vector (except for the overall phase, which is not of physical significance).

The state vector can represent states of *coherent* superposition. The power of the density operator lies in the fact that it can represent *incoherent* superpositions as well. For example, let $|\psi_\alpha\rangle$ be a set of states (without any particular restrictions). Then the density operator

$$\rho = \sum_\alpha P_\alpha |\psi_\alpha\rangle\langle\psi_\alpha| \tag{10.30}$$
(density operator, general)

[21] Arthur Fine, ''Hidden Variables, Joint Probability, and the Bell Inequalities,'' *Physical Review Letters* **48**, 291 (1982) (doi: 10.1103/PhysRevLett.48.291). The precise statement there is ''There exists a factorizable stochastic hidden-variables model for a correlation experiment if and only if there exists a deterministic hidden-variables model for the experiment.'' (Here, ''stochastic hidden-variables model'' means ''locally causal.'')

[22] Tim Maudlin, ''What Bell Did,'' *Journal of Physics A: Mathematical and Theoretical* **47**, 424010 (2014) (doi: 10.1088/1751-8113/47/42/424010).

models the fact that we don't know *which* of the states $|\psi_\alpha\rangle$ the system is in, but we assign a probability or weight P_α to the quantum state $|\psi_\alpha\rangle$ in the mixture defined by ρ. Note that the weights obey

$$\sum_\alpha P_\alpha = 1 \tag{10.31}$$

for proper normalization of the density operator. Another way to say it is this: the state vector $|\psi\rangle$ represents a certain *intrinsic uncertainty* with respect to quantum observables; the density operator can represent uncertainty *beyond* the minimum required by quantum mechanics. Equivalently, the density operator can represent a *statistical ensemble* of identical systems in possibly different states.

A state of the form (10.29) is said to be a **pure state**. One that cannot be written in this form is said to be **mixed**.

10.2.1 Example: Single Qubit

As a simple example, consider a qubit with states $|\mathtt{0}\rangle$ and $|\mathtt{1}\rangle$. The density operators corresponding to the eigenstates are $|\mathtt{0}\rangle\langle\mathtt{0}|$ and $|\mathtt{1}\rangle\langle\mathtt{1}|$; clearly these are pure states. Another pure state is the superposition $|\psi\rangle = (|\mathtt{0}\rangle + |\mathtt{1}\rangle)/\sqrt{2}$, which has the corresponding density operator

$$\rho = \frac{1}{2}\Big(|\mathtt{0}\rangle\langle\mathtt{0}| + |\mathtt{1}\rangle\langle 1| + |\mathtt{0}\rangle\langle\mathtt{1}| + |\mathtt{1}\rangle\langle\mathtt{0}|\Big). \tag{10.32}$$

This density operator is the sum of the density operators for the eigenstates, plus two extra terms that indicated the *purity* of the state or the *coherence* of the superposition. An example of a mixture of the two eigenstates comes from simply removing these last two terms:

$$\rho = \frac{1}{2}\Big(|\mathtt{0}\rangle\langle\mathtt{0}| + |\mathtt{1}\rangle\langle\mathtt{1}|\Big). \tag{10.33}$$

We can see this as a classical mixture of the form (10.30), where the probabilities are $P_{0,1} = 1/2$ for the eigenstates $|\psi_0\rangle = |\mathtt{0}\rangle$ and $|\psi_1\rangle = |\mathtt{1}\rangle$. However, we can equally well regard the same mixed state as a *different* mixture. That is, defining the mixed state

$$\rho' = \frac{1}{2}\Big(|+\rangle\langle +| + |-\rangle\langle -|\Big), \tag{10.34}$$

where

$$|\pm\rangle := \frac{1}{\sqrt{2}}\Big(|\mathtt{0}\rangle \pm |\mathtt{1}\rangle\Big), \tag{10.35}$$

it is not hard to see by direct substitution that $\rho = \rho'$. In fact a *nicer* way to see this is to note that both ρ and ρ' are proportional to the identity operator, expressed in their respective representations. A transformation between representations is given by a unitary operator, which commutes with this density operator. Thus, $\rho' = U\rho U^\dagger = \rho$. Density operators that are proportional to the identity are *special* states, assigning equal classical probabilities to all possible states. We could just as well call states like (10.33) and (10.34) **I-know-nothing states**, and with the intuition that changing basis shouldn't add any information is confirmed by the invariance of I-know-nothing states under unitary transformations.

We can also see that we have to be a bit careful with our above statement, where we said that a mixed state can be regarded as an association of classical probabilities with being in different pure quantum states. Just given a particular density operator, it is not in general possible to uniquely define a pure-state decomposition of the form (10.30). Thus stating that "the state is *really* in a pure state, but we don't quite know *which* one it's in," implies some *extra* information that is not contained in the density operator. Although, of course, you're free to think of such a density operator in this way if it's convenient.

10.2.2 Evolution

Differentiating the density operator and employing the Schrödinger equation $i\hbar\partial_t|\psi\rangle = H|\psi\rangle$, we can write down the equation of motion for the density operator:

$$\begin{aligned}\partial_t\rho &= (\partial_t|\psi\rangle)\langle\psi| + |\psi\rangle\partial_t\langle\psi| \\ &= -\frac{i}{\hbar}H\rho + \frac{i}{\hbar}\rho H \\ &= -\frac{i}{\hbar}[H,\rho].\end{aligned} \qquad \begin{matrix}(10.36)\\ \text{(Schrödinger–von Neumann equation)}\end{matrix}$$

This is referred to as the **Schrödinger–von Neumann equation**. The derivation here assumed a pure state but carries through in the obvious way for arbitrary density operators. Of course, the point is that using the density operator allows us to write down more general evolution equations than those implied by state-vector dynamics. The more general forms are referred to as **Liouville–von Neumann equations** or **master equations**, which we can write in the form

$$\partial_t\rho = \mathcal{L}\rho. \qquad \begin{matrix}(10.37)\\ \text{(master equation, generic form)}\end{matrix}$$

Here, $\mathcal{L}$ is the **Liouvillian superoperator**. We use the term "superoperator" because the Liouvillian represents a higher-dimensional object, since it must represent the commutator above (i.e., it "operates from both sides"). Thinking of the density operator as a two-dimensional matrix as we discuss below, the Liouvillian is effectively a rank-4 tensor.

10.2.3 Expectation Values

We can compute expectation values with respect to the density operator via the trace operation. The trace of an operator A is simply the sum over the diagonal matrix elements with respect to any complete, orthonormal set of states $|\beta\rangle$:

$$\mathrm{Tr}[A] := \sum_\beta \langle\beta|A|\beta\rangle \qquad (10.38)$$

An important property of the trace is that the trace of a product is invariant under cyclic permutations of the product. For example, for three operators,

$$\mathrm{Tr}[ABC] = \mathrm{Tr}[BCA] = \mathrm{Tr}[CAB]. \qquad \begin{matrix}(10.39)\\ \text{(cyclic permutation invariance)}\end{matrix}$$

This amounts to simply an interchange in the order of summations. For example, for two operators, working in a discrete representation,

$$\begin{aligned}\mathrm{Tr}[AB] &= A_{\alpha\beta}B_{\beta\alpha} \\ &= B_{\beta\alpha}A_{\alpha\beta} \\ &= \mathrm{Tr}[BA].\end{aligned} \qquad (10.40)$$

Note that this argument fails if you push it too hard,[23] but it is obviously okay in finite-dimensional spaces. More general permutations [e.g., of the form (10.39)] are obtained by replacements like $B \longrightarrow BC$. We can

[23] A famous paradox is that $\mathrm{Tr}[xp] \neq \mathrm{Tr}[px]$, as a consequence of $[x,p] = i\hbar$. The bigger issue here is that $\mathrm{Tr}[xp]$ and $\mathrm{Tr}[px]$ diverge because it only makes sense to compute them on infinite-dimensional spaces, so it doesn't really make sense to compare them. That is, the trace is not even a well-defined for some operators on infinite-dimensional spaces (like the identity operator).

rewrite the expectation value with respect to a *pure* state by writing it out and inserting an identity,

$$\begin{aligned}\langle A\rangle &= \sum_n \langle\psi|n\rangle\langle n|A|\psi\rangle \\ &= \sum_n \langle n|A|\psi\rangle\langle\psi|n\rangle \\ &= \mathrm{Tr}\big[A|\psi\rangle\langle\psi|\big],\end{aligned} \tag{10.41}$$

or finally,

$$\langle A\rangle = \mathrm{Tr}[A\rho]. \tag{10.42}$$
(expectation value, pure state)

This expression can also of course be written $\mathrm{Tr}[\rho A]$, owing to the permutation property of the trace. Because the trace is a linear operation, this expression extends to the more general form (10.30) of the density operator. Taking an additional average over the ensemble of pure states,

$$\langle\langle A\rangle\rangle = \sum_\alpha P_\alpha \langle\psi_\alpha|A|\psi_\alpha\rangle = \mathrm{Tr}[A\rho], \tag{10.43}$$
(expectation value, ensemble)

where the double angle brackets $\langle\langle\rangle\rangle$ denote the ensemble average over expectation values. For brevity we will drop the extra brackets and simply use single brackets for expectation values with respect to either a pure state or an ensemble ($\langle\langle\rangle\rangle \longrightarrow \langle\rangle$).

10.2.4 The Density Matrix

The physical content of the density operator is more apparent when we compute the elements $\rho_{\alpha\alpha'}$ of the *density matrix* with respect to a complete, orthonormal basis. The density matrix elements are given by

$$\rho_{\alpha\alpha'} := \langle\alpha|\rho|\alpha'\rangle. \tag{10.44}$$
(density matrix)

To analyze these matrix elements, we will assume the simple form $\rho = |\psi\rangle\langle\psi|$ of the density operator, though the arguments generalize easily to arbitrary density operators.

The diagonal elements $\rho_{\alpha\alpha}$ are referred to as *populations*, and give the measurement probability of the system in the state $|\alpha\rangle$:

$$\rho_{\alpha\alpha} = \langle\alpha|\rho|\alpha\rangle = |\langle\alpha|\psi\rangle|^2 . \tag{10.45}$$

The off-diagonal elements $\rho_{\alpha\alpha'}$ (with $\alpha \neq \alpha'$) are referred to as *coherences*, since they give information about the relative phase of different components of the superposition. For example, if we write the state vector as a superposition with explicit phases,

$$|\psi\rangle = \sum_\alpha |c_\alpha|\, e^{i\phi_\alpha}|\alpha\rangle, \tag{10.46}$$

then the coherences are

$$\rho_{\alpha\alpha'} = |c_\alpha c_{\alpha'}|\, e^{i(\phi_\alpha - \phi_{\alpha'})}. \tag{10.47}$$

Notice that for a density operator not corresponding to a pure state, the coherences in general will be the sum of complex numbers corresponding to different states in the incoherent sum. The phases will not in general line up, so that while $|\rho_{\alpha\alpha'}|^2 = \rho_{\alpha\alpha}\rho_{\alpha'\alpha'}$ for a pure state, we expect $|\rho_{\alpha\alpha'}|^2 < \rho_{\alpha\alpha}\rho_{\alpha'\alpha'}$ ($\alpha \neq \alpha'$) for a generic mixed state.

10.2.5 Purity

How can we tell a pure state from a mixed one in general? Notice that the diagonal elements of the density matrix form a probability distribution. Proper normalization thus requires

$$\mathrm{Tr}[\rho] = \sum_\alpha \rho_{\alpha\alpha} = 1. \tag{10.48}$$
(normalization)

We can do the same computation for ρ^2, and we will define the **purity** to be $\mathrm{Tr}[\rho^2]$. For a pure state, the purity is simple to calculate, since $\rho^2 = |\psi\rangle\langle\psi|\psi\rangle\langle\psi| = \rho$:

$$\mathrm{Tr}[\rho^2] = \mathrm{Tr}[\rho] = 1. \tag{10.49}$$
(purity for pure state)

(In fact $\rho^n = \rho$ in a pure state for any nonnegative n.) But for mixed states, $\mathrm{Tr}[\rho^2] < 1$. For example, for the density operator in (10.30),

$$\mathrm{Tr}[\rho^2] = \sum_\alpha P_\alpha^2, \tag{10.50}$$

if we assume the states $|\psi_\alpha\rangle$ to be orthonormal. For equal probability of being in N such states (i.e., an I-know-nothing state), $\mathrm{Tr}[\rho^2] = 1/N$. Intuitively, then we can see that $\mathrm{Tr}[\rho^2]$ drops to zero as the state becomes more mixed—that is, as it becomes an incoherent superposition of more and more orthogonal states. Note also that a pure-state density operator is a projector for some state, while a mixed-state density operator is not (a straight sum of projectors is still a projector, but a weighted sum is not; see Problems problem:projcommute and problem:projsum).

To prove that $\mathrm{Tr}[\rho^2] < 1$ for mixed states, first note that ρ is a Hermitian operator ($\rho = \rho^\dagger$). Thus, ρ may be diagonalized by a unitary transformation, so we may write

$$\rho' = S\rho S^\dagger, \tag{10.51}$$

where ρ' is diagonal and $S^{-1} = S^\dagger$. It is easy to verify that the trace is invariant under unitary transformations, so

$$\mathrm{Tr}[\rho^2] = \mathrm{Tr}[\rho'^2] = \sum_\alpha (\rho'_{\alpha\alpha})^2 \le \sum_\alpha \rho'_{\alpha\alpha} = 1, \tag{10.52}$$

where the inequality comes from noting that $0 \le \rho'_{\alpha\alpha} \le 1$, so that ${\rho'}^2_{\alpha\alpha} \le \rho'_{\alpha\alpha}$. A diagonal pure state has only a single nonzero diagonal element, while a diagonal mixed state necessarily has more than one nonzero diagonal element. Hence, for a mixed state, $\mathrm{Tr}[\rho^2] < 1$. This follows since the diagonal matrix elements are positive,

$$\rho_{\alpha\alpha} = \langle\alpha|\rho|\alpha\rangle = \sum_k P_k |\langle\alpha|\psi\rangle_k|^2 \ge 0, \tag{10.53}$$

and so the equality occurs only for a single term in the sum.

10.2.6 Positivity

We now know some of the properties of the density operator. But given some operator, could it be a density operator? We already mentioned that the density operator must be Hermitian. Thus, it has real eigenvalues and an associated set of orthonormal eigenstates. In its own representation, the density operator can then be written

$$\rho = \sum p_\alpha |\alpha\rangle\langle\alpha|, \tag{10.54}$$

where $|\alpha\rangle$ is the eigenstate with eigenvalue p_α. This of course has the same form as the defining relation (10.30). We can further interpret the p_α as probabilities, since the density operator is *itself* an observable (as it predicts probabilities of measurement outcomes, which can be checked experimentally). Thus the eigenvalues must all be nonnegative, and a an operator (or matrix) that has this property is called a **positive** operator or, more explicitly, a **positive-semidefinite** operator.[24] Positivity of ρ is also equivalent to the requirement that

$$\langle\phi|\rho|\phi\rangle \ge 0 \tag{10.55}$$

[24] An interesting application of this property is to look for cases where classical evolution violates this quantum constraint of "rho-positivity." See Salman Habib, Kurt Jacobs, Hideo Mabuchi, Robert Ryne, Kosuke Shizume, and Bala Sundaram "Quantum-Classical Transition in Nonlinear Dynamical Systems," *Physical Review Letters* **88**, 040402 (2002) (doi: 10.1103/PhysRevLett.88.040402).

for any vector $|\phi\rangle$ in the Hilbert space, a property that is typically abbreviated $\rho \geq 0$. This is obviously true for a pure density operator $\rho = |\psi\rangle\langle\psi|$, and this constraint holds for a mixed state as a linear combination of positive values for an arbitrary ensemble of pure states. Positivity of an operator is sufficient for it to be acceptable as a density operator.

10.2.7 The Density Operator vs. the State Vector

We started off with the axioms of quantum mechanics in Chapter 1), where the state vector $|\psi\rangle$ was the fundamental way to represent the quantum state. And yet now we have this density operator ρ, which in the case of a pure state is equivalent to $|\psi\rangle$, but in the case of mixed states, can represent things that the state vector *can't*. There are a couple of ways to think about this. An old-fashioned view is that quantum mechanics is a theory of statistical predictions, and that the density operator is a convenient bookkeeping tool that lets us keep track of extra uncertainty in a statistical ensemble—uncertainty that is in some sense unnecessary, but a consequence of some ignorance on the part of a physicist. A more modern view is inspired by the need to describe experiments on a *single* quantum object (single atom, ion, nanoresonator, quantum dot, etc.), where the notion of a statistical ensemble is inherently nonsensical. Still, quantum mechanics predicts *probabilities* for a single quantum system. But fundamentally, a quantum system may be in a particular thermal state, which can only be modeled via the density operator if the temperature is nonzero. Or an experimenter may prepare a single quantum system in a particular state; but given a finite amount of time, some level of technical noise in the apparatus, and imperfect physical detectors, the quantum system will never be *perfectly* prepared in a particular pure state. In this case a mixed density operator is needed to describe this experimental uncertainty. Because mixed states can always be thought of as classical averages over pure states, though, the state vector is merely a handy tool, in this modern interpretation. It makes for convenient calculations, provided the impurity of the state is accounted for afterwards. (Remember that the state vector is a lower-dimensional object than the density operator, so especially on a computer it can be much easier to handle $|\psi\rangle$ than ρ.

10.3 Multiple Degrees of Freedom

10.3.1 Merging Hilbert Spaces

Suppose two degrees of freedom are prepared in two quantum states completely independently of each other. This could happen, say, for two particles prepared in separate, distant galaxies. We will refer to the two degrees of freedom as ''particles,'' even though they could correspond to different degrees of freedom of the *same* system, such as the spin and center-of-mass position of an atom, or the spin and spatial profile of a photon.

Labeling the two particles as A and B, if the individual states of the particles are $|\psi\rangle_A$ and $|\psi\rangle_B$, then we can write the composite state as

$$|\psi\rangle = |\psi\rangle_A \otimes |\psi\rangle_B, \tag{10.56}$$

where $\otimes$ denotes the **tensor product** (or **direct product**). To intuitively define this product, think of constructing a matrix from two vectors via $M_{\alpha\beta} = x_\alpha y_\beta$, which we could write in terms of the tenser product as $\mathbf{M} = \mathbf{x} \otimes \mathbf{y}$. Often, this product is written without an explicit tensor-product symbol:

$$|\psi\rangle_A \otimes |\psi\rangle_B \equiv |\psi\rangle_A |\psi\rangle_B \equiv |\psi_A\, \psi_B\rangle. \tag{10.57}$$

The particle labels can even be dropped, since the ordering determines which state applies to which particle.

We can also see the meaning of the tensor product in component form. Let each separate state be expressed in an orthonormal basis as

$$|\psi\rangle_A = \sum_\alpha c_\alpha^{(A)} |\alpha\rangle_A, \qquad |\psi\rangle_B = \sum_\beta c_\beta^{(B)} |\beta\rangle_B. \tag{10.58}$$

Then we can express the composite state as

$$|\psi\rangle = \sum_{\alpha\beta} c_{\alpha\beta} |\alpha_A\, \beta_B\rangle, \tag{10.59}$$

where

$$c_{\alpha\beta} = c_\alpha^{(A)} c_\beta^{(B)}. \tag{10.60}$$

Note that $c_{\alpha\beta}$ is still understood to be a *vector*-like object, with a single index. Thus, there is an implicit (bijective) mapping of the ordered index pair (α, β) to a single index, which we simply denote as $\alpha\beta$.

Similarly, we can write a density operator for two independent particles by the same tensor product:

$$\rho = \rho^{(A)} \otimes \rho^{(B)}. \tag{10.61}$$

We can also write this in component form for the density matrices as

$$\rho_{\alpha\mu\beta\nu} = \rho_{\alpha\beta}^{(A)} \rho_{\mu\nu}^{(B)}, \tag{10.62}$$

where again $\alpha\mu$ and $\beta\nu$ are to be taken as composite indices.

The same tensor-product notation applies to Hilbert spaces. That is, we can write

$$|\psi_A\, \psi_B\rangle \in \mathscr{H}_A \otimes \mathscr{H}_B \tag{10.63}$$

if $|\psi\rangle_A \in \mathscr{H}_A$ and $|\psi\rangle_B \in \mathscr{H}_B$.

10.3.2 Entanglement

The above composite states, described by tensor products of separated states, are called **separable states**. However, not all states are separable, and those that are not separable are called **entangled**.[25] In some sense, entanglement is the ''most quantum'' of all quantum effects.

Thus, we can see that a composite state $|\psi\rangle$ is entangled if and only if it *cannot* be written in the separable form

$$|\psi\rangle = |\psi\rangle_A \otimes |\psi\rangle_B. \tag{10.64}$$

The definition for density operators is somewhat more general: a density operator for a composite system is separable if and only if it can be written in the form

$$\rho = \sum_\alpha P_\alpha \rho_\alpha^{(A)} \otimes \rho_\alpha^{(B)}. \tag{10.65}$$

Unfortunately, given an arbitrary mixed density operator, it is difficult to tell if it corresponds to an entangled state—in fact, this turns out to be an NP-hard problem.[26]

10.3.2.1 Cloning

With the language of entanglement, it is relatively simple to demonstrate the **no-cloning theorem**,[27] which says that the state of a *single* quantum system cannot be copied to another particle. This turns out to be a simple consequence of unitary evolution.

[25] Note that terminology here varies somewhat. What we call ''entangled'' is sometime called ''nonseparable,'' in order to distinguish it from a stronger notion of entanglement that includes a spacelike separation.

[26] Leonid Gurvits, ''Classical deterministic complexity of Edmonds' problem and Quantum Entanglement,'' in *STOC '03: Proceedings of the thirty-fifth annual ACM symposium on Theory of computing* (2003), p. 10 (doi: 10.1145/780542.780545) (arXiv: quant-ph/0303055v1); Sevag Gharibian, ''Strong NP-Hardness of the Quantum Separability Problem,'' *Quantum Information and Computation 10*, 343 (2010) (arXiv: 0810.4507). Quantum states can be organized into a hierarchy that are increasingly difficult to categorize as separable; see Andrew C. Doherty, Pablo A. Parrilo, and Federico M. Spedalieri, ''A complete family of separability criteria,'' *Physical Review A* **69**, 022308 (2004) (doi: 10.1103/PhysRevA.69.022308) (arXiv: quant-ph/0308032).

[27] W. K. Wootters and W. H. Zurek, ''A single quantum cannot be cloned,'' *Nature* **299**, 802 (1982) (doi: 10.1038/299802a0); D. Dieks, ''Communication by EPR devices,'' *Physics Letters A* **92**, 271 (1982).

Let's examine just a simple case. Suppose that cloning is possible on a two-state system from particle A to particle B. Particle B must be in a particular state to begin with, and without loss of generality we may take this to be the "$\mathtt{0}$" state. Then to copy the eigenstates of A, we see that there must be a unitary transformation U such that

$$U|\mathtt{0}\rangle_A|\mathtt{0}\rangle_B = |\mathtt{0}\rangle_A|\mathtt{0}\rangle_B, \qquad U|\mathtt{1}\rangle_A|\mathtt{0}\rangle_B = |\mathtt{1}\rangle_A|\mathtt{1}\rangle_B. \tag{10.66}$$

However, if particle A is in the superposition state

$$|\psi\rangle_A = \frac{1}{\sqrt{2}}\Big(|\mathtt{0}\rangle_A + |\mathtt{1}\rangle_A\Big), \tag{10.67}$$

then we see that the cloning operator gives

$$U|\psi\rangle_A|\mathtt{0}\rangle_B = \frac{1}{\sqrt{2}}\Big(|\mathtt{0}\rangle_A|\mathtt{0}\rangle_B + |\mathtt{1}\rangle_A|\mathtt{1}\rangle_B\Big), \tag{10.68}$$

which is an entangled Bell state. However, what we wanted for cloning to work properly is the *separable* state

$$U|\psi\rangle_A|\mathtt{0}\rangle_B = \frac{1}{2}\Big(|\mathtt{0}\rangle_A + |\mathtt{1}\rangle_A\Big)\Big(|\mathtt{0}\rangle_B + |\mathtt{1}\rangle_B\Big). \tag{10.69}$$

We can see that the problem in this particular example is that U acts nonlocally, and thus induces entanglement between the two particles. In fact, the controlled-NOT (CNOT) gate (which we saw in Section 9.2.4) is a quantum operation that effects the transformations in Eqs. (10.66) (if A and B are in eigenstates, the CNOT flips the state of system B if and only if system A is in state $\mathtt{1}$).

Of course, it *is* possible to clone a state if you already know everything about it (i.e., you have classical knowledge of the state—this is **quantum-state preparation**), or if you have an infinite ensemble of copies. (Copying a state is possible to within some fidelity tolerance for a finite ensemble of copies—this is the idea behind **quantum-state tomography**.[28]) In this case, enough measurements may be made to reconstruct the state of the system arbitrarily well, and of course this procedure does not correspond to a unitary transformation. The problem with the *single* system is that in general, a measurement of the system destroys its state, and a single measurement is not enough to determine the state of the system. Of course, there is no problem with the cloning of the *basis* states, as in Eqs. (10.66); the problem is in cloning general states that are not orthogonal to the basis states. In particular this means that with a bit of *extra* information beyond what is contained in the quantum state (e.g., the state of particle A is either $|\mathtt{0}\rangle_A$ or $|\mathtt{1}\rangle_A$, but not any coherent superposition of the two), cloning may in fact be possible.

10.3.2.2 Quantum-State Teleportation

A problem related to state cloning is that of **teleportation** of quantum states.[29] The idea is that there are two observers (by convention, Alice and Bob), and the idea is that Alice wants to transmit an unknown[30] quantum state $|\psi\rangle_{\mathrm{T}}$ (of, say a single qubit) to Bob. The catch is that only *classical* communication is allowed

[28] The first experimental demonstration was by D. T Smithey, M. Beck, M.G. Raymer and A. Faridani, "Measurement of the Wigner distribution and the density matrix of a light mode using optical homodyne tomography: application to squeezed states and the vacuum," *Physical Review Letters* **70**, 1244 (1993) (doi: 10.1103/PhysRevLett.70.1244). The idea for tomography came from the observation that a state can be determined by its marginal distributions in phase space, as pointed out by K. Vogel and H. Risken, "Determination of quasiprobability distributions in terms of probability distributions for the rotated quadrature phase," *Physical Review A*, **40**, 2847 (1989) (doi: 10.1103/PhysRevA.40.2847).

[29] Charles H. Bennett, Gilles Brassard, Claude Crépeau, Richard Jozsa, Asher Peres, and William K. Wootters, "Teleporting an unknown quantum state via dual classical and Einstein-Podolsky-Rosen channels," *Physical Review Letters* **70**, 1895 (1993) (doi: 10.1103/PhysRevLett.70.1895).

[30] What "unknown" means here is a bit subtle. If the qubit state $|\psi\rangle_{\mathrm{T}}$ is unknown to both Alice and Bob, then they should technically assign the I-know-nothing state $\rho_{\mathrm{T}} = (|+\rangle\langle+| + |-\rangle\langle-|)/2$ to the qubit. But *somebody* must know the state, say an extra observer Chas, who prepared the state and handed it over to Alice. Only Chas can then verify that the state was properly teleported to Bob at the end of the experiment (after many trials of the teleportation protocol). Alternately, in the (upcoming) language of Section 10.3.3, Alice could be teleporting the state of a qubit that is entangled with another inaccessible qubit, in which case Alice effectively doesn't know the state of her qubit; however, we will see that teleportation will preserve the entanglement, so she can still teleport the state without knowing it.

(say, over a radio, or by email). The no-cloning theorem says that because the state of the single qubit is unknown, Alice can't copy it or even completely determine the state (otherwise, the transmission problem would be solved, and would amount to Bob preparing the appropriate state based on a classical recipe sent by Alice). As stated, teleportation is an impossible task, so what is the minimum extra ingredient needed to make this happen? Quantum-state teleportation says that the transmission is possible if Alice and Bob share an entangled pair of qubits (EPR pair). Besides being an entertaining application of entanglement, teleportation is a classic example of how entanglement can be seen as a *resource* (in this case, something like the envelope for sending over the quantum state).

Let's see how this works. We can write the shared Bell state as

$$|\psi\rangle_{\text{B}} = \frac{1}{\sqrt{2}}\Big(|\texttt{00}\rangle + |\texttt{11}\rangle\Big), \tag{10.70}$$

where the left qubit is Alice's, and the right qubit is Bob's (i.e., we could write the kets in the form $|0_{\text{A}}\, 0_{\text{B}}\rangle$). The state that Alice wants to transmit is

$$|\psi\rangle_{\text{T}} = c_+|+\rangle + c_-|-\rangle. \tag{10.71}$$

(The different qubit notations will help to keep the bits straight.) Now here is the teleportation protocol.

0. The initial composite state is

$$|\psi\rangle = |\psi\rangle_{\text{T}}|\psi\rangle_{\text{B}} = \frac{1}{\sqrt{2}}\Big[c_+|+\rangle\Big(|\texttt{00}\rangle + |\texttt{11}\rangle\Big) + c_-|-\rangle\Big(|\texttt{00}\rangle + |\texttt{11}\rangle\Big)\Big]. \tag{10.72}$$

   Notice again that there are three qubits here, and Alice has the left two, while Bob has the rightmost.

1. Alice performs a CNOT operation on her two qubits. Remember that the CNOT operation is defined by

$$\begin{aligned} U_{\text{CNOT}}|\texttt{00}\rangle &= |\texttt{00}\rangle \\ U_{\text{CNOT}}|\texttt{10}\rangle &= |\texttt{11}\rangle, \end{aligned} \tag{10.73}$$

   and so on: the right qubit flips if and only if the left qubit is $|\texttt{1}\rangle$. This amounts to the transformation

$$|\psi\rangle \longrightarrow \frac{1}{\sqrt{2}}\Big[c_+|+\rangle\Big(|\texttt{10}\rangle + |\texttt{01}\rangle\Big) + c_-|-\rangle\Big(|\texttt{00}\rangle + |\texttt{11}\rangle\Big)\Big], \tag{10.74}$$

   assuming we identify $|+\rangle$ with $|\texttt{1}\rangle$.

2. Alice then applies a **Hadamard gate** to the $|\psi\rangle_{\text{T}}$, the qubit to transmit. A Hadamard gate is a fancy way of an operation that we have already seen: in the language of the spin-$^1/_2$ particle on the Bloch sphere, this is a $\pi/2$-pulse (See Section 9.2.2.1), and this is also just the operation of a 50/50 beam splitter [see Eq. (9.52)]. The unitary operation is

$$\begin{aligned} U_{\pi/2}|+\rangle &= \frac{|+\rangle - |-\rangle}{\sqrt{2}} \\ U_{\pi/2}|-\rangle &= \frac{|+\rangle + |-\rangle}{\sqrt{2}}, \end{aligned} \tag{10.75}$$

   and the effect on the total state is

$$|\psi\rangle \longrightarrow \frac{1}{2}\Big[c_+\big(|+\rangle - |-\rangle\big)\Big(|\texttt{10}\rangle + |\texttt{01}\rangle\Big) + c_-\Big(|+\rangle + |-\rangle\Big)\Big(|\texttt{00}\rangle + |\texttt{11}\rangle\Big)\Big]. \tag{10.76}$$

If we reorganize this state, putting together Alice's four possible qubit states, we obtain the state

$$\begin{aligned}|\psi\rangle = \frac{1}{2}\Big[&|{+}\mathtt{1}\rangle\Big(c_+|\mathtt{0}\rangle + c_-|\mathtt{1}\rangle\Big) \\ &+ |{+}\mathtt{0}\rangle\Big(c_+|\mathtt{1}\rangle + c_-|\mathtt{0}\rangle\Big) \\ &- |{-}\mathtt{1}\rangle\Big(c_+|\mathtt{0}\rangle - c_-|\mathtt{1}\rangle\Big) \\ &- |{-}\mathtt{0}\rangle\Big(c_+|\mathtt{1}\rangle - c_-|\mathtt{0}\rangle\Big)\Big] \\ = \frac{1}{2}\Big[&|{+}\mathtt{0}\rangle|\psi\rangle_{\rm T} + |{+}\mathtt{1}\rangle\sigma_x|\psi\rangle_{\rm T} + i|{-}\mathtt{1}\rangle\sigma_y|\psi\rangle_{\rm T} - |{-}\mathtt{0}\rangle\sigma_z|\psi\rangle_{\rm T},\Big]\end{aligned} \tag{10.77}$$

where in the last form we reordered the terms and used the Pauli operators (9.33)

$$\begin{aligned}\sigma_x &= |\mathtt{1}\rangle\langle\mathtt{0}| + |\mathtt{0}\rangle\langle\mathtt{1}| \\ \sigma_y &= i|\mathtt{0}\rangle\langle\mathtt{1}| - i|\mathtt{1}\rangle\langle\mathtt{0}| \\ \sigma_z &= |\mathtt{1}\rangle\langle\mathtt{1}| - |\mathtt{0}\rangle\langle\mathtt{0}|,\end{aligned} \tag{10.78}$$

acting on Bob's qubit in the form of the teleported state $|\psi\rangle_{\rm T} = c_+|\mathtt{1}\rangle + c_-|\mathtt{0}\rangle$.

3. Now Alice measures both of her qubits, and the four possible outcomes correspond to the four terms in the above expression, $|{+}\mathtt{1}\rangle$, $|{+}\mathtt{0}\rangle$, $|{-}\mathtt{1}\rangle$, and $|{-}\mathtt{0}\rangle$. Importantly, Bob at this stage doesn't know the outcome of this measurement, so he can't know which of his four possible states, for example $c_+|\mathtt{0}\rangle + c_-|\mathtt{1}\rangle$ in the first outcome, came to be.

4. Then Alice communicates her measurement result to Bob. Bob can then make use of this to recover the initial state. For example, if the measurement result turns out to be $|{+}\mathtt{0}\rangle$, then Bob already has the right state, and the process is done (again, assuming we identify $|+\rangle$ with $|\mathtt{1}\rangle$). If the measurement result is any of the other three cases, then Bob will receive a modified version of $|\psi\rangle_{\rm T}$. However, he can take advantage of the observation that $\sigma_\alpha^2 = 1$ for any Pauli operator, in order to convert the modified state back to $|\psi\rangle_{\rm T}$ via a (local) unitary operation. Specifically, in the $|{+}\mathtt{1}\rangle$ case he applies σ_x; in the $|{-}\mathtt{1}\rangle$ case he applies $-i\sigma_y$; and in the $|{-}\mathtt{0}\rangle$ case he applies $-\sigma_z$. In any case, Bob is able to reproduce the initial state $|\psi\rangle_{\rm T}$.

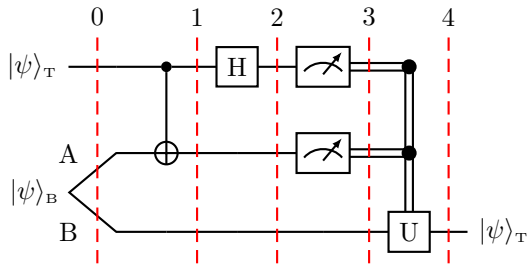
Note that the above procedure carries through for mixed states, since the whole process can be averaged over an ensemble of initial states $|\psi\rangle_{\rm T}$. The procedure just needs to be rewritten in terms of density operators: Bob's four possible states before knowing the result of Alice's measurements are $\rho_{\rm T}$, $\sigma_x\rho_{\rm T}\sigma_x$, $\sigma_y\rho_{\rm T}\sigma_y$, and $\sigma_z\rho_{\rm T}\sigma_z$, expressed in terms of the density operator $\rho_{\rm T} = |\psi\rangle_{\rm T}\langle\psi|_{\rm T}$. Then the entire procedure carries through for mixed states as linear combinations of pure states.

Another important property of quantum-state teleportation is that it preserves entanglement, in the sense that if Alice's qubit is entangled with some other (inaccessible) qubit belonging to Chas, then Alice can teleport her qubit's state, and afterwards Bob's qubit will be entangled with Chas'. The easiest way to see this is to make the replacements $c_\pm \longrightarrow |c_\pm\rangle$ in the initial state $|\psi\rangle_{\rm T}$ in Eq. (10.71), in order to obtain the entangled state

$$|\psi\rangle_{\rm T} = |c_+\rangle|+\rangle + |c_-\rangle|-\rangle. \tag{10.79}$$

(The replacement could even be of the form $c_\pm \longrightarrow a_\pm|c_\pm\rangle$ for arbitrary coefficients $a_\pm$ for more generality.) The whole protocol, being linear in $c_\pm$, carries through as before, and at the end Bob's qubit is now entangled in the same form as in Eq. (10.79).

Since quantum-state teleportation is a simple example of a quantum algorithm, it is common now to represent the protocol in terms of a **quantum circuit diagram**, shown below.



The algorithm flows here from left to right, and the dashed vertical lines label where the result of each step of the algorithm described above may be found. The single lines are "quantum wires," representing the evolution of a quantum two-state system (**qubit**); the double lines are "classical wires," representing the flow of classical information. The CNOT gate is represented by a connection between two qubits, with the controlled qubit having an $\oplus$ symbol (because the closest analogous classical operation is the XOR gate). The single-qubit operations (Hadamard gate and Bob's measurement-dependent unitary operation) are represented by boxes, and the measurements appear as meter symbols. The EPR pair is shown as two qubits sprouting from a common source; this pair is called an **ebit** in quantum circuits.

10.3.3 Open Systems: Church of the Larger Hilbert Space

Now we finally come back to a question that we raised when we discussed the interpretation of the Bell inequality in Section 10.1.3. The EPR pair is a pure, entangled state, and as such, the violation of Bell's inequality rules out a local state for each observer where the spin is well-defined—quantum mechanics is nonlocal. But *this* point depends on more assumptions that can be debated: that the pure Bell state is appropriate, and that both observers agree to this (i.e., they agree to the same state). But to defer that point for a bit, the question that we brought up is, what *can* we say about the local state for each particle? That's something we can address with the density operator.

More broadly, one important function of the density operator is in describing *open* quantum systems—systems interacting with auxiliary systems (**environments** or **reservoirs**) that we don't have access to. Let's now examine a simple model for why the density operator is useful in this sense.

Consider the entangled state

$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|0_A\rangle|0_B\rangle + |1_A\rangle|1_B\rangle\Big) \tag{10.80}$$

between particles (qubits) A and B. Suppose that we have access to particle A, but particle B is locked up in a box, so that we don't know anything about it. The density operator for the composite system is

$$\rho = |\psi\rangle\langle\psi| = \frac{1}{2}\Big(|0_A\rangle|0_B\rangle\langle 0_A|\langle 0_B| + |1_A\rangle|1_B\rangle\langle 1_A|\langle 1_B| + |1_A\rangle|1_B\rangle\langle 0_A|\langle 0_B| + |0_A\rangle|0_B\rangle\langle 1_A|\langle 1_B|\Big) \tag{10.81}$$

We can define the **reduced density operator** that describes *only* particle A by performing a **partial trace** over the state of particle B:

$$\rho_A = \text{Tr}_B[\rho] := \sum_\alpha \langle\alpha_B|\rho|\alpha_B\rangle = \frac{1}{2}\Big(|0_A\rangle\langle 0_A| + |1_A\rangle\langle 1_A|\Big).$$

(reduced density operator) (10.82)

That is, we sum over expectation values with respect to the basis of B's states. Why does this make sense? Well, suppose Q_A is an operator only on A's Hilbert space. Then the reduced density operator can still make any needed prediction involving Q_A via the local expectation value:

$$\langle Q_A\rangle_A = \text{Tr}_A[Q_A\rho_A] = \text{Tr}_{AB}[Q_A\rho_{AB}] \equiv \text{Tr}[Q_A\rho]. \tag{10.83}$$

Here, the second trace is the *global* trace (to reiterate the usual situation). In terms of the example state

(10.81), A's reduced density operator is

$$\rho_A = \mathrm{Tr}_B[\rho] = \frac{1}{2}\Big(|\mathtt{0}_A\rangle\langle\mathtt{0}_A| + |\mathtt{1}_A\rangle\langle\mathtt{1}_A|\Big). \tag{10.84}$$

(reduced density operator, Bell state)

Thus, we can see that the reduced state of particle A corresponds to a *completely incoherent* superposition of the two states (i.e., the I-know-nothing state), even though the composite system carried a completely coherent superposition. Importantly, there is no *pure* state $|\psi\rangle_A$ that gives this density operator.

This was the main point against locality in quantum mechanics that we discussed in Section 10.1.3: The global state ρ in Eq. (10.81) is *much more than* the sum of the parts ρ_A in Eq. (10.84) and its counterpart ρ_B. This is true even if the particles A and B are so distantly separated that it seems that it should be possible to treat them completely independently.

The example here is a simple model for the process of **decoherence**. A quantum system can start in a local state of coherent superposition. But if it interacts with the environment, the coupling causes entanglement between the system and environment, since the interaction is nonlocal. Because we don't have access to the state of the environment, we must trace over it, which reduces the purity of the reduced density operator. Note that we can't keep track of the environment *even in principle*, since it generally has many degrees of freedom. As the interaction continues, the entanglement progresses, driving the reduced density operator towards a completely incoherent superposition. This is, at a simple level, why classical (macroscopic) things behave classically: coupling to the environment destroys quantum coherence.

Conversely, whenever we have a system described by a mixed density operator,

$$\rho = \sum_\alpha P_\alpha |\psi_\alpha\rangle\langle\psi_\alpha|, \tag{10.85}$$

we can always think of it as part of a larger system. We can see this as follows. We will introduce a fictitious environment with orthonormal basis states $|\alpha_\mathrm{E}\rangle$. Then we can write the state vector for the composite system as

$$|\psi_\mathrm{total}\rangle = \sum_\alpha \sqrt{P_\alpha}|\psi_\alpha\rangle|\alpha_\mathrm{E}\rangle. \tag{10.86}$$

(purification of mixed state)

When we compute the total density operator for the composite pure state and trace over the environment, we recover the original density operator (10.85) as the reduced density operator of the larger state. This procedure of switching to a larger pure state is referred to as **purification** or "the doctrine of the Church of the larger Hilbert space."[31] The space of these extra environmental degrees of freedom is often referred to as the **ancilla**.[32] Often, this is a useful picture for thinking about mixed quantum states, especially in quantum-information problems.

10.3.3.1 Subjective States

The above discussions of reduced density operators and purification leads to some interesting consequences—in particular, that different observers may legitimately disagree on the quantum state. That is, the quantum state can be thought of as *subjective*, the state of knowledge of a particular observer.

As a simple example, let's return to the entangled state (10.80) for two particles, and associate the particles with each of two observers (particle A with Alice, B with Bob). Alice's local state is given by the reduced density operator (10.82), and by symmetry Bob's state has the same form—this is assuming that they are separated and keep their corresponding particles to themselves. The original state (10.80) then corresponds to the state according to some omniscient "superobserver," which could be a real observer (who has access to all the knowledge of both Alice and Bob), or a convenient, fictitious observer to facilitate calculation (e.g., so that we could work out the teleportation problem in terms of the global pure state).

[31] Terminology introduced by John Smolin; see Daniel Gottesman and Hoi-Kwong Lo, "From Quantum Cheating to Quantum Security," *Physics Today* **53**, no. 11, 22 (2000) (doi: 10.1063/1.1333282).

[32] Although it just doesn't sound right to my ear, "ancilla" is a singular noun that comes from latin, where it means "hand-maiden," but in contemporary English can mean something that helps to achieve something difficult. (The plural form can be "ancillae" or "ancillas.")

So there is already a difference in states between Alice/Bob and the superobserver, but let's keep going. Suppose now Bob makes a measurement of his state, but he's not going to share the measurement result with Alice—as far as Alice is concerned, Bob and his particle are a black box. But now suppose that Bob's result was $|1\rangle_B$. If Bob knew the initial global state (10.80), then he now knows that the global state is $\rho = |1\rangle_A|1\rangle_B\langle 1|_A\langle 1|_B$ and so his reduced density operator is $\rho_B = |1\rangle_B\langle 1|_B$ (and thus Alice's local state "should be" $\rho_A = |1\rangle_A\langle 1|_A$). But since Alice doesn't have access to this information (or maybe she doesn't even know that Bob made a measurement), her local state *does not change*: it still must be $\rho_A = \mathcal{I}_A/2$, where $\mathcal{I}_A = |1\rangle_A\langle 1|_A + |0\rangle_A\langle 0|_A$ is the identity operator on particle A's Hilbert space. Now, notice that there are two equivalent ways to interpret Alice's state. Her state is the same as before the measurement, so $\rho_A = \mathcal{I}_A/2$ is the local state for a qubit entangled with an "outside" qubit. But also, even if Alice *knows* that Bob made a measurement, but she doesn't know the result of the measurement, she must *incoherently* average over the two possible resulting (local) states, $|1\rangle_A\langle 1|_A$ and $|0\rangle_A\langle 0|_A$. This is, of course, the same local state $\rho_A = \mathcal{I}_A/2$. The state doesn't indicate which is *really* the case.

Yet another valid interpretation of this last situation, where Bob has made a measurement but Alice doesn't know the result, is that Alice can think of Bob as being merely another quantum system. In this case, Bob acts as something of a qubit (with many other attached degrees of freedom) that has become entangled with the B qubit. Alice's local state is still the same, as we have seen, since this entanglement wipes out the coherence of qubit B.[33]

Essentially the same subjective-state phenomenon arise in the protocol for quantum-state teleportation, or at least in a variation where Alice and Bob *know* the state to be teleported. Just before Alice makes her measurement, the state is Eq. (10.77). Bob's local state involves the four possibilities $|\psi\rangle_{\text{T}}$, $\sigma_x|\psi\rangle_{\text{T}}$, $\sigma_y|\psi\rangle_{\text{T}}$, and $\sigma_z|\psi\rangle_{\text{T}}$, and his local state is an incoherent average. This is still the case *after* Alice makes the measurement but *before* sharing the result with Bob. Since Bob's qubit is entangled with one of Alice's, we can guess that Bob's local state at this stage is $\rho_B = \mathcal{I}_B/2$ (and this guess is correct; see Problem 10.12). But according to Alice, Bob's state is a pure state, since she knows which one of the four outcomes came to be. Bob only comes to the same conclusion after receiving the classical communication from Alice. And this is neglecting any probability that Alice is being uncooperative and, with some probability not reporting the correct measurement result, in which case Bob's state would still be mixed after the communication.

This idea of a subjective state is a mild form of a more extreme quantum religion that goes by the name of **quantum Bayesianism**.[34] It can be somewhat uncomfortable to think of the quantum state—something that you can calculate—is a subjective quantity, since physics usually deals in objectivity. But we've seen how this notion can arise quite naturally in the context of multiple observers and a single experiment on a simple composite quantum system. There are limits to the subjectivity, of course. For example, if two observers insist that a given quantum system is in a *pure* state, they should at least agree on *which* pure state that is. We will return to Bayesian inference in quantum mechanics in Section 11.3.

10.4 Indistinguishability and Identical Particles

In the case of multiple, identical particles, we have to be careful with the quantum state. In particular, in some sense it should not matter if two identical particles are interchanged—the identicality of the particles means that a physical system should be invariant under the interchange of a pair of identical particles. More precisely, there are certain Hermitian operators that refer to, say, one of a pair of identical particles, but these do not necessarily correspond to observables. The symmetry of identical particles is often referred to

[33] This situation is an instance of **Wigner's friend** (or Alice's friend, as it were), where Wigner pondered as a thought experiment the measurement of a quantum system by his friend. Should he think of the friend as observing a quantum object, or should he think of the friend+object as in terms of a joint quantum state of interacting systems? Wigner pondered this situation in the context of consciousness and quantum mechanics. See Eugene P. Wigner, "Remarks on the Mind–Body Question," in *The Scientist Speculates*, I. J. Good, Ed. (Heinemann, 1961), p. 284; reprinted in Eugene Wigner, *Symmetries and Reflections* (Indiana University Press, 1967), p. 171; and in *Quantum Theory and Measurement*, John Archibald Wheeler and Wojciech Hubert Zurek, Eds. (Princeton, 1983) p. 168 (ISBN: 0691083150).

[34] See for example, Rüdiger Schack, Todd A. Brun, and Carlton M. Caves, "Quantum Bayes rule," *Physical Review A* **64** 014305 (2001) (doi: 10.1103/PhysRevA.64.014305); Christopher A. Fuchs, "Quantum Mechanics as Quantum Information (and only a little more)," arXiv.org preprint (arXiv: quant-ph/0205039).

as **indistinguishability**, but this concept is slightly different.[35] We will be careful about this distinction and defer the discussion of indistinguishability until after some calculations. In any case, the symmetry of multiple-particle systems under exchange of identical particles is typically enforced in nonrelativistic quantum mechanics by a quantum-state structure that *looks* a lot like entanglement, but isn't really the same.[36] Consider the two-particle state

$$|\psi\rangle = |(\psi_1)_A\,(\psi_2)_B\rangle. \tag{10.87}$$

That is, particle A is in state $|\psi_1\rangle$, and particle B is in state $|\psi_2\rangle$. This state is appropriate for *distinguishable* particles. But if the two particles are *indistinguishable*, the state must be invariant under exchange of the particle labels,

$$|\psi\rangle = |(\psi_2)_A\,(\psi_1)_B\rangle, \tag{10.88}$$

which for this state would imply that $|\psi_1\rangle = |\psi_2\rangle$. It is hardly satisfactory for every indistinguishable particle to be in the same state, so we can introduce an explicit symmetrization (antisymmetrization) as follows:

$$|\psi\rangle_\pm = \frac{1}{\sqrt{2}}\Big(|(\psi_1)_A\,(\psi_2)_B\rangle \pm |(\psi_2)_A\,(\psi_1)_B\rangle\Big). \tag{10.89}$$

The symmetry here under a swap of the particle labels is called **exchange symmetry**. In the case of the minus sign, the particle exchange is accompanied by a factor (-1), amounting to just an overall phase, which is certainly permissible. The idea is the same as that of the parity operator; given that two applications of the particle-exchange operator is just the identity, the operator should have eigenvalues ± 1. The idea can be extended to more that two particles, where the $+1$ eigenvalue means invariance under all permutations, and the -1 eigenvalue means invariance under even permutations and invariance except for a minus sign for odd permutations.

What happens when we try to superpose these states? We can see that

$$\frac{1}{\sqrt{2}}\Big(|\psi\rangle_+ + |\psi\rangle_-\Big) = |(\psi_1)_A\,(\psi_2)_B\rangle, \tag{10.90}$$

and so we end up in a state that's no good. Evidently, we can't superpose states corresponding to different symmetrizations. Thus, we must postulate that once a pair of particles obey a certain symmetrization rule, they must *always* do so. (This is equivalent to the statement that the operator corresponding to the exchange operation commutes with the Hamiltonian.) Of course, the particles corresponding to the + sign in (10.89) are **bosons**, and those corresponding to the − sign are **fermions**. It can be shown that the different particles correspond to different classes of spins—half-integer-spin particles are fermions, while integer-spin particles are bosons, according to the **spin–statistics theorem**,[37] something we will return to shortly. Again, Eq. (10.89) is suggestive of an entangled state, but only in a trivial sense, since it is nonsensical to speak of separate identities for the two particles. It is completely, fundamentally impossible to tell them apart. Another way to see this is that even with an *unsymmetrized* state vector, we can always impose the symmetrization via the representation:

$$\frac{1}{\sqrt{2}}\Big(\langle(x_1)_A\,(x_2)_B| \pm \langle(x_2)_A\,(x_1)_B|\Big)|\psi\rangle = \frac{1}{\sqrt{2}}\left[\psi(x_1,x_2) \pm \psi(x_2,x_1)\right]. \tag{10.91}$$

Here, x_1 and x_2 represent two different position coordinates, it is the ordering of the arguments that determines which particle is associated with which position. Another, more specific criterion for deciding whether

[35] For more on indistiguishability of identical particles, see S. J. van Enk, "Thermalizing two identical particles," (arXiv: 1810.05147) (2018); D. Dieks, "Quantum statistics, identical particles and correlations," *Synthese* **82**, 127 (1990) (doi: 10.1007/BF00413672); D. Dieks and A. Lubberdink, "How Classical Particles Emerge From the Quantum World," *Foundations of Physics* **41**, 1051 (2011 (doi: 10.1007/s10701-010-9515-2).

[36] The presentation here follows parts of David J. Griffiths, *Introduction to Quantum Mechanics* (Prentice–Hall, 1995), Chapter 5, p. 177; Asher Peres, *Quantum Theory: Concepts and Methods* (Kluwer, 1995), Section 5-4, p. 126; and lecture notes by M. Baranger and J. Negele. See also Daniel F. Styer, "Common misconceptions regarding quantum mechanics," *American Journal of Physics* **64**, 31 (1996).

[37] W. Pauli, "The Connection Between Spin and Statistics," *Physical Review* **58**, 716 (1940) (doi: 10.1103/PhysRev.58.716).

a state like (10.89) is entangled is whether or not it can be ''used'' in the sense of teleporting a quantum state; this state can't be used in this way.[38]

So then here is an interesting (but intentionally deceptive!) question. Recall the Bell state for a two spin-$^1/_2$ particles (10.2),

$$|0\ 0\rangle = \frac{1}{\sqrt{2}}\Big(|+\rangle|-\rangle - |-\rangle|+\rangle\Big). \tag{10.92}$$

This is antisymmetric as required for fermions. In fact, any state such as $|+\rangle|+\rangle$ vanishes under this same antisymmetrization—it simply *isn't allowed*. So, what we've just shown is that in the two-spin fermionic representation, the Bell state (10.92) is the *only* possible state. Does this mean that the Bell state is an artifact of exchange symmetry, and that we shouldn't think of this state as entangled? Further, does this mean that *any* pair of electrons is spin-anticorrelated as a consequence of exchange antisymmetry (even if they've never interacted)? Well, no to both of these, although we won't fully explain the flaw in this reasoning for a bit. But for now, note that the EPR experiment doesn't depend on the indistinguishability of particles, so there is no problem in principle there. The real point, however, is that physically, the state (10.92) isn't a complete representation of the two-particle state.[39] More on this soon.

10.4.1 Exchange "Force"

One consequence of indistinguishability is an interference effect that looks something like an effective force between indistinguishable particles. This effect, the **exchange ''force''** or, more properly, **exchange interaction**, is particularly important in understanding atomic and molecular structure, condensed matter systems, quantum degenerate gases, and astrophysics (where ''degeneracy pressure'' prevents white dwarfs and neutron stars from collapsing).

Consider two particles A and B in respective states $|\psi_1\rangle$ and $|\psi_2\rangle$, which we assume to be orthonormal. For distinguishable particles, the composite state is

$$|\psi\rangle = |(\psi_1)_A\,(\psi_2)_B\rangle. \tag{10.93}$$

The joint spatial probability density is

$$P(A \text{ at } x_A, B \text{ at } x_B) = |\langle x_A\, x_B|\psi\rangle|^2 = |\psi_1(x_A)|^2|\psi_2(x_B)|^2 \quad \text{(distinguishable)}, \tag{10.94}$$

where $\psi_1(x_A) = \langle x_A|(\psi_1)_A\rangle$ and $\psi_2(x_B) = \langle x_B|(\psi_2)_B\rangle$. If we choose not to distinguish between the particles, we can compute the probability of finding one at x and the other at x',

$$\begin{aligned} P(1 \text{ particle at } x,\ 1 \text{ particle at } x') &= P(A \text{ at } x,\ B \text{ at } x') + P(A \text{ at } x',\ B \text{ at } x) \\ &= |\psi_1(x)|^2|\psi_2(x')|^2 + |\psi_1(x')|^2|\psi_2(x)|^2 \quad \text{(distinguishable)}. \end{aligned} \tag{10.95}$$

This expression facilitates comparison with the indistinguishable case.

Now consider indistinguishable particles, either bosons or fermions

$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|(\psi_1)_A\,(\psi_2)_B\rangle \pm |(\psi_2)_A\,(\psi_1)_B\rangle\Big), \tag{10.96}$$

[38] Note, however, that the opposite has been argued; see N. Killoran, M. Cramer, and M.B. Plenio, ''Extracting Entanglement from Identical Particles,'' *Physical Review Letters* **112**, 150501 (2014) (doi: 10.1103/PhysRevLett.112.150501). They argue that while the exchange-symmetric state itself may not be directly useful as an entangled state, it has entanglement that may be ''extracted'' using something like a beam splitter. However, in a second-quantized picture, it is natural to view the beam splitter as *creating* entanglement, even for a single incident photon (in this case the output modes are entangled); see S. J. van Enk ''Single-particle entanglement,'' *Physical Review A* **72**, 064306 (2005) (doi: 10.1103/PhysRevA.72.064306).

[39] In fact, the root of the problem is that we took spin as an experimental fact that was missing from quantum mechanics, and we spliced it in to fix things up. In a formulation of quantum mechanics where spin arises naturally (i.e., second quantization), problems like this don't show up. In the present formalism (first quantization), the spin labels can be unphysical if they're abused. The first-quantized fix for the apparent paradox here is in Section 10.4.2.

In this case the joint spatial probability density becomes

$$\begin{aligned} P(A \text{ at } x_A, B \text{ at } x_B) &= |\langle x_A\, x_B|\psi\rangle|^2 \\ &= \frac{1}{2}\Big(|\psi_1(x_A)|^2|\psi_2(x_B)|^2 + |\psi_2(x_A)|^2|\psi_1(x_B)|^2 \\ &\qquad \pm 2\mathrm{Re}[\psi_1^*(x_A)\psi_2^*(x_B)\psi_2(x_A)\psi_1(x_B)]\Big) \quad \text{(bosons/fermions).} \end{aligned} \tag{10.97}$$

Again, we must drop the particle labels, so

$$\begin{aligned} P(1 \text{ particle at } x, 1 \text{ particle at } x') &= |\psi_1(x)|^2|\psi_2(x')|^2 + |\psi_2(x)|^2|\psi_1(x')|^2 \\ &\qquad \pm 2\mathrm{Re}[\psi_1^*(x)\psi_2^*(x')\psi_2(x)\psi_1(x')] \quad \text{(bosons/fermions).} \end{aligned} \tag{10.98}$$

The final interference term is the **exchange term**. Note that it is nonvanishing only if the two wave functions $\psi_1(x)$ and $\psi_2(x)$ overlap.

To see the effect of the exchange term, consider the probability density when $x = x'$. For distinguishable particles, the probability density is simply

$$P(\text{both at } x) = 2|\psi_1(x)|^2|\psi_2(x)|^2, \tag{10.99}$$
(distinguishable particles)

while in the indistinguishable case,

$$\begin{aligned} P(\text{both at } x) &= 2|\psi_1(x)|^2|\psi_2(x)|^2 \pm 2\mathrm{Re}[|\psi_1(x)|^2|\psi_2(x)|^2] \\ &= \begin{cases} 4|\psi_1(x)|^2|\psi_2(x)|^2 & \text{(bosons)} \\ 0 & \text{(fermions)} \end{cases} \end{aligned}$$

(exchange interaction) (10.100)

Thus, the probability density for being at the same position *doubles* with respect to the distinguishable case for bosons, and vanishes for fermions. Thus, it is common to speak of the attractive "**exchange force**," or **exchange interaction** between bosons, and the repulsive "force" between fermions. This effect is not a force, however; it is simply an interference effect due to the symmetry properties under exchange. In particular, if two noninteracting particles "collide" and then separate, there is no scattering or net phase shift after the crossing of the particles due to the exchange interaction. However, these *would* occur if the exchange interaction really could be modeled as a force (instead, the exchange interaction affects the details of the particles spatial distributions only while they are overlapping).[40]

10.4.1.1 Mean-Squared Separation

We can also see this effect, by computing the expectation value of the squared separation $(x_A - x_B)^2$ between the two particles:

$$\left\langle (x_A - x_B)^2 \right\rangle = \left\langle x_A^2 \right\rangle + \left\langle x_B^2 \right\rangle - 2\langle x_A x_B \rangle\,. \tag{10.101}$$

For distinguishable particles, again in the state

$$|\psi\rangle = |(\psi_1)_A\,(\psi_2)_B\rangle, \tag{10.102}$$

we find

$$\left\langle (x_A - x_B)^2 \right\rangle = \left\langle x_A^2 \right\rangle_1 + \left\langle x_B^2 \right\rangle_2 - 2\langle x_A\rangle_1\langle x_B\rangle_2\,, \tag{10.103}$$

[40] W. J. Mullin and G. Blaylock, "Quantum statistics: Is there an effective fermion repulsion or boson attraction?" *American Journal of Physics* **71**, 1223 (2003) (doi: 10.1119/1.1590658).

where $\langle x\rangle_{1,2} := \langle\psi_{1,2}|x|\psi_{1,2}\rangle$. Note that this result is invariant under exchange of particle labels. Of course, we can also write

$$\big\langle (x_A - x_B)^2\big\rangle = \big\langle x^2\big\rangle_1 + \big\langle x^2\big\rangle_2 - 2\langle x\rangle_1\langle x\rangle_2\,, \tag{10.104}$$
(distinguishable particles)

since in the expectation values, the distinction between x_A and x_B is no longer necessary.

For identical particles in the state

$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|(\psi_1)_A\,(\psi_2)_B\rangle \pm |(\psi_2)_A\,(\psi_1)_B\rangle\Big), \tag{10.105}$$

we first of all see that the sum of the first two terms in (10.104) remains the same,

$$\big\langle x_A^2\big\rangle + \big\langle x_B^2\big\rangle = \big\langle x^2\big\rangle_1 + \big\langle x^2\big\rangle_2\,, \tag{10.106}$$

since, for example,

$$\big\langle x_A^2\big\rangle = \frac{1}{2}\Big(\big\langle x_A^2\big\rangle_1 + \big\langle x_A^2\big\rangle_2\Big) = \frac{1}{2}\Big(\big\langle x^2\big\rangle_1 + \big\langle x^2\big\rangle_2\Big). \tag{10.107}$$

The cross term takes the form

$$\langle x_A x_B\rangle = \frac{1}{2}\Big[\langle x_A\rangle_1\langle x_B\rangle_2 + \langle x_A\rangle_2\langle x_B\rangle_1 \pm 2\mathrm{Re}[\langle x_A x_B\rangle_{12}]\Big], \tag{10.108}$$

where

$$\begin{aligned}
\langle x_A x_B\rangle_{12} &:= \langle(\psi_1)_A\,(\psi_2)_B|x_A x_B|(\psi_2)_A\,(\psi_1)_B\rangle \\
&= \langle(\psi_1)_A|x_A|(\psi_2)_A\rangle\langle(\psi_2)_B|x_B|(\psi_1)_B\rangle \\
&= \langle\psi_1|x|\psi_2\rangle\langle\psi_2|x|\psi_1\rangle \\
&= |\langle\psi_1|x|\psi_2\rangle|^2 \\
&=: |\langle x\rangle_{12}|^2\,.
\end{aligned} \tag{10.109}$$

Thus, for identical particles, we have

$$\big\langle (x_A - x_B)^2\big\rangle = \big\langle x^2\big\rangle_1 + \big\langle x^2\big\rangle_2 - 2\langle x\rangle_1\langle x\rangle_2 \mp 2\,|\langle x\rangle_{12}|^2\,, \tag{10.110}$$
(bosons/fermions)

which differs from the distinguishable case by the last term. Thus, we see that on average, the separation between two bosons is *smaller* than the separation between two distinguishable particles, which is smaller yet for two identical fermions. This result is consistent with the previous analysis of the probability distributions.

10.4.1.2 Indistinguishability

The exchange interaction shows the main consequence of having identical particles. It is only when they ''interact'—in having spatially overlapped wave functions—that the exchange interaction is important. This brings up the concept of **indistinguishable** particles. If two bosons are confined to a trap, they can be in the same trapped state. The exchange interaction will be in force, causing them to be closer on average than for nonidentical particles. And because they are identical and in the same state, they in fact are completely indistinguishable, even in principle. The same can be said of a pair of fermions in a trap, although antisymmetry requires that they not occupy exactly the same state (either the spin or vibrational state must differ, due to the **Pauli exclusion principle**). Nevertheless, the exchange antisymmetry and the corresponding antisymmetric occupation of a pair of trap modes makes for indistinguishable fermions.

However, if a pair of identical particles is widely separated such that the single-particle wave functions do not overlap, then the exchange interaction is not in effect, as we have seen. As long as they stay separated, you could even use the distinguishable-particle quantum state (10.87), and make perfectly valid predictions. In this case it is the fact that the different particles have access to different sets of states that makes them

effectively distinguishable. Even more deeply, you could perform an experiment involving only one of the particles but not the other one. So when you work with a single particle, say an electron, you don't have to worry about the fact that it is exchange-antisymmetric with every other electron in the universe (which should come as a huge relief).

A related subtlety is in what it means to swap two particles under the exchange symmetry. It is common to speak of the exchange symmetry in terms of a kind of parity operation, where the particle labels are swapped, and the physical states pick up a phase of 0 or π during the swap. But this is a *mathematical* exchange of labels. If you really want to *physically* exchange two particles, other phases are possible.[41] For example, suppose that you want to *physically* exchange a pair of electrons. You could do this by performing a π rotation of the two-particle system. This means that there are effectively two π rotations, one on each particle, and the net phase on the pair particles is the combination of these phases. This is the same phase accumulation as a 2π rotation of a single particle. But we know that spin-$1/2$ particle picks up a minus sign under a 2π rotation, so the rotation-exchange here gives the minus sign expected for fermion exchange. But not so fast! For consistency we also have to exchange the spin states, and so the rotation must apply to each spin as well. The two spins will accumulate another net phase that is identical to the first phase (another minus sign). The two phases exactly cancel, and there is no exchange phase. The point here is that there *is* an exchange phase, but corresponding to the mathematical exchange of labels. A *physical* exchange of two particles may be accompanied by geometric and dynamical phases (as discussed in Chapter 4. But the exchange phase occurs independently of the details of a physical exchange: the dynamical phase depends the speed and paths of the exchange and the geometric phase depends on the paths but not speed. Because the exchange phase is independent of these details, it is an example of a **topological phase**.

10.4.2 Internal vs. External Degrees of Freedom

One more complication: we have so far been treating *spinless* particles, but the situation is more complicated for two fermions, say, electrons of spin 1/2. In this case, we must have an antisymmetrized state vector, now of the form

$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|(\psi_1)_A\,(\psi_2)_B\rangle|(m_1)_A\,(m_2)_B\rangle - |(\psi_2)_A\,(\psi_1)_B\rangle|(m_2)_A\,(m_1)_B\rangle\Big), \tag{10.111}$$

where the $m_{1,2}$ are the quantum numbers for the projections of the spins along the z-axis. Treating the spin degrees of freedom separately, we recall that there are two types of two-electron states. The **singlet state** is antisymmetric in the spin,

$$|0\,0\rangle = \frac{1}{\sqrt{2}}\Big(|\uparrow_A\downarrow_B\rangle - |\downarrow_A\uparrow_B\rangle\Big), \tag{10.112}$$

while the **triplet states** are symmetrized in the spin:

$$\begin{aligned} |1\,1\rangle &= |\uparrow_A\uparrow_B\rangle \\ |1\,0\rangle &= \frac{1}{\sqrt{2}}\Big(|\uparrow_A\downarrow_B\rangle + |\downarrow_A\uparrow_B\rangle\Big) \\ |1\,{-1}\rangle &= |\downarrow_A\downarrow_B\rangle. \end{aligned} \tag{10.113}$$

Here, we are also labeling the states by the composite quantum numbers $|S\,m_S\rangle$. Since we need only antisymmetrize the *total* state, we can see that singlet states imply *symmetric* states in the external degree of freedom, while triplet states require *antisymmetric* states. Thus, for two electrons, we can see both an attractive and a repulsive exchange interaction, if the electrons are respectively in a spin singlet or spin triplet state (corresponding to antialigned or aligned spins, respectively). Fermions can in some sense act like fermions or bosons, and the same holds true for bosons. More carefully, we should really relabel the results (10.100) and (10.110) for the exchange interaction in terms of symmetry or antisymmetry of the

[41] For more details, see S. J. van Enk, "Exchanging identical particles and topological quantum computing," (arXiv: 1810.05208) (2018).

spatial wave function instead of in terms of bosonic or fermionic particles; for example,

$$\langle (x_A - x_B)^2 \rangle = \langle x^2 \rangle_1 + \langle x^2 \rangle_2 - 2\langle x \rangle_1 \langle x \rangle_2 \mp 2\,|\langle x \rangle_{12}|^2$$

(symmetric/antisymmetric spatial wave function) (10.114)

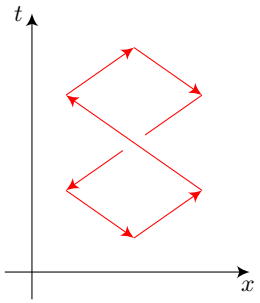
should replace Eq. (10.110).

Note that this view of the exchange interaction in accounting for both spin and spatial degrees of freedom also addresses the apparent paradox with the Bell state (10.92). The entangled spins are not the whole story; we really should include the external state of the particles, in which case *any* spin combination is possible. Thus, the anticorrelated spin-entangled state is *not* just a consequence of exchange antisymmetry.

10.4.3 Spin and Statistics

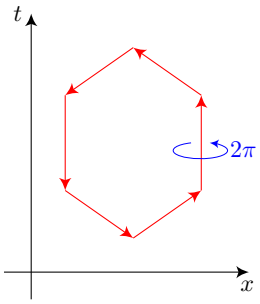
An important part of the discussion above is that bosons and fermions are respectively associated with plus and minus signs under identical-particle exchange. The spin–statistics theorem that we mentioned says that bosons are associated with integer spins, while fermions are associated with half integer spins. This can be justified via the following argument.[42]

Consider the space-time diagram below. One way to look at this is as the worldline of a particle moving around in a closed path in space-time.



If you view this diagram differently, moving only in the positive direction along the time axis, it is a process where initially a particle/antiparticle pair are created (the antiparticle running with a backwards arrow; an antiparticle is a particle moving backwards through time, as discussed later in Section 19.2.3). Then there is a particle exchange (here, in a counter-clockwise rotation), and then finally the pair annihilates.

Setting aside the issue of whether exchanging a particle/antiparticle pair is equivalent to exchanging a pair of identical particles (it turns out to be, which can be seen by rotating the diagram by 90° in spacetime), the crux of the argument is to deform the worldline continuously into the form shown below.



However, something extra is needed: rather than thinking about the worldline as merely a path, think of it more as a ribbon, as a bookkeeping trick to keep track of rotations of the particle. The above worldlines

[42] This follows part of the argument given by John Preskill, *Lecture Notes for Physics 219: Quantum Computation* (14 June 2004), Section 9.3 (`http://www.theory.caltech.edu/~preskill/ph219/topological.pdf`). Although the ribbon-based topological idea occurs earlier, for example in Richard P. Feynman and Steven Weinberg, *Elementary Particles and the Laws of Physics: The 1986 Dirac Memorial Lectures* (Lecture notes compiled by Richard MacKenzie and Paul Doust) (Cambridge University Press, 1987), pp. 56-9 (ISBN: 0521340004), Preskill's argument is particularly clear, elegant, and direct.

are topologically equivalent (equivalent under continuous deformation) provided the particle undergoes a 2π rotation (the rotation could be accounted for in various ways, but let's stick with this one). This is something that you have to try to see it work out: take a belt or other belt-like object, give one end a 2π rotation with respect to the other, and then buckle the ends together. You should see that it can be rearranged to match either diagram above.

Now, the exchange is equivalent to a 2π rotation of the particle, and such a rotation is associated with a phase factor $(-1)^{2S}$ for a spin-S particle. To see this, note that such a rotation about, say, the z-axis is induced by the operator $\exp(-i2\pi S_z/\hbar)$ [Eq. (7.131)]. This is $\exp[-i\pi(2m)] = (-1)^{2m}$ in terms of the m quantum number, and the phase $(-1)^{2m}$ agrees with $(-1)^{2S}$ for every value of m. This argument gives the (topological) exchange phase in terms of the rotation phase that we already studied. Of course, the caveats from before still apply: a *physical* realization of this worldline in general involves extra geometric and dynamical phases. But as a conceptual process useful for deriving a topological phases, we can ignore these complications.

Finally, note that the spin–statistics relation is something that *only* comes out of relativistic theory. In this argument, the relativistic part is of course the existence of antiparticles.

10.5 Exercises

Problem 10.1

The point of this problem is to see how to construct a hidden-variable theory that matches the quantum-mechanical prediction for a *single* spin-1/2 particle.

(a) Given a particle in state

$$|\psi\rangle = |+\rangle_{\hat{\alpha}}, \tag{10.115}$$

which is the $m = +1/2$ eigenstate along the direction $\hat{\alpha}$,

$$\sigma(\hat{\alpha})|+\rangle_{\hat{\alpha}} = (+1)|+\rangle_{\hat{\alpha}}, \tag{10.116}$$

where as usual $\sigma(\hat{\alpha}) = \boldsymbol{\sigma} \cdot \hat{\alpha}$ is the rotation of σ_z in the same sense as the $\hat{z}$ axis is rotated to the $\hat{\alpha}$ axis.

Compute the quantum-mechanical prediction for the expectation value $\left\langle \sigma(\hat{\beta}) \right\rangle = \left\langle \boldsymbol{\sigma} \cdot \hat{\beta} \right\rangle$, where $\hat{\beta}$ is the orientation of the detector (different in general from the preparation axis $\hat{\alpha}$). Use θ to denote the angle between $\hat{\alpha}$ and $\hat{\beta}$.

(b) Now define the hidden-variable prediction by

$$\left\langle \sigma(\hat{\beta}, \lambda) \right\rangle_{\lambda} = \int d\hat{\lambda}\, f(\hat{\lambda})\, \sigma\big(\hat{\beta}, \hat{\lambda}\big), \tag{10.117}$$

where the hidden-variable integration will be limited to the unit sphere, parameterized by the unit vector $\hat{\lambda}$. The idea will be to design this average to reproduce the quantum result for the state (10.115), so there is an implicit dependence on the quantum state (and thus $\hat{\alpha}$) buried in $\sigma(\hat{\beta}, \hat{\lambda})$.

Suppose that we take

$$\sigma\big(\hat{\beta}, \hat{\lambda}\big) = \mathrm{sgn}\big(\hat{\beta}' \cdot \hat{\lambda}\big), \tag{10.118}$$

where $\hat{\beta}'$ is yet to be specified. Note that the variable here has the allowed values ± 1, in agreement with the quantum possibilities (this doesn't quite work out for $\hat{\beta}' \cdot \hat{\lambda} = 0$, but this is a set of measure zero, and so won't affect the integration... close enough). Also take $f(\hat{\lambda})$ to be uniform over the upper half-sphere, and zero otherwise. Argue that, under these assumptions,

$$\left\langle \sigma(\hat{\beta}, \lambda) \right\rangle_{\lambda} = 1 - \frac{2\theta'}{\pi}, \tag{10.119}$$

where θ' is the angle between $\hat{\alpha}$ and $\hat{\beta}'$. Thus show how to choose $\hat{\beta}'$ (as a function of $\hat{\alpha}$ and $\hat{\beta}$) to reproduce the quantum prediction from part (a).

Problem 10.2

The point of this problem is to work through a famous variation on the Bell theorem that is slightly more complicated to set up but easier to work through mathematically. Consider the following combination of correlation functions

$$\mathscr{C} := C(\hat{x}, \hat{+}) + C(\hat{x}, \hat{-}) + C(\hat{y}, \hat{+}) - C(\hat{y}, \hat{-}), \tag{10.120}$$

referring to the four unit vectors $\hat{x}$, $\hat{y}$, and

$$\hat{\pm} := \frac{\hat{x} \pm \hat{y}}{\sqrt{2}}. \tag{10.121}$$

(a) First let's work through the quantum-mechanical prediction for this measurement. Remembering the correlation functions are defined in terms of Pauli spin matrices as

$$C(\hat{\alpha}, \hat{\beta}) = \left\langle \sigma_1(\hat{\alpha})\, \sigma_2(\hat{\beta}) \right\rangle, \tag{10.122}$$

show that $\mathscr{C} = -2\sqrt{2}$ using the calculated value of $C(\hat{\alpha}, \hat{\beta})$ for a Bell state

$$|\psi\rangle = \frac{|+\rangle_1|-\rangle_2 - |-\rangle_1|+\rangle_2}{\sqrt{2}}. \tag{10.123}$$

(b) Now the reason for the particular choice of four orientations is that there is a simple way to handle the *operator* combination underlying $\mathscr{C}$. To do this, start by showing that

$$\sigma(\hat{\pm}) = \frac{\sigma(\hat{x}) \pm \sigma(\hat{y})}{\sqrt{2}}. \tag{10.124}$$

Then show that

$$\sigma_1(\hat{x})\sigma_2(\hat{+}) + \sigma_1(\hat{x})\sigma_2(\hat{-}) + \sigma_1(\hat{y})\sigma_2(\hat{+}) - \sigma_1(\hat{y})\sigma_2(\hat{-}) = \sqrt{2}\,\sigma_1(\hat{x})\sigma_2(\hat{x}) + \sqrt{2}\,\sigma_1(\hat{y})\sigma_2(\hat{y}), \tag{10.125}$$

and then compute $\mathscr{C}$ with respect to the Bell state using this latter operator combination. Obviously your result should match what you got in (a).

(c) Now to derive a bound satisfied by local hidden-variable theories. Remember that now we interpret the correlation function as an average over the values of the hidden-variables λ, and the σ_j are *functions* with well-defined values of the arguments:

$$C(\hat{\alpha}, \hat{\beta}) = \Big\langle \sigma_1(\hat{\alpha}, \lambda)\, \sigma_2(\hat{\beta}, \lambda) \Big\rangle_\lambda . \tag{10.126}$$

Working with the unaveraged experimental results, show that the combination

$$A_x B_+ + A_x B_- + A_y B_+ - A_y B_- \tag{10.127}$$

can only have the values ± 2 in any given experiment, where we are using the shorthands

$$A_x := \sigma_1(\hat{x}, \lambda), \qquad B_+ := \sigma_2(\hat{+}, \lambda), \tag{10.128}$$

and similarly for A_y and B_-.

(d) Finally, use the result of (c) along with

$$|\langle X \rangle| \leq \langle |X| \rangle \tag{10.129}$$

for any average over a variable quantity X to derive the **CHSH inequality** (for Clauser, Horne, Shimony, Holt)[43]

$$|\mathscr{C}| \leq 2, \tag{10.130}$$

in which case we have shown that quantum mechanics is incompatible with a local hidden-variable explanation of this experiment.

(e) Note that the argument in (c) and (d) leading to the CHSH inequality (10.130) does not depend on the relative orientations of the axis $\hat{x}$, $\hat{y}$, and $\hat{\pm}$, but merely that the corresponding hidden variables occur in a particular combination. (The motivation for the particular choice of orientations was to simplify the quantum-mechanical calculation.) Thus, it holds for any set of four axes, say $\hat{\alpha}$, $\hat{\beta}$, $\hat{\alpha}'$, and $\hat{\beta}'$, so that we can write

$$\big|C(\hat{\alpha}, \hat{\alpha}') + C(\hat{\alpha}, \hat{\beta}') + C(\hat{\beta}, \hat{\alpha}') - C(\hat{\beta}, \hat{\beta}')\big| \leq 2. \tag{10.131}$$

Show that this form of the CHSH inequality implies the Bell inequality.

[43] John F. Clauser, Michael A. Horne, Abner Shimony, and Richard A. Holt, ‘‘Proposed Experiment to Test Local Hidden-Variable Theories,’’ *Physical Review Letters* **23**, 880 (1969) (doi: 10.1103/PhysRevLett.23.880).

Problem 10.3

Consider the following entangled state (called a **GHZ state**[44]) of three spin-1/2 particles:

$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|+++\rangle - |---\rangle\Big). \tag{10.132}$$

We can assume the particles to be distinguishable and labeled as particles 1, 2, and 3 in the order they appear in the ket.

(a) Show that this state is a simultaneous eigenstate of the operators $\sigma_{1x}\sigma_{2y}\sigma_{3y}$, $\sigma_{1y}\sigma_{2x}\sigma_{3y}$, $\sigma_{1y}\sigma_{2y}\sigma_{3x}$, and $\sigma_{1x}\sigma_{2x}\sigma_{3x}$, and find the eigenvalue in each case. (Note that $\sigma_{1\alpha}$ is the σ_α Bloch operator for particle 1, and so on for particles 2 and 3.)

(b) Now suppose that you make joint measurements of the three particles in each of the four combinations specified in (a). Suppose also that you try to describe the measurement results in terms of a local hidden-variable theory. Let's use A_α, B_β, and C_γ to denote the respective hidden-variable counterparts to $\sigma_{1\alpha}$, $\sigma_{2\beta}$, and $\sigma_{3\gamma}$. Then write down what you should expect for the measurement combinations $A_xB_yC_y$, $A_yB_xC_y$, $A_yB_yC_x$, and $A_xB_xC_x$, in order for them to match quantum mechanics. By considering the product of the first three measurement combinations, show that you obtain a contradiction (so that again, quantum mechanics cannot be explained in terms of local hidden variables).

Problem 10.4

Bell's theorem is usually discussed in terms of entangled spin-1/2 particles, but it applies quite generally, to the (correlated) eigenstates of any two quantum systems. Specifically, take $|m\rangle$ and $|n\rangle$ to be two states of a quantum system (which has other states as well) such that $\langle m|n\rangle = 0$, and consider the one-parameter family of operators[45]

$$F(\alpha) := e^{i\alpha}|m\rangle\langle n| + e^{-i\alpha}|n\rangle\langle m|. \tag{10.133}$$

(a) Find *three* distinct eigenvalues and corresponding eigenvectors of $F(\alpha)$.

(b) Show that $F(\alpha)$ and $F(\alpha')$ cannot simultaneously have definite values, provided $\alpha - \alpha'$ is not an integer multiple of π.

(c) Now take $|\mu\rangle$ and $|\nu\rangle$ to be two states of a different quantum system such that $\langle\mu|\nu\rangle = 0$, and define the analogous operator

$$\Phi(\beta) := e^{i\beta}|\mu\rangle\langle\nu| + e^{-i\beta}|\nu\rangle\langle\mu|. \tag{10.134}$$

Suppose the two systems are entangled in the state

$$|\psi\rangle = \frac{|m\rangle|\nu\rangle - |n\rangle|\mu\rangle}{\sqrt{2}}. \tag{10.135}$$

Compute the correlation function

$$C(\alpha,\beta) := \langle\psi|F(\alpha)\Phi(\beta)|\psi\rangle \tag{10.136}$$

for this entangled state.

(d) Now complete the argument: write down an inequality involving $C(\alpha,\beta)$ assuming the experiment is explainable by a local hidden-variables theory, and which is violated by quantum mechanics.

[44] After the original conception by D. M. Greenberger, M. A. Horne, and A. Zeilinger, "Going Beyond Bell's Theorem," in *Bell's Theorem, Quantum Theory and Conceptions of the Universe*, M. Kafatos, Ed. (Springer, 1989), p. 69 (doi: 10.1007/978-94-017-0849-4_10) (arXiv: 0712.0921); for the three-particle state and an experimental realization with photons, see also Dik Bouwmeester, Jian-Wei Pan, Matthew Daniell, Harald Weinfurter, and Anton Zeilinger, "Observation of Three-Photon Greenberger-Horne-Zeilinger Entanglement," *Physical Review Letters* **82**, 1345 (1999) (doi: 10.1103/PhysRevLett.82.1345) (arXiv: quant-ph/9810035).

[45] This variation on Bell's theorem is from Asher Peres, "Unperformed experiments have no results," *American Journal of Physics* **46**, 745 (1978) (doi: 10.1119/1.11393).

Problem 10.5

A way of producing a Bell state of two photons comes from the spontaneous decay of an atom from an S state ($L = 0$, where L is the quantum number for orbital angular momentum) to a lower P state ($L = 1$), and then to another S state (typically the ground state). This is called an "S-P-S cascade."

(a) Indicate the three possible decay paths. Assuming both decays occur as electric-dipole transitions, write down the *relative* amplitudes for each double-transition as products of Clebsch–Gordan coefficients, using the expression (7.263) that we derived in class for $\langle \alpha\ J\ m_J | \hat{\varepsilon} \cdot j^*(\mathbf{k}) | \alpha'\ J'\ m'_J \rangle$ for the atomic-transition amplitude. Also give numerical values for the relative amplitudes (including the correct signs). To be definite, you can associate the primed quantum numbers with the initial state and the unprimed numbers with the post-decay state, but either way should produce the same relative amplitudes.

(b) Now to come back to a part of multipole emission that we glossed over—the radiated field. Recalling the multipole interaction Hamiltonian (7.225),

$$H_{\text{int}} = -\frac{1}{2\pi} \int d^3k\, \tilde{\mathbf{j}}(-\mathbf{k}) \cdot \tilde{\mathbf{A}}(\mathbf{k}) = -\frac{1}{2\pi} \int d^3k\, \tilde{\mathbf{j}}^*(\mathbf{k}) \cdot \tilde{\mathbf{A}}(\mathbf{k}), \tag{10.137}$$

for our purposes this says that electric-dipole radiation, which couples to the field via the polarization vector $\hat{\varepsilon}$, will have the same rank-1 tensor symmetry. That is, for a polarization basis vector $\hat{\epsilon}_q$ that appears in the atomic matrix element, this corresponds to radiation emitted in the pattern $Y^{-q}_{\ell'=1}(\hat{k})$. Well, except that it's not *quite* that simple, because this *would* be the emission pattern for a scalar radiation field, but we have a *vector* radiation field. Assuming radiation of a transverse vector potential (as appropriate for Coulomb gauge), it turns out that the correspoding angular distribution is specified by the **vector spherical harmonics**, defined in terms of the regular spherical harmonics by

$$\mathbf{X}^m_l(\theta, \phi) := -\frac{i}{\sqrt{l(l+1)}}\, \mathbf{r} \times \nabla Y^m_l(\theta, \phi). \tag{10.138}$$

That is, the radiation pattern (including the polarization of the radiation field) is given by $\mathbf{X}^{-q}_1(\hat{k})$ instead of $Y^{-q}_1(\hat{k})$.

Take advantage of this observation that the spherical harmonic $\mathbf{X}^{-q}_1(\hat{k})$ gives the relative amplitude for photon emission into direction $\hat{k}$ to argue that if you only count emission events along one particular direction (which one?), one of the decay paths is excluded. Of course, if you only count emission along *exactly* one direction, the rate at which you generate photon Bell states would tend to zero; however, you can approximate this situation as well as you like, at the expense of the rate at which you generate EPR pairs. Also, feel free to look up the appropriate vector spherical harmonics in lieu of calculation (just make sure the conventions are the same as given here!).

(c) Labeling the emitted photon by $|-q\rangle$, where $-q$ is the same label as in the spherical harmonic of part (b) (i.e., use the labels $|\pm\rangle$ for the emitted photons), write down a state vector representing the generated photon Bell state corresponding to the situation in part (b), *given* that an appropriate pair of photons were emitted in the proper directions. How is this state different from the state generated by a decay into a pair of spin-$\frac{1}{2}$ particles? Can you interpret any difference?

Problem 10.6

Consider the matrix

$$\rho = \begin{bmatrix} A & 0 \\ 0 & D \end{bmatrix}. \tag{10.139}$$

(a) What is required of ρ for it to be a density matrix?

(b) What is required of ρ for it to be a *pure* density matrix?

Now consider the matrix

$$\rho' = \begin{bmatrix} A & B \\ C & D \end{bmatrix}. \tag{10.140}$$

(c) What is required of ρ' for it to be a density matrix?

(d) What is required of ρ' for it to be a *pure* density matrix?

Problem 10.7

Show that under Hamiltonian evolution,

$$\partial_t \rho = -\frac{i}{\hbar}[H, \rho], \tag{10.141}$$

the purity $\mathrm{Tr}[\rho^2]$ is a constant of the motion.

Problem 10.8

For a single qubit/spin-1/2 system, it turns out that an arbitrary density operator may be written in terms of the Pauli matrices as

$$\rho = \frac{1}{2}\big(1 + \mathbf{r}\cdot\boldsymbol{\sigma}\big), \tag{10.142}$$

where $|\mathbf{r}| \le 1$ and the $\mathcal{I}$ is the identity operator on the qubit Hilbert space.

(a) Show this by writing out the right-hand side as a 2×2 matrix, and showing that it parameterizes an arbitrary matrix with the correct properties to be a density matrix. (What are the properties?)

(b) By computing $\langle\boldsymbol{\sigma}\rangle$, show that $\mathbf{r}$ is in fact the Bloch vector.

(c) Show that the purity is related to the length of the Bloch vector by

$$\mathrm{Tr}[\rho^2] = \frac{1}{2}\big(1 + |\mathbf{r}|^2\big). \tag{10.143}$$

In particular, pure states have $|\mathbf{r}| = 1$, with mixed states $0 \le |\mathbf{r}| < 1$ (so that $1/2 \le \mathrm{Tr}[\rho^2] < 1$).

(d) What is the Bloch vector for the I-know-nothing state (proportional to the identity)?

Problem 10.9

(a) Consider a spin-1/2 particle in a quantum state given by the density operator ρ, and in particular in terms of the density matrix elements $\rho_{\pm\pm}$ and $\rho_{\pm\mp}$ in the representation of the eigenstates of S_z. Give the probability (in terms of density-matrix elements) for a measurement of S_x, S_y, or S_z to give the result $+\hbar/2$ (i.e., do three separate calculations but stay in the same representation).

(b) Repeat the calculation of (a) for a $j = 1$ particle to give the result $+\hbar$ under the same conditions (representation of J_z's eigenstates, consider measurements along each axis).

Problem 10.10

Consider the Boltzmann-distribution density operator

$$\rho = Z^{-1}e^{-\beta H} = Z^{-1}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)}|n\rangle\langle n|, \tag{10.144}$$

where $\beta = 1/k_{\mathrm{B}}T$, H is the harmonic-oscillator Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2, \tag{10.145}$$

and

$$Z = \mathrm{Tr}[e^{-\beta H}] = \sum_n e^{-\beta\hbar\omega(n+1/2)} \tag{10.146}$$

is the partition function.

(a) Compute the expected energy $\langle H\rangle$ and the expected occupation number $\langle n\rangle$. Note that a good way to start is to first compute the partition function, and then show that $\langle H\rangle = -\partial_\beta \log Z$.

(b) Use Mehler's formula for the Hermite-polynomial sum[46]

$$\sum_{n=0}^{\infty} \frac{(z/2)^n}{n!} H_n(x)H_n(y) = \frac{1}{\sqrt{1-z^2}} \exp\left[\frac{2xyz - (x^2+y^2)z^2}{1-z^2}\right] \tag{10.147}$$

to derive the expression

$$\rho(x,x') = \frac{1}{\sqrt{\pi x_{\mathrm{s}}^2 \coth(\beta\hbar\omega/2)}} \exp\Big[-\coth(\beta\hbar\omega)\big(x^2+x'^2\big)/2x_{\mathrm{s}}^2 + \mathrm{csch}(\beta\hbar\omega)\big(xx'/x_{\mathrm{s}}^2\big)\Big] \tag{10.148}$$

for the density matrix $\rho(x,x') = \langle x|\rho|x'\rangle$ in the position representation, where

$$x_{\mathrm{s}} = \sqrt{\frac{\hbar}{m\omega}} \tag{10.149}$$

is the usual length scale for the harmonic oscillator.

What is the position uncertainty for this thermal state? Check the asymptotic regimes of small and large temperature, and give a sensible interpretation for the expression you derive in the two limits.

Problem 10.11

Consider a pair of qubits labeled A and B, interacting via the Hamiltonian

$$H = \epsilon\Big(|\mathtt{1}\rangle_A\langle\mathtt{1}|_A + |\mathtt{1}\rangle_B\langle\mathtt{1}|_B\Big) - \delta\Big(|\mathtt{1}_A\,\mathtt{1}_B\rangle\langle\mathtt{1}_A\,\mathtt{1}_B| + |\mathtt{0}_A\,\mathtt{0}_B\rangle\langle\mathtt{0}_A\,\mathtt{0}_B|\Big). \tag{10.150}$$

That is, each qubit separately has energy levels of 0 and ϵ, and there is an energetic preference for the qubits to align if $\delta > 0$.

(a) Write down an expression for the density operator of the pair in a thermal state of temperature T (see Problem 10.10), assuming they are indistinguishable bosons.

(b) Is this state entangled? Explain why or why not.

Problem 10.12

For the quantum-state teleportation problem (Section 10.3.2.2), compute Bob's local state (i.e., Bob's reduced density operator ρ_{B}) before Alice makes her local measurement (and, of course, before communicating the measurement results to Bob).

Problem 10.13

In the problem of quantum-state teleportation (Section 10.3.2.2), suppose Bob knows that it's April Fool's Day, and so Alice will lie to him about the measurement result with probability $\epsilon \ll 1$. In this case what is the final (corrupted) teleported state in this scenario? (In the case that Alice is lying, you may assume she picks one of the three "wrong" measurement results at random.)

[46] Harry Bateman, *Higher Transcendental Functions*, vol. II (McGraw–Hill, 1953), p. 194, Eq. (22), available at `http://resolver.caltech.edu/CaltechAUTHORS:20140123-104529738`.

Problem 10.14

Alice teleports the state of a single qubit to Bob using the normal protocol. To make things easier, Bob has a brand new Teleport-O-Matic® teleportation receiver. All he has to do is feed in his half of the shared EPR pair into the machine's super convenient Input-O-Matic® input slot and voilà, the machine reads (and deletes) the email from Alice containing her measurement result, takes care of the required unitary operations on his end, and the qubit pops out in the teleported state. Bob is now thrilled because he now has time to do all those things that he never had time for, because unitary operations are an awful lot of back-breaking work, with flaky lasers and knobs and little doohickeys and whatnot. Unfortunately for Bob, just after the qubit pops out, he receives a message from the manufacturer, saying that his unit has a manufacturing defect. The manufacturer's information says:

- Whenever the machine needs to correct the state *only* by swapping $|\mathtt{0}\rangle \longleftrightarrow |\mathtt{1}\rangle$ (or in the case where it needs to perform *no* correction), it works just fine, BUT...
- The relative-phase corrector has a bug that makes the machine freak out, so that whenever the machine needs to change a relative phase, the machine freezes and *doesn't* apply any swapping operation (whether or not it was needed). It also *scrambles the relative phase* in this case—it performs the operation $a|\mathtt{0}\rangle+b|\mathtt{1}\rangle \longrightarrow a|\mathtt{0}\rangle+e^{i\phi}b|\mathtt{1}\rangle$, where ϕ is random and uniformly distributed, as far as anyone knows. (If it seems easier to you, you can think of the scrambling operation as $a|\mathtt{0}\rangle + b|\mathtt{1}\rangle \longrightarrow a|\mathtt{0}\rangle \pm b|\mathtt{1}\rangle$, where the sign is random; the final answer will come out the same.)

What is the state of Bob's teleported qubit after he gets the note from the manufacturer? Assume that because the Teleport-O-Matic® helpfully deleted Alice's email and Bob didn't bother to read it, Bob has no way of knowing what was the result of Alice's measurement.

Problem 10.15

Suppose that we have brainstormed a half-baked, modified teleportation scheme to clone a quantum state. Starting with three qubits in the GHZ state given in Eq. (10.132),

$$|\psi\rangle = \frac{1}{\sqrt{2}}\Big(|+++\rangle - |---\rangle\Big), \tag{10.151}$$

Alice is to keep the first one, gives the second one to Bob, and gives the third to Casey. She does the same local operations to her shared qubit and qubit to teleport $|\psi\rangle_{\text{T}}$ that she would in the standard teleportation protocol. Then she communicates the usual two classical bits of information to both Bob and Casey, and asks them to perform local unitary operations as appropriate in order to reconstruct $|\psi\rangle_{\text{T}}$.

(a) The no-cloning theorem says this procedure can't work as we envision. Analyze the procedure to show that it indeed doesn't work, and indicate why not.

(b) However, show that Bob can apply a (local) unitary operation to his qubit, measures its state, and send the result to Casey, then Casey can use the information to receive the teleported state from Alice.

Problem 10.16

In the quantum-state-teleportation protocol, suppose that Alice's Hadamard-O-Matic® has gotten out of whack, and makes a small error of the form

$$\begin{aligned} U_{\pi/2+\epsilon}|+\rangle &= \frac{|+\rangle(1+\epsilon) - |-\rangle(1-\epsilon)}{\sqrt{2}} \\ U_{\pi/2+\epsilon}|-\rangle &= \frac{|+\rangle(1-\epsilon) + |-\rangle(1+\epsilon)}{\sqrt{2}} \end{aligned} \tag{10.152}$$

in implementing the Hadamard gate, where $\epsilon \ll \pi/2$.

(a) First assume that Alice and Bob are unaware of the error. Does the error necessarily lead to an error in Bob's final teleported state? Justify your answer either way.

(b) Does your conclusion from (a) change if both Alice and Bob know that the Hadamard-O-Matic® implements the less-than-ideal operator $U_{\pi/2+\epsilon}$? Again, justify.

Problem 10.17

A *classical* analogue of the quantum-state-teleportation protocol goes as follows. Suppose Alice has a coin with two states, heads ("+") and tails ("−") prepared in an unknown (to Alice and Bob) state, which is heads with a probability p_+, and tails with probability p_-, with $p_+ + p_- = 1$.

Before the teleportation, Alice and Bob share a correlated pair of classical coins; they are either both heads (with probability 1/2) or both tails (also with probability 1/2); initially neither Alice nor Bob know the state of the pair, except that they are in this classical correlated superposition state.

To teleport the state, Alice makes a measurement that tells her only if her two coins are the same or different (her Coin-O-Matic® can indicate whether the coins are the same or different without revealing whether the coins are individually heads or tails). She communicates this (single bit of) classical information to Bob, who is able to recover the teleported state.

(a) Write down a density operator ρ_{T} for the state to be teleported. (To be concrete, this state is not known to Alice but is known to an external observer Chas; write down the state from Chas' point of view, who will verify the teleportation occurred correctly.) Use standard quantum-mechanical (Dirac) notation throughout this problem.

(b) Write down a density operator ρ_{S} representing the (classical) correlated state of the shared coin pair.

(c) What is Bob's local state for his coin before any measurement or communication?

(d) What is Bob's local state for his coin after knowing the results of Alice's measurement? Describe how Bob can recover the state ρ_{T} for his coin using the bit of information from Alice.

Note that you *can* work this part out formally in terms of a POVM, but you don't *have* to; you can simply read off the (correct) result from the state.

(e) What is Alice's local state for her two coins at the end of the teleportation process?

(f) This classical-state teleportation protocol has a lot in common with the quantum counterpart. While it doesn't transmit the state of a qubit—it only transmits one continuous variable p_+, rather than the two variables it would take to transmit the coordinates on the Bloch sphere—repeating this procedure twice transmits an equivalent amount of information in terms of continuous variables, using an equivalent number of classical bits. The state is teleported even though unknown to Alice and Bob, just as in the quantum case. Describe how *quantum*-state teleportation differs from this classical version.

Problem 10.18

Consider a pair of identical, noninteracting, spinless particles, each in an eigenstate of the harmonic-oscillator Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2. \tag{10.153}$$

(You may assume that the particles are not in the same eigenstate.) Compute the mean-squared separation $\langle (x_A - x_B)^2 \rangle$ in the cases where the particles are distinguishable, indistinguishable bosons, or indistinguishable fermions.

Problem 10.19

A classic application of the exchange interaction is the helium atom, which has two electrons (spin-1/2

fermions) bound to the nucleus. If the electron spins form one of the triplet states (symmetric spin state), then the helium atom is called **orthohelium** state; otherwise if the spins are in the singlet state (antisymmetric spin combination), then the helium is said to be **parahelium**. Since it is relatively difficult for spins to change orientation (without some external perturbation), these spin configurations are relatively long-lived.

(a) Which spin variety has the lowest energy state, parahelium or orthohelium? Explain your reasoning, based on the exchange symmetry of the total quantum state.

(b) Now compare the helium atom to a fictitious helium atom with distinguishable electrons (call it ''delium''). How do the parahelium energies compare to those of paradelium? How do the orthohelium energies compare to those of orthodelium? Again, explain your reasoning in each case.

Chapter 11

Quantum Measurements

11.1 Born's Rule Revisited

Before, in Section 1.5, we talked about Born's rule as defining the probabilities and outcomes of a measurement of a quantum observable. To recap, suppose that we have an observable Q, which is a Hermitian operator on the quantum Hilbert space. The eigenvectors of Q are $|q\rangle$, with corresponding eigenvalues q. Then a measurement of Q yields the outcome q with probability

$$P(q) = |\langle q|\psi\rangle|^2, \tag{11.1}$$

if the state just before the measurement is $|\psi\rangle$. This measurement outcome is accompanied by the change

$$|\psi\rangle \longrightarrow |q\rangle \tag{11.2}$$

in the quantum state.

11.1.1 Measurement Probabilities as Expectations

Now let's cast Born's rule into more general language, which will make it suitable for use with both mixed states and more general measurements. First, the measurement probability can be rewritten

$$P(q) = \langle\psi|q\rangle\langle q|\psi\rangle, \tag{11.3}$$

and then identifying the projection operator

$$P_q = |q\rangle\langle q| \tag{11.4}$$

for the q eigenstate, the measurement probability becomes the expectation value of the projector:

$$P(q) = \langle\psi|P_q|\psi\rangle = \langle P_q\rangle\,. \tag{11.5}$$
(measurement probability)

This result also holds in terms of the density operator,

$$P(q) = \langle P_q\rangle = \mathrm{Tr}[P_q\rho], \tag{11.6}$$
(measurement probability)

even for mixed states. The change in the state (11.2) is then expressed as

$$|\psi\rangle \longrightarrow \frac{P_q|\psi\rangle}{\sqrt{\langle\psi|P_q|\psi\rangle}} = \frac{P_q|\psi\rangle}{\sqrt{\langle\psi|P_qP_q|\psi\rangle}} \tag{11.7}$$
(state collapse)

in terms of the projector. Note that the denominator cannot vanish, because the measurement probability could not have vanished for the outcome q. Also, note that the projection $P_q|\psi\rangle$ is not a normalized state if $|\psi\rangle \neq |q\rangle$, and so the division is necessary to renormalize it. Note that the result is a *nonlinear* function of $|\psi\rangle$, which is sometimes a useful fact. Also, we can write the state-collapse operation as

$$\rho \longrightarrow \frac{P_q \rho P_q}{\mathrm{Tr}[P_q \rho P_q]} \tag{11.8}$$
(state collapse)

in terms of the density operator.

Because the measurement can be represented in terms of projectors, this type of measurement is called a **projective measurement** or **von Neumann measurement**.

Now for some interpretation. The ''products'' of quantum mechanics can thus always be though of in terms of *expectation values*—these are the things that are experimentally testable. As we have seen, this includes probabilities of measurement outcomes, and expectation values like $\langle Q\rangle, \langle Q^2\rangle$, and so on (remember that moments are determined by and give information equivalent to the measurement probabilities). Another way to say this is: **Quantum mechanics is a theory that maps operators to probabilities** via the state $|\psi\rangle$ or ρ.

11.1.2 Positive Operators

But if expectation values of projectors determine probabilities, what about *other* operators? In particular, a **positive operator** or **positive-semidefinite operator** is a good candidate for generalizing projectors in this sense. An operator Π (*not* the parity operator here!) is positive semidefinite if

$$\langle\psi|\Pi|\psi\rangle \geq 0 \tag{11.9}$$

for every vector $|\psi\rangle$ in the Hilbert space on which Π operates. This condition is often written as simply ''$\Pi \geq 0$.'' In this case, the expectation value of Π can in principle determine a probability (given the extra constraint that the expectation value is at most 1).

There are some other useful properties of Π, given that it is a positive operator:

- Π is Hermitian.
- Because every expectation value $\langle\psi|\Pi|\psi\rangle$ is a linear combination of eigenvalues of Π (because ψ may be written in the representation of Π's eigenvectors), then all of Π's eigenvalues π_j must satisfy $\pi_j \geq 0$.
- Π has a decomposition of the form
$$\Pi = \Omega^\dagger \Omega \tag{11.10}$$
for an operator Ω. Since Π may be written in terms of its orthonormal basis as
$$\Pi = \sum_j \pi_j |\pi_j\rangle\langle\pi_j|, \tag{11.11}$$
then we can write
$$\Omega = \sum_j \omega_j |\pi_j\rangle\langle\pi_j|, \tag{11.12}$$
provided
$$\omega_j^* \omega_j = \pi_j. \tag{11.13}$$
(While the π_j are real and nonnegative, the ω_j may not be.) For example, the projector P_q has the decomposition $P_q = P_q^2$.

11.1.3 POVMs

Now we can go ahead and state a more general formulation of a measurement:

- Measurement probabilities are defined in terms of positive operators

$$\Pi_j = \Omega_j^\dagger \Omega_j, \tag{11.14}$$

with each operator corresponding to a different measurement outcome. The operators Ω_j that make up the positive operators are called **Kraus operators**.

- The probability of the jth measurement outcomes is given in terms of the expectation value

$$P(j) = \langle \Pi_j \rangle \,, \tag{11.15}$$
(POVM measurement probability)

whether in terms of the state vector as $\langle\psi|\Pi_j|\psi\rangle$ or density operator as $\mathrm{Tr}\Pi_j\rho$.

- In the jth measurement outcome, the change (11.7) in the state generalizes to

$$|\psi\rangle \longrightarrow \frac{\Omega_j|\psi\rangle}{\sqrt{\langle\psi|\Pi_j|\psi\rangle}} = \frac{\Omega_j|\psi\rangle}{\sqrt{\langle\psi|\Omega_j^\dagger\Omega_j|\psi\rangle}}, \tag{11.16}$$
(POVM state collapse)

because the norm of the state $\Omega_j|\psi\rangle$ matches the probability of the outcome.

- Alternatively, the state collapse may be written

$$\rho \longrightarrow \frac{\Omega_j \rho \Omega_j^\dagger}{\mathrm{Tr}[\Omega_j \rho \Omega_j^\dagger]} \tag{11.17}$$
(POVM state collapse)

in terms of the density operator ρ. In either this case or the case of a pure state, the Kraus operator specifies the effect of the measurement outcome on the quantum state. Note that there may be many possible Kraus operators Ω_j corresponding to the same positive operator Π_j, because any unitarily transformed operator $U\Omega_j$ can serve equally well in the same role. Thus there are different possible measurement effects on the quantum state, corresponding to the same set of measurement probabilities.

- A set of operators defines a complete set of measurement outcomes if

$$\sum_j P(j) = \sum_j \langle \Pi_j \rangle = 1. \tag{11.18}$$

This is basically saying that the operators define a "probability measure." For this condition to hold for every state $|\psi\rangle$ or ρ, the condition

$$\sum_j \Pi_j = 1 \tag{11.19}$$
(POVM completeness)

must hold, where the "1" on the right-hand side is the identity operator on the Hilbert space. This is a **completeness** requirement on the set of positive operators. Under this conditions the Π_j define a **positive-operator-valued measure** or **POVM**. This is like a probability measure, but instead assigns **operators** to measurement outcomes instead of probabilities. Then quantum mechanics assigns probabilities to the measurement outcomes via expectation values.

Of course any given complete set of positive operators may or may not correspond to a physically meaningful measurement; it is up to you, the physicist, to design a physically useful POVM to model a measurement.

11.1.4 Axiomatic Implications

It looks like we may have just gone and mucked with Born's rule, one of the axioms of quantum mechanics that we started off with. And indeed we did. In this case it's useful to discuss a couple of relevant results (which we will do without proof), to see the implications of generalized measurements.

The first result is **Naimark's theorem** (or **Neumark's theorem**),[1] which says that any POVM may be constructed via a unitary operation plus a projective measurement. The main implication of course is that measurements generalized to POVMs are compatible with the axioms of quantum mechanics as previously stated. Intuitively, this means that POVMs that are *not* projective correspond to *indirect* measurements. That is, suppose we want to make an indirect measurement on a system represented by $|\psi\rangle$. First, the state interacts with *another* system $|\mathrm{E}\rangle$ (for the ''environment''), and the two systems become entangled via the interaction. Then an observer makes a projective measurement, but *only* on the environment. This of course destroys the entanglement and provides (partial) information about the system state $|\psi\rangle$ (with more entanglement typically yielding more complete information). In this way, for example, a realistic position measurement can leave the system in a state of nonzero position uncertainty. Another good example of an indirect measurement is scattering a photon from an atom, and then measuring the photon with a photodetector to gain some information about the atom (such as its position, in a ''Heisenberg microsope'').

The other result to mention now is **Gleason's theorem**.[2] Suppose that you have a set of positive operators Π_j that makes up a POVM. Then Gleason's theorem says that the *only* way to assign probabilities via these operators is through the trace $\mathrm{Tr}[\Pi_j\rho]$ with respect to some positive semidefinite operator ρ, which we can interpret as the density operator. This says that the density operator can be regarded as more fundamental than the state vector, as far as representing the state of the system; it also mostly *replaces* Born's rule as an axion, requiring only the assumptions that the Π_j means something and the assumptions underlying the notion of probability and that quantum mechanics should predict them (assumptions already implicit in Born's rule).

11.2 Quantum State Discrimination

A good example of a POVM comes in the problem of **quantum state discrimination**.[3] The setup is as follows. Suppose a quantum system is prepared in one of two pure states $|\psi_0\rangle$ or $|\psi_1\rangle$, but we don't know which. However, we want to find out by making measurements.

The simplest case is when the states are orthogonal, $\langle\psi_1|\psi_0\rangle = 0$. This is trivial because there are projectors

$$P_0 = |\psi_0\rangle\langle\psi_0|, \qquad P_1 = |\psi_1\rangle\langle\psi_1|, \tag{11.20}$$

such that

$$P_i P_j = \delta_{ij} P_j. \tag{11.21}$$

These projectors make up the POVM (*projector*-valued measure, in fact); the measurement outcome indicates the state, and even leaves the state untouched after the measurement.

In the general case, $\langle\psi_1|\psi_0\rangle \neq 0$. This is nontrivial because the states can't be discriminated unambiguously via projectors ($P_i P_j \neq \delta_{ij} P_j$). To start, let's call p_0 the probability that the state is $|\psi_0\rangle$ and p_1 the probability that the state is $|\psi_1\rangle$. That is, the state of the system is

$$\rho = p_0|\psi_0\rangle\langle\psi_0| + p_1|\psi_1\rangle\langle\psi_1|, \tag{11.22}$$

because the uncertainty in the state preparation is a *classical* uncertainty, leading to a mixed quantum state.

[1] Asher Peres, *Quantum Theory: Concepts and Methods* (Springer, 1995), Section 9-6, p. 285.

[2] Andrew M. Gleason, ''Measures on the closed subspaces of a Hilbert space,'' *Indiana University Mathematics Journal* **6**, 885 (1957) (doi: 10.1512/iumj.1957.6.56050). For a simplified derivation, see Paul Busch, ''Quantum States and Generalized Observables: A Simple Proof of Gleason's Theorem,'' *Physical Review Letters* **91**, 120403 (2003) (doi: 10.1103/PhysRevLett.91.120403). For interesting commentary, see H. Barnum, C. M. Caves, J. Finkelstein, C. A. Fuchs, and R. Schack, ''Quantum probability from decision theory?'' *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* **456**, 1175 (1997) (doi: 10.1098/rspa.2000.0557).

[3] Here we are following parts of the tutorial by Stephen M. Barnett and Sarah Croke, ''Quantum state discrimination,'' *Advances in Optics and Photonics* **1**, 238 (2009) (doi: 10.1364/AOP.1.000238).

11.2.1 Two-Outcome Measurement

Now let's try to set up a POVM, with operators Π_0 and Π_1 that respectively indicate that the state is $|\psi_0\rangle$ and $|\psi_1\rangle$. To decide what the POVM operators (projectors, in this case) should be, consider the probability of making an error (i.e., misidentifying the state):

$$P_{\text{error}} = P(\psi_0)P(1|\psi_0) + P(\psi_1)P(0|\psi_1). \tag{11.23}$$

Here, $P(\psi_j)$ is the probability that the state is $|\psi_j\rangle$, and $P(i|\psi_j)$ is the probability of getting the measurement result i given that the state was actually $|\psi_j\rangle$. From the definitions of these probabilities, we can rewrite the error probability as

$$P_{\text{error}} = p_0\langle\psi_0|\Pi_1|\psi_0\rangle + p_1\langle\psi_1|\Pi_0|\psi_1\rangle. \tag{11.24}$$

Then using $\Pi_1 = 1 - \Pi_0$ and writing the expectation values in terms of a trace,

$$P_{\text{error}} = p_0 - \text{Tr}\Big[\Big(p_0|\psi_0\rangle\langle\psi_0| - p_1|\psi_1\rangle\langle\psi_1|\Big)\Pi_0\Big]. \tag{11.25}$$

The second term is of the form $\text{Tr}[Q\Pi_0]$; in order to *minimize* the error probability we should *maximize* the value of the trace.

To proceed with the error minimization, note that this operator Q is Hermitian but not generally positive. It thus has one positive and one negative eigenvalue, which we can call $q_\pm$, with corresponding eigenvectors $|\pm\rangle$. Then notice that the error probability is minimized by picking

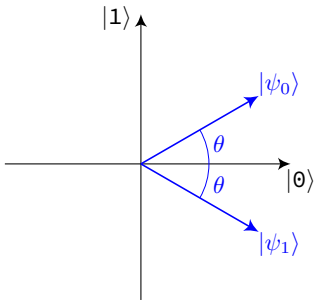
$$\Pi_0 = |+\rangle\langle+|, \tag{11.26}$$

which of course is a projection operator (with $\Pi_1 = |-\rangle\langle-|$ to form a POVM).

To compute the error probability, we will need to compute the eigenvalue q_+. Although $|\psi_0\rangle$ and $|\psi_1\rangle$ are not orthogonal, they define a two-dimensional vector space. We can thus choose an orthonormal basis $\{|\mathtt{0}\rangle, |\mathtt{1}\rangle\}$ such that

$$\begin{aligned} |\psi_0\rangle &= \cos\theta|\mathtt{0}\rangle + \sin\theta|\mathtt{1}\rangle \\ |\psi_1\rangle &= \cos\theta|\mathtt{0}\rangle - \sin\theta|\mathtt{1}\rangle, \end{aligned} \tag{11.27}$$

with $\theta \in (0, \pi/4)$. Intuitively, the state $|\mathtt{0}\rangle$ is geometrically in between the two states to discriminate, and $|\mathtt{1}\rangle$ is the orthogonal state, as shown below.



Then, for example, we can write the inner product

$$\langle\psi_1|\psi_0\rangle = \cos^2\theta - \sin^2\theta = \cos 2\theta, \tag{11.28}$$

which corresponds to the intuitive from the diagram. Now if we write the projectors as matrices in the $\{|\mathtt{0}\rangle, |\mathtt{1}\rangle\}$ representation, we have

$$\Big(|\psi_0\rangle\langle\psi_0|\Big) = \begin{bmatrix} \cos^2\theta & \cos\theta\sin\theta \\ \cos\theta\sin\theta & \sin^2\theta \end{bmatrix} \tag{11.29}$$

and

$$\Big(|\psi_1\rangle\langle\psi_1|\Big) = \begin{bmatrix} \cos^2\theta & -\cos\theta\sin\theta \\ -\cos\theta\sin\theta & \sin^2\theta \end{bmatrix} \tag{11.30}$$

Then the operator we need to consider is

$$(Q) = \Big(p_0|\psi_0\rangle\langle\psi_0| - p_1|\psi_1\rangle\langle\psi_1|\Big) = \begin{bmatrix} (p_0-p_1)\cos^2\theta & \cos\theta\sin\theta \\ \cos\theta\sin\theta & (p_0-p_1)\sin^2\theta \end{bmatrix}. \tag{11.31}$$

The eigenvalues are (Problem 11.1)

$$q_\pm = \frac{1}{2}\left(p_0 - p_1 \pm \sqrt{1-4p_0p_1\cos^2 2\theta}\right). \tag{11.32}$$

Then since $\Pi_0 = |+\rangle\langle+|$ and $Q = q_+|+\rangle\langle+| + q_-|-\rangle\langle-|$, the error probability (11.25) is

$$P_{\text{error}} = p_0 - \text{Tr}[Q\Pi_0] = p_0 - q_+ = \frac{p_0+p_1}{2} - \frac{1}{2}\sqrt{1-4p_0p_1\cos^2 2\theta}, \tag{11.33}$$

or

$$P_{\text{error}} = \frac{1}{2}\left(1 - \sqrt{1-4p_0p_1|\langle\psi_1|\psi_0\rangle|^2}\right). \tag{11.34}$$

(Helstrom bound)

This error is called the **Helstrom bound**, which is the minimum error that can be made by projective measurements.

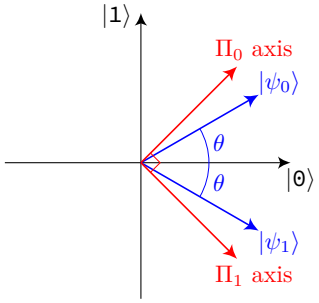
To interpret these results, first suppose $p_0 = p_1 = 1/2$. In this case, the operator is

$$(Q) = \begin{bmatrix} 0 & \cos\theta\sin\theta \\ \cos\theta\sin\theta & 0 \end{bmatrix}, \tag{11.35}$$

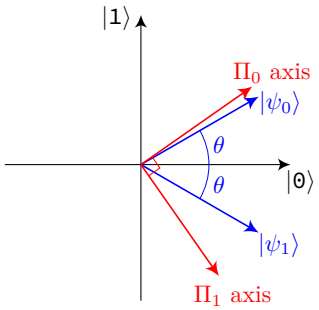
which has the same form as the Hamiltonian of a symmetric double-well potential. The eigenvectors are thus [Eq. (3.49)]

$$|q_\pm\rangle = \frac{|0\rangle \pm |1\rangle}{\sqrt{2}}. \tag{11.36}$$

The projectors Π_0 and Π_1 should correspond to these two directions, and are thus orthogonal and equally spaced about $|\psi_0\rangle$ and $|\psi_1\rangle$, as shown in the diagram below.



In the case $p_0 \neq p_1$, the projection axes are still orthogonal, but will not have the same orientation. Intuitively, if $p_0 > p_1$ then we should have a smaller error in the case of a Π_0 measurement, in which case the Π_0 axis should better match the $|\psi_0\rangle$ axis, as shown below.



11.2.1.1 Physical Realization

At this point, it may make the above treatment seem a little less abstract if we discuss how you might realize this state discrimination experimentally. A convenient two-state quantum system is a photon (Section3.4.2). Suppose that Alice prepares a photon in one of two linear-polarization states, with polarization axes separated by 2θ. Alice points the photon in Bob's direction, and Bob will try to figure out in which of the two polarization states Alice prepared the photon. To be specific about the assumptions: Bob knows the two possible polarization axes that Alice is using, and also the probabilities p_0 and p_1 that she will choose one or the other polarization state, but he doesn't know in advance which state she chose in advance.

In the case of orthogonal ($2\theta = 90°$) polarization states, Bob doesn't have any problem, assuming he has access to an ideal polarizer. He aligns it with one of the axes, say $|\psi_0\rangle$, in which case the polarizer realizes the $\Pi_0 = |\psi_0\rangle\langle\psi_0|$ projective measurement: if the photon passes through the polarizer, Bob knows that Alice prepared the $|\psi_0\rangle$ state; if the polarizer blocks the photon, then the only other possibility is that Alice prepared the $|\psi_1\rangle$ state.

In the case of *non*orthogonal ($0 < 2\theta < 90°$) polarization states, this strategy leaves some ambiguity. If Bob aligns the polarizer to the $|\psi_0\rangle$ axis, and the photon passes through, then he can't conclude with certainty that the state was $|\psi_0\rangle$, because the $|\psi_1\rangle$ polarization has a nonzero projection onto the polarizer axis—this leads to an error probability of $\cos^2 2\theta$ if the photon was actually in $|\psi_1\rangle$. (On the other hand, for this particular setup, Bob *can* conclude with certainty that the polarization state was $|\psi_1\rangle$ if the polarizer *blocks* the photon.)

Then the above treatment says that the optimal measurement strategy, given that we set up a measurement with only two outcomes, is to *still* use the linear polarizer. But the strategy that minimizes the error probability in the symmetric ($p_0 = p_1$) case is to misalign both the pass and block axes of the polarizer symmetrically away from the two polarization states—it turns out to be better to distribute the error between the two possibilities rather than to concentrate the error into one state.

11.2.2 Unambiguous Discrimination

In the above treatment of state discrimination, the assumptions were that we wanted a *definite* answer after the measurement, and we then proceeded to minimize the error associated with the measurement procedure. Quantum mechanics can provide a which-state answer that is *error-free*, but of course at a cost. This is the problem of **unambiguous quantum-state discrimination**.[4] Because the states to discriminate are not orthogonal, in the previous discrimination problem the best we could do is to choose two orthogonal projectors $\Pi_0 = |+\rangle\langle+|$ and $\Pi_1 = |-\rangle\langle-|$. Because the projection axes ultimately did not align with the states to discriminate, the projective measurements involved error. But now suppose we try to *eliminate* completely any errors. To do this, we should choose measurement operators such that

$$\begin{aligned} \langle\psi_1|\Pi_0|\psi_1\rangle &= 0 \\ \langle\psi_0|\Pi_1|\psi_0\rangle &= 0. \end{aligned} \tag{11.37}$$

That is, the probability for the measurement to ''fire'' in the wrong state is zero. In that case, a measurement result corresponding to Π_0 means that the state is *definitely* $|\psi_0\rangle$, and a Π_1 result means that the state is *definitely* $|\psi_1\rangle$.

Going back to the expressions (11.27) for the two states in the $\{|\mathtt{0}\rangle, |\mathtt{1}\rangle\}$ basis, repeated here,

$$\begin{aligned} |\psi_0\rangle &= \cos\theta|\mathtt{0}\rangle + \sin\theta|\mathtt{1}\rangle \\ |\psi_1\rangle &= \cos\theta|\mathtt{0}\rangle - \sin\theta|\mathtt{1}\rangle, \end{aligned} \tag{11.38}$$

[4]Here we are again following parts of the tutorial by Stephen M. Barnett and Sarah Croke, *op. cit.*; the original papers to consider this problem are: I. D. Ivanovic, ''How to differentiate between non-orthogonal states,'' *Physics Letters A* **123**, 257 (1987) (doi: 10.1016/0375-9601(87)90222-2); D. Dieks, ''Overlap and distinguishability of quantum states,'' *Physics Letters A* **126**, 303 (1988) (doi: 10.1016/0375-9601(88)90840-7); and Asher Peres, ''How to differentiate between non-orthogonal states,'' *Physics Letters A* **128**, 19 (1988) (doi: 10.1016/0375-9601(88)91034-1). The case of unequal probabilities for the two states was considered by Gregg Jaeger and Abner Shimony, ''Optimal distinction between two non-orthogonal quantum states,'' *Physics Letters A* **197**, 83 (1995) (doi: 10.1016/0375-9601(94)00919-G)

we can construct orthogonal vectors

$$\begin{aligned} |\oplus\rangle &= \sin\theta|\mathtt{0}\rangle + \cos\theta|\mathtt{1}\rangle \qquad \Longrightarrow \qquad \langle\oplus|\psi_1\rangle = 0 \\ |\ominus\rangle &= \sin\theta|\mathtt{0}\rangle - \cos\theta|\mathtt{1}\rangle \qquad \Longrightarrow \qquad \langle\ominus|\psi_0\rangle = 0. \end{aligned} \tag{11.39}$$

Of course, these vectors do not form an orthogonal pair:

$$\langle\ominus|\oplus\rangle = \sin^2\theta - \cos^2\theta = -\cos 2\theta \neq 0. \tag{11.40}$$

However, we can proceed by choosing unambiguous projectors

$$\Pi_0 = a_0|\oplus\rangle\langle\oplus|, \qquad \Pi_1 = a_1|\ominus\rangle\langle\ominus|, \tag{11.41}$$

for some constants a_0 and a_1. These two projectors project in nonorthogonal directions, and so they cannot form a complete POVM for any choice of a_0 and a_1. To see this explicitly, note that the $|\mathtt{0}\rangle\langle\mathtt{0}|$ components of Π_0 and Π_1 are $a_0\sin^2\theta$ and $a_1\sin^2\theta$, respectively. The $|\mathtt{1}\rangle\langle\mathtt{1}|$ components of Π_0 and Π_1 are $a_0\cos^2\theta$ and $a_1\cos^2\theta$, respectively. For completeness, these operators should sum to the identity, which gives $a_0 + a_1 = 1/\sin^2\theta = 1/\cos^2\theta$, which is only possible in the case of orthogonal vectors $\langle\psi_1|\psi_0\rangle = 0$.

Then to complete the POVM, we need a *third* measurement operator, which we can define by

$$\Pi_? := 1 - \Pi_0 - \Pi_1. \tag{11.42}$$

This information doesn't discriminate between the two possible states, and so we can call it the "I don't know" outcome: it is the price we have to pay for demanding unambiguous state discrimination. The probability for this outcome to occur is

$$P(?) = \mathrm{Tr}[\Pi_?\rho], \tag{11.43}$$

with the quantum state (11.22)

$$\rho = p_0|\psi_0\rangle\langle\psi_0| + p_1|\psi_1\rangle\langle\psi_1|. \tag{11.44}$$

Thus,

$$P(?) = p_0\langle\psi_0|\Pi_?|\psi_0\rangle + p_1\langle\psi_1|\Pi_?|\psi_1\rangle, \tag{11.45}$$

and using the I-don't-know operator (11.42) and the orthogonality conditions (11.37), we find

$$P(?) = p_0 + p_1 - p_0\langle\psi_0|\Pi_0|\psi_0\rangle - p_1\langle\psi_1|\Pi_1|\psi_1\rangle. \tag{11.46}$$

Now computing products of the vectors (11.38) and (11.39) gives $\langle\psi_0|\Pi_0|\psi_0\rangle = 4a_0\sin^2\theta\cos^2\theta$ and $\langle\psi_1|\Pi_1|\psi_1\rangle = 4a_1\sin^2\theta\cos^2\theta$, so that

$$P(?) = 1 - (p_0a_0 + p_1a_1)\sin^2 2\theta \tag{11.47}$$

after using $2\sin\theta\cos\theta = \sin 2\theta$.

11.2.2.1 Symmetric Case

To proceed, let's simplify things by assuming that the two states are equally likely, $p_0 = p_1 = 1/2$. Then the probability of an inconclusive outcome is

$$P(?) = 1 - \frac{(a_0 + a_1)}{2}\sin^2 2\theta. \tag{11.48}$$

To get a good overview of where we stand, it's handy to write out the measurement operators in matrix form. The discriminating operators are

$$\big(\Pi_0\big) = a_0\begin{bmatrix} \sin^2\theta & \sin\theta\cos\theta \\ \sin\theta\cos\theta & \cos^2\theta \end{bmatrix}, \qquad \big(\Pi_1\big) = a_1\begin{bmatrix} \sin^2\theta & -\sin\theta\cos\theta \\ -\sin\theta\cos\theta & \cos^2\theta \end{bmatrix}, \tag{11.49}$$

in the $\{|\mathtt{0}\rangle, |\mathtt{1}\rangle\}$ basis, in that order. Then the inconclusive operator is

$$(\Pi_?) = \begin{bmatrix} 1-(a_0+a_1)\sin^2\theta & (a_1-a_0)\sin\theta\cos\theta \\ (a_1-a_0)\sin\theta\cos\theta & 1-(a_0+a_1)\cos^2\theta \end{bmatrix}. \tag{11.50}$$

We need this operator to be positive, so not all values of $a_{0,1}$ are permissible. Remember that we chose $0 < \theta < \pi/4$, so that $\cos^2\theta > \sin^2\theta$, so our main constraint is

$$a_0 + a_1 \leq \frac{1}{\cos^2\theta}. \tag{11.51}$$

Of course, we minimize the possibility of an inconclusive outcome by maximizing $a_{0,1}$, so we will choose the equality:

$$a_0 + a_1 = \frac{1}{\cos^2\theta}. \tag{11.52}$$

Then the probability (11.48) that we fail to discriminate the state is

$$P(?) = 1 - \frac{\sin^2 2\theta}{2\cos^2\theta} = \cos 2\theta = |\langle\psi_1|\psi_0\rangle|, \tag{11.53}$$

(optimal inconclusive probability)

which is just the state overlap. Then by symmetry we should choose $a_0 = a_1$, so that the discriminating operators (11.41) become

$$\Pi_0 = \frac{|\oplus\rangle\langle\oplus|}{2\cos^2\theta} = \frac{|\oplus\rangle\langle\oplus|}{1+|\langle\psi_1|\psi_0\rangle|}, \qquad \Pi_1 = \frac{|\ominus\rangle\langle\ominus|}{2\cos^2\theta} = \frac{|\ominus\rangle\langle\ominus|}{1+|\langle\psi_1|\psi_0\rangle|}. \tag{11.54}$$

The inconclusive operator is

$$\Pi_? = \big(1-\tan^2\theta\big)|\mathtt{0}\rangle\langle\mathtt{0}|, \tag{11.55}$$

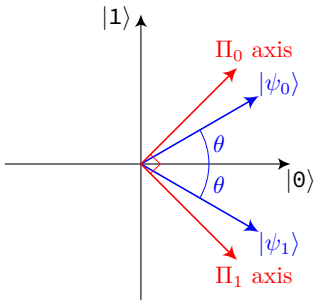
which is easiest to see from Eq. (11.50). With a bit more algebra, we can rewrite this operator as

$$\Pi_? = \frac{2|\langle\psi_1|\psi_0\rangle|}{1+|\langle\psi_1|\psi_0\rangle|}|\mathtt{0}\rangle\langle\mathtt{0}|, \tag{11.56}$$

in coordinate-independent form.

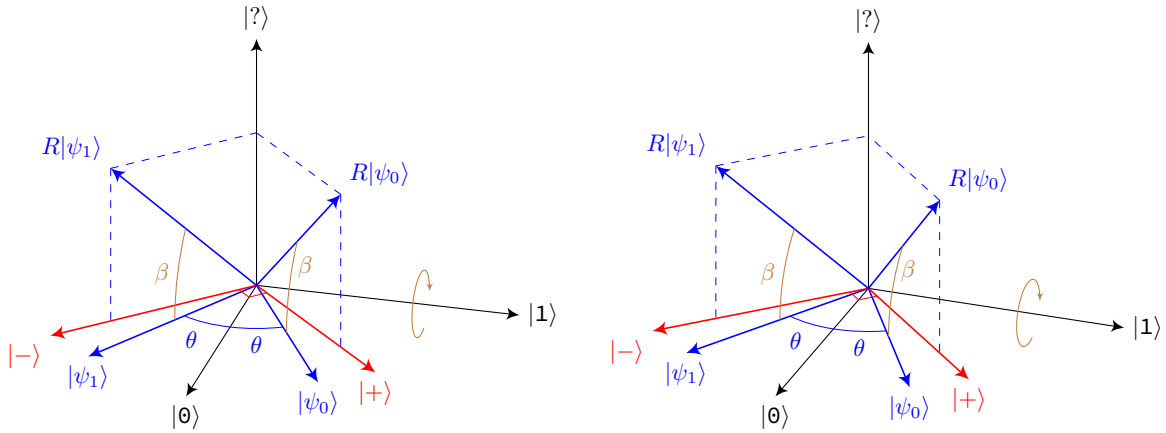
11.2.2.2 Geometric Interpretation

The above mathematical solution has a nice geometric interpretation.[5] Let's go back to the setup for state discrimination in the *ambiguous* case, where we used two orthogonal projectors. The optimal projectors were symmetrically placed about the two possible states, in the equal-likelihood case $p_0 = p_1$, as shown again below.



[5] B. Huttner, A. Muller, J. D. Gautier, H. Zbinden, and N. Gisin, "Unambiguous quantum measurement of nonorthogonal states," *Phys. Rev. A* **54**, 3783 (1996) (doi: 10.1103/PhysRevA.54.3783).

Now let's extend the $\{|0\rangle, |1\rangle\}$ space into three dimensions, calling the third dimension $|?\rangle$. The same vectors are again shown in the $|0\rangle$–$|1\rangle$ plane below, with the $|\pm\rangle$ vectors still representing the orthogonal projection axes.[6]



Now consider additionally a *rotation* of the possible states $|\psi_0\rangle$ and $|\psi_1\rangle$ by an angle β about the $|1\rangle$ axis as shown (technically, this is a rotation by $-\beta$ with right-hand rules). The idea is that, with just the right rotation angle, the projections of the rotated vectors $R|\psi_{0,1}\rangle$ into the $|0\rangle$–$|1\rangle$ plane fall on the $|\pm\rangle$ orthogonal projection directions, as shown. Of course, now the rotated vectors *also* have some projection along the $|?\rangle$ direction. But if we then make a projective measurement, we can get the two definite outcomes $|\psi_{0,1}\rangle$ (corresponding to the $|\pm\rangle$ directions), with the possibility of an inconclusive outcome (corresponding to the $|?\rangle$ direction).

To work through this, we can start again with the expressions (11.27) for the two states in the $|\pm\rangle$ basis, repeated here:

$$\begin{aligned} |\psi_0\rangle &= \cos\theta|0\rangle + \sin\theta|1\rangle \\ |\psi_1\rangle &= \cos\theta|0\rangle - \sin\theta|1\rangle. \end{aligned} \tag{11.57}$$

With the rotation about the $|1\rangle$ axis, these become

$$\begin{aligned} R|\psi_0\rangle &= \cos\theta\cos\beta|0\rangle + \sin\theta|1\rangle + \cos\theta\sin\beta|?\rangle \\ R|\psi_1\rangle &= \cos\theta\cos\beta|0\rangle - \sin\theta|1\rangle + \cos\theta\sin\beta|?\rangle. \end{aligned} \tag{11.58}$$

Now we need to rewrite this in the orthogonal measurement basis. Recalling $|\pm\rangle = (|0\rangle \pm |1\rangle)/\sqrt{2}$, this means

$$|0\rangle = \frac{|+\rangle + |-\rangle}{\sqrt{2}}, \qquad |1\rangle = \frac{|+\rangle - |-\rangle}{\sqrt{2}}. \tag{11.59}$$

Putting these into Eqs. (11.58),

$$\begin{aligned} R|\psi_0\rangle &= \frac{1}{\sqrt{2}}\big(\cos\theta\cos\beta + \sin\theta\big)|+\rangle + \frac{1}{\sqrt{2}}\big(\cos\theta\cos\beta - \sin\theta\big)|-\rangle + \cos\theta\sin\beta|?\rangle \\ R|\psi_1\rangle &= \frac{1}{\sqrt{2}}\big(\cos\theta\cos\beta - \sin\theta\big)|+\rangle + \frac{1}{\sqrt{2}}\big(\cos\theta\cos\beta + \sin\theta\big)|-\rangle + \cos\theta\sin\beta|?\rangle. \end{aligned} \tag{11.60}$$

The condition for the rotated states to project down to the orthogonal projectors amounts to them being orthogonal to the *opposing* projector—that is, we want $R|\psi_0\rangle \perp |-\rangle$ and $R|\psi_1\rangle \perp |+\rangle$. Both of these happen if we choose the rotation angle β such that

$$\cos\beta = \tan\theta. \tag{11.61}$$

[6] Why are you seeing double in this figure? See the explanation in the usage chapter, starting on p. 20.

Under this choice of rotation angle, Eqs. (11.60) become

$$\begin{aligned} R|\psi_0\rangle &= \sqrt{2}\sin\theta|+\rangle + \sqrt{\cos 2\theta}|?\rangle \\ R|\psi_1\rangle &= \sqrt{2}\sin\theta|-\rangle + \sqrt{\cos 2\theta}|?\rangle \end{aligned} \tag{11.62}$$

after some simplification.

After the rotation, the idea is to implement a projective measurement with projectors

$$P_0 = |+\rangle\langle+|, \qquad P_1 = |-\rangle\langle-|, \qquad P_? = |?\rangle\langle?|. \tag{11.63}$$

Obviously in either case of the real state being $|\psi_0\rangle$ or $|\psi_1\rangle$, the probability of the inconclusive outcome is

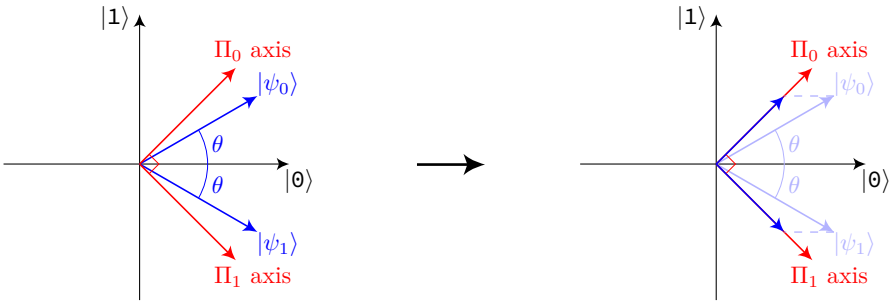
$$P(?) = \cos 2\theta = |\langle\psi_1|\psi_0\rangle|, \tag{11.64}$$

in agreement with the result (11.53) of the POVM analysis.

Now one last question. From this geometric interpretation, what should the observer's quantum state be after a measurement returns the inconclusive result? (The state in the $|\mathtt{0}\rangle$–$|\mathtt{1}\rangle$ basis, that is.) Is it possible to obtain further information by repeating a state-discrimination measurement?[7]

11.2.2.3 Physical Realization

Now let's go back to the discussion of Section 11.2.1.1 about the physical realization of a quantum-state-discrimination experiment. To adapt the experiment to the unambiguous version is actually pretty simple, at least in principle. The previous situation in the ambiguous version of the experiment is shown below on the left. One way to interpret the "problem" of the nonorthogonal polarization states, is that there is "too much" of each polarization along the $|\mathtt{0}\rangle$ axis. So suppose that we could reduce the components of $|\psi_0\rangle$ and $|\psi_1\rangle$ along the $|\mathtt{0}\rangle$ direction, as shown in the diagram below to the right.



Physically, this can be accomplished by passing the photons through a medium that partially absorbs only light that is polarized along the $|\mathtt{0}\rangle$ direction. The thickness of the medium can be fine-tuned to provide just the right amount of attenutation for any given value of θ. Then look what happened: the problem has been reduced to the case of two orthogonal polarization states, for which we can make an error-free measurement. The price, of course, is that the two initial states $|\psi_0\rangle$ and $|\psi_1\rangle$ are no longer normalized, because the photons were absorbed by the medium with some probability. That absorption even corresponds to the $\Pi_?$ outcome, because the absorbed photon can't provide any information about the polarization being in the $|\psi_0\rangle$ vs. $|\psi_1\rangle$ direction. (Of course, the final polarizer has to be modified so that it gives a which-polarization measurement, which can be realized by a polarizing beam splitter and a pair of photodetectors.)

[7] First, remembering that the final state should refer to the $|\mathtt{0}\rangle$–$|\mathtt{1}\rangle$ plane, the inconclusive result is orthogonal to this plane, which has no particular orientation. Reasonable guesses then include just 0 (null vector) or the I-don't-know state (density operator proportional to the identity). The first answer is what you expect from the geometric picture, but the second result is more sensible for the POVM setup, which only refers to the $|\mathtt{0}\rangle$–$|\mathtt{1}\rangle$ plane.

11.2.3 Quantum Cryptography

The problem of discriminating between two nonorthogonal states might seem like a strange and artificial one, but besides making for an interesting example of a POVM, it does have an important application: that of **quantum cryptography**. The idea is that Alice wants to send Bob a secure message, encoded in binary. There is no *classical* way to send the message (even with classical cryptographic techniques) that guarantees that the message was not intercepted, copied, and sent on to Bob. In quantum mechanics, the no-cloning theorem suggests that it might be possible to make a guaranteed secure transmission of information. Indeed this is possible, and while there are many schemes for quantum cryptography, nonorthogonal states play a central role.[8]

In general, quantum-mechanical techniques are much more costly than standard classical encryption based on prime factorization of large numbers. However, classical encryption relies on Alice and Bob having some shared information, which we can call the **encryption key** (or keys), to make the encryption work. Short of hand-delivery to Bob, though Alice can't guarantee the secure transmission of the key, and so one of the main applications of quantum cryptography is secure distribution of keys, or **quantum key distribution** (QKD).

If Alice tries to send Bob some information as a (classical) bit stream by encoding the bits in terms of a pair of *orthogonal* states $|\psi_0\rangle$ and $|\psi_1\rangle$ comes when we consider an eavesdropper (by convention, named "Eve"). Bob can receive and discriminate the orthogonal states perfectly in principle. But this means that if Eve can guess the basis in which the message is being sent, she can perform a man-in-the-middle attack by intercepting a data stream, decoding the data, and then sending a perfect copy on to Bob. This doesn't violate the no-cloning theorem, because the extra information that the state is one or the other element of a pure-state basis is enough to allow cloning (and indeed is what allows Bob to decode it perfectly).

This is where, perversely, the *unreliability* of discriminating *nonorthogonal* states becomes an asset. Suppose Alice encodes the bit stream in nonorthogonal states $|\psi_0\rangle$ and $|\psi_1\rangle$. Bob will fail to receive the bit in a fraction $|\langle\psi_1|\psi_0\rangle|$ of cases. This is no problem, because Alice can transmit a bunch of extra bits, and Bob can report which bits didn't work out (over an *insecure* channel, since information about rejected bits can't help Eve). The net result is Alice and Bob share a common set of random bits. This could be the basis for a classical encryption key, or they could send information, for example, by `XOR`ing the message with random bits, and a second `XOR` at the other end with the same random bits will recover the information. (In this simple scheme, the random bits can't be reused, because Eve could look to see which bits aren't changing very often in successive messages to infer information about what is being transmitted.)

Now what happens when Eve tries to listen in on the data stream? She will randomly be unsuccessful at decoding a bit at the same rate as Bob, in which case she won't be able to clone the bit and send it along to Bob. Thus, she will have to fudge these bits, and at best a fraction $|\langle\psi_1|\psi_0\rangle|/2$ on average will disagree with the original bit stream. Bob will then decode the molested data stream, and will be unsuccessful at decoding a *different* fraction $|\langle\psi_1|\psi_0\rangle|$ of bits than Eve. At the end of the process, Bob's bits will differ from Alice's, even after rejection. Then some of the extra random information sent over the secure channel by Alice can be used as a message from Bob back to Alice to validate the QKD channel. The smoking gun alerting Alice and Bob to Eve's presence is that Alice won't be able to decode the test message to match the original bit stream. Eve doesn't have the full encryption key, so she can't even intercept and modify the test message to make Alice think the channel is secure. So in the case where the test message works, the encryption key was sent successfully, with a guarantee that nobody has a copy of it. Pretty cool.

11.2.4 Discriminating Coherent States

Another good and relatively simple example of unambiguous quantum state discrimination is between two coherent states.[9] For example, suppose that a quantum harmonic oscillator is prepared in either the $|\alpha\rangle$ or $|-\alpha\rangle$ coherent state. For simplicity, we will assume throughout that $\alpha \in \mathbb{R}$. Remember that these are Gaussian states (separated in position, in this case), and therefore nonorthogonal.

[8] Charles H. Bennett, "Quantum cryptography using any two nonorthogonal states," *Physical Review Letters* **68**, 3121 (1992) (doi: 10.1103/PhysRevLett.68.3121).

[9] See, for example, S. J. van Enk, "Unambiguous state discrimination of coherent states with linear optics: Application to quantum cryptography," *Physical Review A* **66**, 042313 (2002) (doi: 10.1103/PhysRevA.66.042313).

The procedure for distinguishing the coherent states is to introduce a *second* harmonic oscillator in coherent state $|i\alpha\rangle$ (i.e., with the same displacement amplitude, but displaced in momentum instead of position). Then the two possible composite states are

$$|\psi_\pm\rangle = |\pm\alpha\rangle|i\alpha\rangle. \tag{11.65}$$

The idea will be to construct the POVM indirectly, through a unitary operation followed by a projective measurement. The unitary operation has the effect

$$U|\alpha\rangle|i\alpha\rangle = |0\rangle|i\sqrt{2}\alpha\rangle \tag{11.66}$$

in the first case, and

$$U|-\alpha\rangle|i\alpha\rangle = |-\sqrt{2}\alpha\rangle|0\rangle \tag{11.67}$$

for the alternate possibility. This transformation is not such an obvious one, so we will take care to justify it. This is a nonlocal unitary operation that mixes the two systems. It has a general form

$$U|\alpha_1\rangle|\alpha_2\rangle = |\beta_1\rangle|\beta_2\rangle, \tag{11.68}$$

which we can write as a transformation of the coefficients as

$$\begin{bmatrix} \beta_2 \\ \beta_1 \end{bmatrix} = U \begin{bmatrix} \alpha_2 \\ \alpha_1 \end{bmatrix} \tag{11.69}$$

for a unitary matrix U. For Eqs. (11.66) and (11.67), the matrix is given by

$$\begin{bmatrix} \beta_2 \\ \beta_1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 & i \\ i & 1 \end{bmatrix} \begin{bmatrix} \alpha_2 \\ \alpha_1 \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} \alpha_2 + i\alpha_1 \\ \alpha_1 + i\alpha_2 \end{bmatrix}. \tag{11.70}$$

In the more general case, the unitary matrix can have the form

$$\begin{bmatrix} \beta_2 \\ \beta_1 \end{bmatrix} = \begin{bmatrix} r & \tau \\ \tau^* & r^* \end{bmatrix} \begin{bmatrix} \alpha_2 \\ \alpha_1 \end{bmatrix}, \tag{11.71}$$

provided they satisfy

$$|r|^2 + |\tau|^2 = 1. \tag{11.72}$$

This is the transformation for the field amplitudes at the outputs of an optical beam splitter in terms of the inputs. The reflection and transmission amplitudes (2.137) of a square barrier have the same form (see the Stokes relations in Problem 2.28, and also how the coefficients work out in the case of a delta barrier in Problem 2.31). The optical analogy here points to an important implementation of this discrimination problem, because quantized optical waves are harmonic oscillators, and coherent states are the appropriate states to model coherent light (e.g., the output of a laser). Then the transformations (11.66) and (11.67) correspond to mixing the optical state to discriminate with a local reference field on a beam splitter; all the light goes into one or the other output port, depending on which coherent state we started with. (The other output is left only with vacuum fluctuations.) Since we haven't worked with the quantized electromagnetic field, we will also justify this transformation in terms of a linear coupling between two oscillators.

Once the transformation in Eqs. (11.66) and (11.67) have been effected, the measurement is simply an energy measurement of both oscillators. If both oscillators are found to be in the ground state then the result is inconclusive; otherwise we have discriminated the input state with certainty. Recalling the expansion (5.82) of a coherent state in the energy representation,

$$\langle n|\alpha\rangle = \frac{\alpha^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}, \tag{11.73}$$

the probability for the measurement to find the oscillator in the ground state is

$$|\langle 0|\alpha\rangle|^2 = e^{-|\alpha|^2}. \tag{11.74}$$

To adapt this to the present problem, we should make the replacement $\alpha \longrightarrow \sqrt{2}\alpha$, so that the probability of the inconclusive outcome is

$$P(?) = |\langle 0|\sqrt{2}\alpha\rangle|^2 = e^{-2|\alpha|^2}. \tag{11.75}$$

Note that from this expression for the probability, we can rewrite it as

$$P(?) = |\langle 0|\sqrt{2}\alpha\rangle|^2 = |\langle 0|2\alpha\rangle| = |\langle -\alpha|\alpha\rangle|, \tag{11.76}$$

which is exactly analogous to the inconclusive probability (11.53) in the qubit case.

11.3 Quantum Measurement as Bayesian Inference

With the introduction of POVMs as generalizations of quantum (von Neumann) measurements, it's useful to compare this to the *classical* analogue: classical Bayesian inference. In both the classical and quantum cases, the acquisition of data *refines* the information that one has about a system, modifying classical or quantum probabilities. This is a mild form of the Bayesian view of quantum mechanics; more details on this modern view of quantum measurement may be gleaned from more hardcore Bayesians.[10]

11.3.1 Bayes' Rule

Bayes' rule is the centerpiece of statistics from the Bayesian point of view, and its derivation is deceptively simple. The starting point is the definition of the **conditional probability** $P(B|A)$, the probability of event B occuring *given* that event A occurred:

$$P(A \wedge B) =: P(B|A)\, P(A). \tag{11.77}$$
(definition of conditional probability)

Read this as follows: $P(A \wedge B)$ is the probability that event A occurred *and* event B occurred, and this is the same as the probability of B occurring *given* that A has definitely occurred, but we must multiply by the probability that A occurred. [If A and B are independent, then by definition $P(B|A) = P(B)$ and $P(A \wedge B) = P(A)\, P(B)$].

Now writing Eq. (11.77) out for both $P(A \wedge B)$ and $P(B \wedge A)$ and equating the results, we can derive a relation between the conditional probabilities $P(A|B)$ and $P(B|A)$:

$$P(A|B) = \frac{P(B|A)\, P(A)}{P(B)}. \tag{11.78}$$

This is, in fact, **Bayes' rule**. It looks simple enough, but all the subtlety is in the *interpretation*, which we will facilitate by replacing B by one possible outcome D_α out of a set $\{D_\alpha\}$ of all possible, disjoint outcomes:

$$P(A|D_\alpha) = \frac{P(D_\alpha|A)P(A)}{P(D_\alpha)}. \tag{11.79}$$
(Bayes' rule)

The basic interpretation is that in learning that an outcome D_α (the "data" resulting from a measurement or experiment) actually occurred out of a set $\{D_\alpha\}$ of possible measurement outcomes, we can *refine* the probability we assign to A, reflecting our updated knowledge. The various factors are:

1. The **prior**: $P(A)$ represents the probability *assigned* to event A—*prior* to knowing the outcome of the measurement—based on any knowledge or assumptions. This probability is *not* conditioned on D_α, so it is also called the **unconditioned probability**.

[10] Rüdiger Schack, Todd A. Brun, and Carlton M. Caves, "Quantum Bayes rule," *Physical Review A* **64** 014305 (2001) (doi: 10.1103/PhysRevA.64.014305); Christopher A. Fuchs, "Quantum Mechanics as Quantum Information (and only a little more)," arXiv.org preprint (arXiv: quant-ph/0205039). This second paper is interesting overall, but also worth reading *just* for the quote from Hideo Mabuchi on p. 13.

2. The **likelihood function**: $P(D_\alpha|A)$ is the probability that the particular measurement outcome, or event D_α would occur, given that A actually happened. ''Likelihood'' here points to the observation that, if we observe D_α, a larger value of $P(D_\alpha|A)$ makes the event A more ''likely,'' or better able to ''explain'' the observed data.

3. The **renormalization factor**: $P(D_\alpha)$ is the (unconditioned) probability of the measurement outcome D_α, by which we must divide for the result to come out correctly. This is computed most simply by summing over the probabilities of a complete, nonintersecting set of outcomes A_β conditioned on D_α, weighted by the probabilities that the A_β occur:

$$P(D_\alpha) = \sum_\beta P(D_\alpha|A_\beta)\, P(A_\beta). \tag{11.80}$$

   This this basically the same as saying $P(D_\alpha \wedge \text{anything}) = P(D_\alpha)$.

4. The **posterior**: $P(A|D_\alpha)$ is the *refined* probability for the event A, now that we know that the measurement outcome D_α has occurred.

The posterior probability thus reflects the information *gained* or *revealed* by the occurrence of data D_α.

11.3.2 Example: The Monty Hall "Paradox"

A standard but useful example of applying Bayes' rule is the **Monty Hall problem**. This is standard almost to the point of being trite, but still this is a useful example in setting up our comparison to quantum measurement. The problem is inspired by the game show *Let's Make a Deal*, of which the host was Monty Hall. Typically on the show, Monty Hall would give some prize to a contestant, and then offer the contestant the opportunity to trade the prize in hand for some other prize hidden behind a door, curtain, cover, etc. Sometimes the hidden prize would be much more valuable, sometimes it would be a real stinker (a ''zonk'' prize, like a can of beans).[11]

There is an interesting back-story to this problem. Marylin vos Savant had a weekly column in a syndicated newspaper magazine, where she would answer questions, math puzzles and so on (having gained fame as having a record-high IQ). This was a problem that a reader posed; her solution caused something of an uproar, even among people who presumably should have known better.[12] The solution that vos Savant originally gave was absolutely correct, and she explained it in multiple compelling ways. In (slight) fairness to some of the objectors, we should be more precise about the assumptions involved in the problem, and see how Bayesian inference provides a nice interpretation of this problem.

The rules of the game are as follows:

1. You're a contestant on the game show *Let's Make a Deal*, and you are shown three doors; we will call them doors 1, 2, and 3.

2. Behind one door is a brand-new car, and behind the other two are goats (the zonks). We will suppose that you like cars very much, but you're less fond of goats: they smell funny and make you sneeze. We will also suppose that the prizes are randomly distributed, one behind each of the three doors, and that the problem is invariant under any permutation of the door labels.

3. You pick a door; we will call that one ''door 1'' without loss of generality. You stand to gain whatever is behind that door.

4. Monty opens up one of the other two doors to reveal a goat; without loss of generality we will call this door 3. We will assume the host knowingly and intentionally revealed a goat, and if he could do this in multiple ways, he would pick either possibility at random.

[11] A good example of the show is here: `https://www.youtube.com/watch?v=T5QYTrDReTo`. Marvel at the merch and fashion sense of yesteryear.

[12] The original problem, with many responses and her (priceless) reactions are online at `https://web.archive.org/web/20110728182056/http://www.marilynvossavant.com/articles/gameshow.html`. Imagine if this were a modern, online publication, what the comment section would look like! Monty Hall himself discusses the uproar at the time and how the problem was only loosely based on what he did on the show here: `https://www.youtube.com/watch?v=c1BSkquWkDo`.

5. The problem is: is it to your advantage to switch to door 2, or should you stay with door 1?

The answer (or "paradox"), somewhat counterintuitively, is that you double your chances of successfully winning the car if you switch doors[13]. This result is not hard to work out using Bayes' rule:

- **Prior:** we will define the three events C_α, which is the event where the car is behind door α. Since the arrangement is random,
$$P(C_\alpha) = \frac{1}{3} \qquad (\forall_{\alpha\in\{1,2,3\}}). \tag{11.81}$$

- **Data:** the outcome event, or data, that gives us information is D_3, which will be our shorthand for the goat being behind door 3 *and* the host chose to reveal door 3 if there were multiple choices for revealing a goat. If the car were behind door 1, then there are goats behind doors 2 and 3, so the host would have a 50% chance of opening door 3:
$$P(D_3|C_1) = \frac{1}{2}. \tag{11.82}$$
If the car were behind door 2, then opening door 3 would be the only choice,
$$P(D_3|C_2) = 1, \tag{11.83}$$
while if the car were behind door 3, opening door 3 wouldn't be an option:
$$P(D_3|C_3) = 0. \tag{11.84}$$
The probability for D_3 to occur is given by summing over all conditional probabilities for D_3, weighted by the probability of each conditioning event to occur:
$$P(D_3) = \sum_\alpha P(D_3|C_\alpha)\,P(C_\alpha) = \frac{1}{2}\cdot\frac{1}{3} + 1\cdot\frac{1}{3} + 0\cdot\frac{1}{3} = \frac{1}{2}. \tag{11.85}$$

- **Posterior:** Now, given the information revealed by Monty's choice, we can compute the *posterior* probability distribution for the car to be behind each door:
$$\begin{aligned} P(C_1|D_3) &= \frac{P(D_3|C_1)\,P(C_1)}{P(D_3)} = \frac{1}{3} \\ P(C_2|D_3) &= \frac{P(D_3|C_2)\,P(C_2)}{P(D_3)} = \frac{2}{3} \\ P(C_3|D_3) &= \frac{P(D_3|C_3)\,P(C_3)}{P(D_3)} = 0. \end{aligned} \tag{11.86}$$

Clearly it is to your advantage to switch to door 2, since the probability of finding the car there is double what it was before. Note that, by opening one of the doors while avoiding the car, Monty *gave you some information* about the location of the car. In applying Bayes' rule, you *infer* or back out the information content from Monty's act, adjusting your probabilities appropriately. In doing so, the probability distribution the car's location changed discontinuously: the distribution was initially uniform, then changed to the distribution in Eqs. (11.86). This is quite reminiscent of the collapse of a quantum state after a quantum measurement.

11.3.2.1 Quantum Language

In fact, we can easily recast this same problem in the notation of quantum-mechanical measurement as represented by POVMs quite, as a simple example of how quantum measurement generalizes Bayesian inference. This is the identical problem, though, so there won't be anything quantum-mechanical about this version of the problem except for notation. This is simply an exercise to emphasize the similarity of quantum measurements to Bayes' rule.

[13] See Problem 11.4 for another standard example of a counterintuitive result, analyzed via Bayes' rule.

- **Prior:** The three outcomes (car behind door α) can correspond to the states $|\alpha\rangle$, with projection operators $P_\alpha := |\alpha\rangle\langle\alpha|$. The initial state is equiprobable with no quantum coherence, and so the appropriate density operator is simply the I-know-nothing state:

$$\rho = \frac{1}{3}(P_1 + P_2 + P_3). \tag{11.87}$$

- **Data:** The ''generalized quantum measurement'' here involves seeing which door Monty opens to reveal a goat. For example, the revelation of a goat behind door 3 can be represented by the Kraus operator (taking the place of the classical likelihood function)

$$\Omega_3 := \frac{1}{\sqrt{2}}P_1 + P_2. \tag{11.88}$$

Thus, $\Omega_3^\dagger\Omega_3 = \frac{1}{2}P_1 + P_2$, and a POVM could be completed, for example, by the alternate possibility $\Omega_2 = \frac{1}{\sqrt{2}}P_1 + P_3$, where Monty shows off the goat behind door 2. How did we get this? The idea here in constructing Ω_3 is that $\Omega_3^\dagger\Omega_3$ is going to take over the role of the classical likelihoods (11.82)–(11.84). So we need to choose the positive measurement operator $\Omega_3^\dagger\Omega_3$ to have the same likelihoods along the diagonal. This is because we're doing a *classical* measurement; a more general measurement operator need not be diagonal.

To verify explicitly that the operator Ω gives the right conditional probabilities for the each of the outcomes, given by the appropriate trace $\mathrm{Tr}[\Omega_3\rho\Omega_3^\dagger]$, we can treat the three possibilities in the density operator (11.87) separately by setting the density operator equal to the appropriate projector, $\rho = P_\alpha$:

$$\begin{aligned} P(D_3|C_1) &= \mathrm{Tr}[\Omega_3 P_1 \Omega_3^\dagger] = \mathrm{Tr}\left[\frac{P_1^2}{2}\right] = \frac{1}{2} \\ P(D_3|C_2) &= \mathrm{Tr}[\Omega_3 P_2 \Omega_3^\dagger] = \mathrm{Tr}[P_2^2] = 1 \\ P(D_3|C_3) &= \mathrm{Tr}[\Omega_3 P_3 \Omega_3^\dagger] = 0. \end{aligned} \tag{11.89}$$

The only operator algebra is to note that for orthogonal projectors, $P_\alpha P_\beta = \delta_{\alpha\beta}P_\alpha$. These are, of course, the same classical probabilities as in Eqs. (11.82)–(11.84), and this is precisely the justification for defining this operator. (See Problem 11.7 for a justification via a projective-measurement representation of this problem.)

- **Posterior:** Now the **conditioned state** ρ_c is given by the POVM transformation

$$\rho_c = \frac{\Omega_3\rho\Omega_3^\dagger}{\mathrm{Tr}[\Omega_3\rho\Omega_3^\dagger]} = \frac{\left(\frac{P_1}{\sqrt{2}} + P_2\right)\frac{1}{3}(P_1 + P_2 + P_3)\left(\frac{P_1}{\sqrt{2}} + P_2\right)}{\mathrm{Tr}\left[\left(\frac{P_1}{\sqrt{2}} + P_2\right)\frac{1}{3}(P_1 + P_2 + P_3)\left(\frac{P_1}{\sqrt{2}} + P_2\right)\right]} = \frac{\left(\frac{P_1}{2} + P_2\right)}{\mathrm{Tr}\left[\frac{P_1}{2} + P_2\right]} = \frac{1}{3}P_1 + \frac{2}{3}P_2. \tag{11.90}$$

Finally, the posterior, or conditioned, probabilities of finding the car behind each door is given by a similar trace, where the projector P_α defines the outcome of finding the car behind door α in a *subsequent* measurement:

$$\begin{aligned} P_c(C_1) &\equiv P(C_1|D_3) = \mathrm{Tr}[P_1\rho_c P_1] = \frac{1}{3} \\ P_c(C_2) &\equiv P(C_2|D_3) = \mathrm{Tr}[P_2\rho_c P_2] = \frac{2}{3} \\ P_c(C_3) &\equiv P(C_3|D_3) = \mathrm{Tr}[P_3\rho_c P_3] = 0. \end{aligned} \tag{11.91}$$

These are the same probabilities that we obtained using Bayes' rule in standard form. Of course, because the unconditioned and conditioned density operators and Kraus operators were all diagonal, this

is all just classical inference: the diagonal elements of ρ are the classical priors; the diagonal elements of ρ_c are the classical posteriors; the diagonal elements of $\Omega_3^\dagger\Omega_3$ are the classical likelihoods; and $\mathrm{Tr}[\Omega_3\rho\Omega_3^\dagger]$ is the normalization factor. Quantum mechanics is more general in allowing off-diagonal elements in these operators, representing quantum coherences before and/or after the measurement (and possibly induced by the measurement).

11.3.3 Quantum Inference from Data

To summarize and also generalize the Monty Hall example, we can recast the POVM reduction as a ''quantum Bayes' rule.'' Assume we have a set D_α of Kraus operators that are comprised in a POVM. Then the αth measurement outcome converts the quantum state ρ into the conditioned state ρ_c according to

$$\rho_c = \frac{D_\alpha \rho D_\alpha^\dagger}{\mathrm{Tr}[D_\alpha \rho D_\alpha^\dagger]}. \tag{11.92}$$

We can identify elements here that are generalizations of the classical Bayes' Rule:

1. The **prior**: in this case is the initial density operator ρ.
2. The **reduction**: the operators D_α and $D_\alpha^\dagger$ act as generalized likelihoods $P(D_\alpha|A)$ in the classical case, which effects the change in the probability in response to the occurrence of D_α (regarded as an event). As we saw in the Monty Hall example, these quantum operators can be constructed to be equivalent to the classical conditional probabilities.
3. The **renormalization factor**: we then renormalize the probability by dividing by $\mathrm{Tr}[D_\alpha \rho D_\alpha^\dagger]$, which is just the probability $P(D_\alpha)$ in the classical case. This step of course ensures a normalized, conditioned density operator, which we of course need for a sensible probability distribution.
4. The **posterior**: the conditioned state ρ_c then reflects our knowledge of the quantum state given the αth outcome of the measurement, in the same way that $P(A|D_\alpha)$ reflects the probability for outcome A given the event D_α.

The obvious but superficial difference here is that the classical rule describes the change in the assigned probability for a *single* event A, whereas the quantum rule handles *all possible* outcomes of a future measurement all at once. While similar, the quantum and classical rules can't quite be cast in the same form since the quantum rule is both more general in handling *coherent* superpositions (quantum probabilities) and different in that measurements on some aspects of a system must disturb complementary aspects (quantum backaction). We can conclude this interlude by noting a number of points regarding how one can use the quantum Bayes' rule as a framework for thinking about quantum measurement.[14] While bordering on the philosophical, this is a handy framework for thinking about measurements in modern experiments, particularly where single quantum systems and multiple, sequential measurements are involved.

- The quantum state ρ *is* the information about a quantum system according to a particular observer.
- A quantum measurement *refines* the observer's information about the system, and thus modifies the density operator.
- This removes any problems with ''collapse of the wave function'' as a discontinuous process. The wave function is, in fact, literally in the observer's head, and the collapse is just an update of information.
- This view is particularly useful in considering multiple observers for the same system, both performing their own measurements but possibly not sharing their results. The obvious example for this is quantum-state teleportation, and analyzing Bob's state before and after Alice communicates to him the results of her measurement.

[14] see Christopher A. Fuchs, *op. cit.* for *much* additional detail.

- The price of all this is the potentially distasteful feature of *subjective*, or *observer-dependent* quantum states (as we discussed before in Section 10.3.3.1). Actually, this shouldn't be unreasonable in the case of multiple observers; however, even multiple observers with access to *all* the same measurement results could disagree on the details of the quantum state, because they may have begun with different prior states. There *are* a number of important objective features, however. For example, the data (measurement results) are objective—as are the rules for incorporating data—and as the observers continue to incorporate more data, their states should converge (at least in the aspects reflected by the measurements): with sufficient data, eventually the information from the data should completely swamp the prior. Further, in constructing priors, both observers should either agree that the probability of a particular measurement outcome is either zero or nonzero, even if they disagree on the exact probability: an assigned probability of zero is the only really claim that is absolutely falsifiable by future measurements. Finally, there are objective ways of constructing prior states, such as the *maximum-entropy principle*, which chooses the state with the least information that is consistent with all known constraints[15] (though in practice determining and implementing constraints can be a tricky business[16]).

- In any quantum or classical measurement, the knowledge should increase, or at least it shouldn't *decrease*. For example, in a quantum projective measurement, a mixed state always transforms to a pure state, with correspondingly less uncertainty (i.e., the uncertainty reduced to the quantum-mechanical minimum), though of course once in a pure state a projection can only modify the state without increasing knowledge. Essentially the same is true of general POVMs.[17]

- The information gained in a quantum measurement is *not* about some pre-existing reality (i.e., hidden variables), but rather in the measurement, the uncertainty *for predictions of future measurements* decreases.

[15] E. T. Jaynes, *Probability Theory: The Logic of Science* (Cambridge, 2003).

[16] Jos Uffink, ''The Constraint Rule of the Maximum Entropy Principle,'' *Studies in History and Philosophy of Modern Physics* **27**, 47 (1996) (doi: 10.1016/1355-2198(95)00022-4).

[17] see Christopher A. Fuchs, *op. cit.* for proofs.

11.4 Exercises

Problem 11.1

Show that the eigenvalues of the matrix

$$Q = \begin{bmatrix} (p_0 - p_1)\cos^2\theta & \cos\theta\sin\theta \\ \cos\theta\sin\theta & (p_0 - p_1)\sin^2\theta \end{bmatrix} \tag{11.93}$$

may be written

$$q_\pm = \frac{1}{2}\left(p_0 - p_1 \pm \sqrt{1 - 4p_0p_1\cos^2 2\theta}\right), \tag{11.94}$$

in the case p_0 and p_1 are probabilities satisfying $p_0 + p_1 = 1$.

Note that the eigenvalues of a 2×2 matrix may always be written

$$q_\pm = \frac{\mathrm{Tr}[Q]}{2} \pm \sqrt{\left(\frac{\mathrm{Tr}[Q]}{2}\right)^2 - \det[Q]}. \tag{11.95}$$

Problem 11.2

Consider the unambiguous quantum-state discrimination problem in the symmetric case of equal probability $p_0 = p_1 = 1/2$ of being prepared in $|\psi_0\rangle$ or $|\psi_1\rangle$.

A physical realization that we discussed in Section 11.2.1.1 is to pass the quantum particle through a medium that absorbs particles, but only if they are in the $|\mathtt{0}\rangle$ state. Then the discrimination between $|\psi_0\rangle$ and $|\psi_1\rangle$ can be accomplished via a projective measurement in the $|\pm\rangle$ basis.

(a) **Briefly** justify the operator

$$\Pi_{\mathrm{abs}} = 1 - \exp\left(-\frac{L}{L_{\mathrm{c}}}|\mathtt{0}\rangle\langle\mathtt{0}|\right) \tag{11.96}$$

as representing the passage of the quantum system through such an absorbing medium of length L, given a characteristic absorption length L_{c}.

(b) How is the inconclusive measurement operator $\Pi_?$ related to Π_{abs}? As part of your solution you should give an expression for the value of L required to realize the optimal case.

(c) Write down expressions for the remaining measurement operators Π_0, Π_1 that implement the optimal measurement in this physical realization.

Problem 11.3

Your shiny new POVM-O-Matic® takes a qubit (spin-1/2 particle) as an input and performs a measurement according to some POVM, and spits out the measurement result and the collapsed qubit. Suppose that you use the POVM that came with it (other POVMs cost extra; even though they're cheaper if you subscribe to the POVM-of-the-month club, you blew all your money on the POVM-O-Matic®, 'cause it's as expensive as all get-out). Anyway, the built-in POVM is

$$\Pi_0 = \sigma^\dagger\sigma, \qquad \Pi_1 = 1 - \Pi_0, \qquad \sigma := \frac{\sigma_x - i\sigma_y}{2}, \tag{11.97}$$

where σ_x and σ_y are the usual Pauli operators.

(a) Start with a general state in terms of the Bloch vector $\langle\boldsymbol{\sigma}\rangle$, and not necessarily a pure state:

$$\rho = \frac{1}{2}\big(\mathcal{I} + \langle\boldsymbol{\sigma}\rangle\cdot\boldsymbol{\sigma}\big). \tag{11.98}$$

Compute the probabilities of each measurement outcome in terms of the Bloch-vector components.

(b) Give the final state in terms of the Bloch vector after a measurement resulting in the Π_0 outcome. Use the Kraus operator $\Omega = \sigma$ for Π_0 to compute the final state.

(c) Give the final state in terms of the Bloch vector after a measurement resulting in the Π_1 outcome. Use the Kraus operator $\Omega = \sigma^\dagger$ for Π_1 to compute the final state.

Problem 11.4

Suppose that a (fictitious) serious disease called Bayes' syndrome affects 0.1% of the population. Suppose also that you are tested for Bayes' syndrome. The test has a false-positive rate of 0.1% and a false-negative rate of 0.1% (i.e., for either outcome the test is correct 99.9% of the time). If you test positive for Bayes' syndrome, what is the probability that you actually have the disease?

Use Bayes' rule to calculate the answer, identifying the various factors (prior, posterior, likelihood). Surprisingly, the answer turns out to be 50%. The reason is that the prior knowledge of the situation is that you are very *unlikely* to have the disease, and because it is so skewed, the prior strongly influences the posterior expectation.

Problem 11.5

Compute the same probability in Problem 11.4, but after two statistically independent tests (i.e., with uncorrelated errors) turn up positive, assuming both tests have the same error rates.

Problem 11.6

As of 29 March 2020, the testing protocol in Oregon for the SARS-CoV-2 virus[18] stated that a nasopharyngeal swab is acceptable (but not preferred) for a rRT-PCR test (real-time reverse transcription-polymerase chain reaction test, which looks for virus RNA). This is a likely collection method in the absence of severe symptoms. An early (rough) estimate[19] gives a **sensitivity** (probability of correctly giving a positive diagnosis) of around 60%. (The **specificity**, or probability of correctly giving *negative* diagnosis, is presumably close to 100% for a genetic test.[20])

If the prior is based on the infected fraction of the population (out of an Oregon population of about 4 million, there are an estimated 800 infected people,[21] so a negative test result doesn't say much about the probability of someone being infected (it's still low).

However, suppose that a patient presents with symptoms that could also be explained by influenza or bacterial pneumonia, and suppose we crudely estimate the prior probability of SARS-CoV-2 infection to be 50% given the symptoms. Compute the probability of actually being infected in the case of a negative test result from a nasopharyngeal swab. What about a more invasive test based on bronchoalveolar lavage fluid (sensitivity around 90%)?

Problem 11.7

Repeat the Monty Hall problem in the language of quantum mechanics, but use only pure states and projective measurements in your treatment, extending the Hilbert space to include the state of Monty Hall himself prior to revealing what is hidden behind door 3. In doing this, justify the operator

$$\Omega = \frac{1}{\sqrt{2}} P_1 + P_2 \tag{11.99}$$

[18] https://web.archive.org/web/20200327194726/https://www.oregon.gov/oha/PH/LABORATORYSERVICES/Pages/COVID-19.aspx

[19] Wenling Wang *et al.*, "Detection of SARS-CoV-2 in Different Types of Clinical Specimens," *Journal of the American Medical Association*, published online March 11, 2020 (doi: 10.1001/jama.2020.3786).

[20] https://www.fda.gov/media/136151/download

[21] https://govsite-assets.s3.amazonaws.com/VooxlwVoTey3aArqqFkG_Oregon-COVID-19-Projections-2020-03-23.pdf

as an appropriate representation of Monty Hall's revelation of a goat behind door 3. Since there is a projective measurement on an auxiliary system (Monty Hall), who has "interacted" with the doors, this problem gives an example of Naimark's theorem in action.

Problem 11.8

In the problem of quantum-state discrimination for coherent states (Section 11.2.4), the treatment relied on the existence of a unitary operator effecting the transformations (11.66) and (11.67):

$$\begin{aligned} U|\alpha_1\rangle|\alpha_2\rangle &= |\beta_1\rangle|\beta_2\rangle \\ U|-\alpha\rangle|i\alpha\rangle &= |-\sqrt{2}\alpha\rangle|0\rangle. \end{aligned} \tag{11.100}$$

The action of this operator can be justified in a slightly different way by consider a pair of identical, but coupled harmonic oscillators of the form

$$H = \frac{p_1^2 + p_2^2}{2m} + \frac{k}{2}\left(x_1^2 + x_2^2\right) + \frac{\kappa}{2}(x_1 - x_2)^2. \tag{11.101}$$

The coupling constant κ is assumed to be small ($\kappa \ll k$), and this can be regarded as the weak-coupling limit of an arbitrary coupling function. Transforming into normal-mode coordinates

$$x_\pm := \frac{x_1 \pm x_2}{\sqrt{2}}, \qquad p_\pm := \frac{p_1 \pm p_2}{\sqrt{2}}, \tag{11.102}$$

the Hamiltonian (11.101) becomes

$$H = \frac{p_+^2 + p_-^2}{2m} + \frac{k}{2}x_+^2 + \frac{1}{2}(k + 2\kappa)x_-^2. \tag{11.103}$$

This is a pair of *uncoupled* oscillators, but with slightly different spring constants (thus oscillation frequencies). Note that because this amounts to a pair of uncoupled harmonic oscillators, it is sufficient to consider the *classical* oscillator motion.

To get a feel for the dynamics, consider some special combinations of initial conditions:

(a) Write down the (classical) solution corresponding to the initial conditions $p_{10} = p_{20} = 0$, $x_{10} = x_{20} \neq 0$, and interpret the solutions.

(b) Do the same for initial conditions $p_{10} = p_{20} = 0$, $x_{10} = -x_{20} \neq 0$.

(c) Do the same for $p_{10} = 0$, $x_{20} = 0$. In particular, you should find solutions of the form

$$\begin{aligned} x_1(t) &= \sqrt{2}x_{10}\cos[(1 + \kappa/2)t]\cos(\kappa t/2 + \pi/4) \\ x_2(t) &= \sqrt{2}x_{10}\sin[(1 + \kappa/2)t]\cos(\kappa t/2 - \pi/4), \end{aligned} \tag{11.104}$$

which you can interpret as kinetic energy moving back and forth between the two oscillators.

(d) Now justify the unitary transformations above, based on the solution from part (c). For example, the initial condition should mimic the state $|\alpha\rangle|i\alpha\rangle$, and the unitary transformation comes after $1/4$ of a period of the slow oscillation of the motion between the two oscillators.

Chapter 12

Static Theory of Perturbations

12.1 Setup

Perturbation theory is an enormously important approximation method in physics. Suppose that we have a time-independent Hamiltonian H_0 that is completely solved—we know all its eigenvalues and eigenvectors. Such systems are fairly rare, requiring a high degree of symmetry in order to be able to solve the eigenvalues and eigenvectors in closed form (though it can be possible to employ these techniques to numerical solutions as well). Now suppose we have another Hamiltonian

$$H = H_0 + \lambda V, \tag{12.1}$$
(perturbed Hamiltonian)

in terms of the **interaction potential** V. We will assume that V is ''small,'' in the sense that V should not make a huge difference in the eigenvalues and eigenvectors of H vs. H_0, but we will have to be more precise about what this means as we go along. The parameter λ is a bookkeeping parameter that is both conventional and handy. It will help to keep track of the order of the perturbative approximation, and it gives a nice way to connect the two Hamiltonians by taking the limit $\lambda \longrightarrow 0$. However, it is not *necessarily* a ''small'' parameter; generally the idea is to set $\lambda = 1$ at the end of the calculation, so that the perturbation energy is really just V.

The common derivation for deriving the perturbation series is to write the perturbed eigenvalue as

$$E = E_0 + \lambda\,\Delta E_1 + \lambda^2\,\Delta E_2 + \cdots \tag{12.2}$$

and the corresponding perturbed eigenstate as

$$|\psi\rangle = |\psi_0\rangle + \lambda\,\Delta|\psi\rangle_1 + \lambda^2\,\Delta|\psi\rangle_2 + \cdots\,. \tag{12.3}$$

Clearly, the setup is such that $E \longrightarrow E_0$ and $|\psi\rangle \longrightarrow |\psi_0\rangle$ in the limit $\lambda \longrightarrow 0$. The idea is to find the corrections ΔE_n and $\Delta|\psi\rangle_n$, and the procedure amounts to finding the roughest approximation ΔE_1, which is then used to derive $\Delta|\psi\rangle_1$. These are then used to derive the next corrections ΔE_2 and $\Delta|\psi\rangle_2$. The procedure continues, clawing your way up order by order in a morass of indices, while the process becomes rapidly more complicated. To avoid this, we will use an operator-based method to derive closed expressions at all orders all at once.[1]

12.2 Resolvent Operator

The operator method that we will use to proceed is based on the resolvent operator. The utility of the resolvent extends far beyond what we will do here, to nonperturbative approximation methods, as well as

[1] Here we will follow the resolvent method outlined by Albert Messiah, *Quantum Mechanics* (Wiley, 1958) Sections XVI.15-17, pp. 712–20 (ISBN: 0486409244); this formalism was derived originally by Tosio Kato, ''On the Convergence of the Perturbation Method. I,'' *Progress of Theoretical Physics* **4**, 514 (1949) (doi: 10.1143/ptp/4.4.514).

exact and approximate solutions in time-dependent problems, particularly in problems involving transitions to the continuum. The **resolvent operator** is defined in the complex plane in terms of the *time-independent* Hamiltonian H by

$$G(z) := \frac{1}{z - H}. \tag{12.4}$$
(resolvent operator)

Expanding into a basis $|n\rangle$ of discrete eigenstates of H (i.e., multiplying by the identity $\sum_n |n\rangle\langle n| = 1$), we have the alternate expression

$$G(z) = \sum_n \frac{|n\rangle\langle n|}{z - E_n}. \tag{12.5}$$

Thus, $G(z)$ has a simple pole at each eigenvalue E_n of H (a simple pole at $z = a$ is a divergence of the form $(z-a)^{-1}$, or in other words, one where multiplication by $(z-a)$ removed the divergence). In the case of a continuum of states, where the eigenvalues cluster together into a continuous interval along the real line, $G(z)$ has instead a branch cut. For example, for the hydrogen atom, which has both bound and unbound (ionized) states, $G(z)$ has poles at each bound-state energy, but a branch cut beginning at the smallest ionization energy (i.e., $E = 0$) and extending to $+\infty$ along the real axis. There are some subtleties in dealing with branch cuts in $G(z)$, but here we will mostly ignore these, as we will be dealing only with perturbations to discrete states (we will also assume that there is no degeneracy to the eigenstates, at least for the moment). However, away from the real axis, the resolvent operator is analytic (in the sense that all its matrix elements are analytic functions away from the real axis).

12.2.1 Perturbation Series for the Resolvent

Again, let's start with a quantum system described by Hamiltonian (12.1),

$$H = H_0 + \lambda V, \tag{12.6}$$

where H_0 is the unperturbed Hamiltonian, and with interaction λV shifting the eigenstates of H_0. We then have two resolvents, one corresponding to the perturbed Hamiltonian and given by the original definition (12.4), and one corresponding to the unperturbed system,

$$G(z) := \frac{1}{z - H}, \qquad G_0(z) := \frac{1}{z - H_0}.$$
(perturbed and unperturbed resolvent operators) (12.7)

Now we will want to relate these two operators. Starting with $B = A + (B - A)$ for arbitrary A and B, we multiply on the left by B^{-1} and on the right by A^{-1} to obtain the identity

$$\frac{1}{A} = \frac{1}{B} + \frac{1}{B}(B - A)\frac{1}{A}. \tag{12.8}$$

Letting $A = z - H_0 - \lambda V$ and $B = z - H_0$, we find

$$G(z) = G_0(z) + \lambda G_0(z) V G(z). \tag{12.9}$$
(perturbed resolvent)

Note that this (implicit) expression is still *exact* at this stage. To derive a perturbation series, we simply iterate it, putting the entire right-hand side expression into the $G(z)$ on the right-hand side, for example to obtain

$$G(z) = G_0(z) + \lambda G_0(z) V G_0(z) + \lambda^2 G_0(z) V G_0(z) V G(z). \tag{12.10}$$

This iteration can be continued *ad infinitum* to obtain the series

$$G = G_0 + \lambda G_0 V G_0 + \lambda^2 G_0 V G_0 V G_0 + \lambda^3 G_0 V G_0 V G_0 V G_0 + \cdots . \tag{12.11}$$
(Born expansion)

This is called the **Born series** for the resolvent. Writing out the whole series explicitly,

$$G(z) = \sum_{n=0}^{\infty} \lambda^n G_0(z)\big[VG_0(z)\big]^n. \tag{12.12}$$
(Born expansion)

Perturbation approximations amount to truncating this series after some number of terms, in the hopes that the successive terms in the series are getting smaller. This corresponds to, at some point in the finite iteration of a form like that in Eq. (12.10), that in the last term we can simply approximate $G(z)$ by $G_0(z)$. It is not guaranteed, however, that the successive terms in the perturbation series will continue getting smaller, or that the series will converge. However, often useful results with relatively little pain can be obtained from just the first correction or two.

12.3 Perturbation Series for the Projector

To proceed with the setup of perturbation theory, let's denote the (perturbed) eigenstate of H as $|\psi\rangle$ with eigenvalue E, while the eigenstate of H_0 as $|\psi_0\rangle$, with eigenvalue E_0:

$$H|\psi\rangle = E|\psi\rangle, \qquad H_0|\psi_0\rangle = E_0|\psi_0\rangle. \tag{12.13}$$

We will also define projection operators for both the perturbed and unperturbed states

$$P := |\psi\rangle\langle\psi|, \qquad P_0 := |\psi_0\rangle\langle\psi_0|,$$
(pertubed/unperturbed-state projectors) (12.14)

as well as the projection operator for *all of the other* unperturbed states:

$$Q_0 := 1 - P_0. \tag{12.15}$$
(complementary unperturbed projector)

Again, we are assuming that $|\psi\rangle$ has no degeneracy (i.e., it is the unique state with energy E, and there are no energies arbitrarily close by); we will come back to fix this restriction later.

Now the idea is to develop a perturbation series for the projection operator P of the form

$$P = P_0 + \sum_{n=1}^{\infty} \lambda^n \, \delta P_n, \tag{12.16}$$
(projector perturbation series)

where the corrections δP_n are yet to be determined.

12.3.1 Cauchy Integral Formula

To compute the correction terms to the projector in Eq. (12.16), we will use the Cauchy integral formula. Consider a closed, simply connected contour γ in the complex plane, and let $f(z)$ be a function analytic everywhere inside γ. Then an integral around the contour vanishes,

$$\oint_\gamma f(z)\, dz = 0, \tag{12.17}$$

and **Cauchy's integral formula** states that on the same contour,

$$f(a) = \frac{1}{2\pi i} \oint_\gamma \frac{f(z)}{z-a}\, dz, \tag{12.18}$$
(Cauchy integral formula)

under the assumption a is a point interior to the closed contour γ, and that the integration proceeds once counterclockwise around the contour (a clockwise integration implies an extra minus sign, and multiple passes

around a would imply an integer multiplying factor on the left-hand side). The common terminology is that the function $f(z)/(z-a)$ has a **simple pole** at $z=a$, and $f(a)$ is the **residue** of the function $f(z)/(z-a)$ at the pole. Remarkably, both results are *independent of the contour*, so long as the above conditions hold.

The form (12.18) for the integral formula is standard, but also a bit strange from the point of view of applying it to integrals, because the divergence in the integrand is typically not separated out so automatically. An alternate way to write this formula is the **residue theorem**,

$$\oint_\gamma g(z)\,dz = 2\pi i\,\mathrm{Res}[g(a)], \tag{12.19}$$
(residue theorem)

where the **residue** of $g(z)$ at a simple pole at $z=a$ is given by

$$\mathrm{Res}[g(a)] = \lim_{z\to a}(z-a)\,g(z), \tag{12.20}$$
(residue definition)

assuming that this limit exists (i.e., for a simple pole at $z=a$). This formula of course assumes the same conditions on the contour γ, and if there are multiple poles enclosed by the contour, the result should sum over all of their residues.

12.3.1.1 Application to the Resolvent

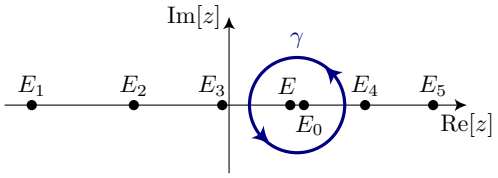
Recalling that $G(z) = 1/(z-H)$ has isolated, simple poles at the discrete eigenvalues of H, we will take the contour γ to enclose the pole at $z=E$ once counterclockwise, and we will take it to *not* enclose any other poles. In this case, from Eq. (12.5), the residue of the enclosed pole is $|\psi\rangle\langle\psi| = P$, and thus

$$P = \frac{1}{2\pi i}\oint_\gamma G(z)\,dz. \tag{12.21}$$

Similarly, we can write that

$$P_0 = \frac{1}{2\pi i}\oint_\gamma G_0(z)\,dz, \tag{12.22}$$

but here it is crucial to notice that we are using the *same* contour γ. This is justified by the "smallness" of the perturbation λV, since the pole at $z=E_0$ should be sufficiently close to the one at $z=E$ that γ can be taken to enclose both of these *without* enclosing any others, as illustrated below.



Then we can apply the same integration as in Eqs. (12.21) and (12.22) to the Born series (12.12), in which case we can match up the terms to those in Eq. (12.16) with equivalent powers of λ, which gives the correction operators

$$\delta P_n = \frac{1}{2\pi i}\oint_\gamma G_0(VG_0)^n\,dz. \tag{12.23}$$

Now note that we have developed something with a more complicated pole structure. Since each G_0 has a simple pole at E_0, it follows that δP_n has a pole of order $n+1$ at E_0 [i.e., it diverges at E_0 as $1/(z-E_0)^{n+1}$].

12.3.2 Laurent Series for the Unperturbed Resolvent

To proceed with evaluating the contour integral (12.23), which involves possibly many instances of $G_0(z)$, we need to better organize $G_0(z)$ with respect to its singular behavior at $z=E_0$. Starting with the general

expression (12.5), we can separate out the unperturbed state $|\psi_0\rangle$ to write

$$G_0(z) = \frac{|\psi_0\rangle\langle\psi_0|}{z - E_0} + \sum_{\alpha\neq 0} \frac{|\alpha\rangle\langle\alpha|}{z - E_\alpha}, \tag{12.24}$$

where the remaining sum explicitly excludes $|\psi_0\rangle$. Now noting the expansion

$$\frac{1}{z - E_\alpha} = \sum_{k=1}^{\infty} \frac{(-1)^{k-1}(z - E_0)^{k-1}}{(E_0 - E_\alpha)^k}, \tag{12.25}$$

which is a **Laurent expansion** due to the singular first term, we can use this in Eq. (12.24) to write

$$G_0(z) = \frac{|\psi_0\rangle\langle\psi_0|}{z - E_0} + \sum_{k=1}^{\infty}(-1)^{k-1}(z - E_0)^{k-1} \sum_{\alpha\neq 0} \frac{|\alpha\rangle\langle\alpha|}{(E_0 - E_\alpha)^k}. \tag{12.26}$$

To simplify the last summation over the ''other'' unperturbed states, note that we can write

$$\sum_{\alpha\neq 0} \frac{|\alpha\rangle\langle\alpha|}{(E_0 - E_\alpha)^k} = \left(\sum_{\alpha\neq 0} \frac{|\alpha\rangle\langle\alpha|}{E_0 - E_\alpha}\right)^k = \Big(Q_0 G_0(E_0) Q_0\Big)^k = Q_0 G_0^k(E_0) Q_0, \tag{12.27}$$

where we are making use of the observation that Q_0 removes any contribution of $|\psi_0\rangle$ from $G_0(z)$, also that Q_0 is a projector, so $Q_0^2 = Q_0$, and finally that $[Q_0, G_0] = 0$. Using this result in Eq. (12.26), we come to

$$G_0(z) = \frac{|\psi_0\rangle\langle\psi_0|}{z - E_0} + \sum_{k=1}^{\infty}(-1)^{k-1}(z - E_0)^{k-1} Q_0 G_0^k(E_0) Q_0. \tag{12.28}$$

It is handy to write this expression more compactly as

$$G_0(z) = \sum_{k=0}^{\infty}(-1)^{k-1}(z - E_0)^{k-1} S_k, \tag{12.29}$$

if we define the symbol

$$S_k := \begin{cases} -P_0, & k = 0 \\ Q_0 G_0^k(E_0) Q_0 = \dfrac{Q_0}{(E_0 - H_0)^k}, & k > 0. \end{cases} \tag{12.30}$$

The last expression for the $k > 0$ case is justified since Q_0 is a projector on an eigenspace of H_0, so it commutes with $(z - H_0)^{-1}$. In this way the contour integral (12.23) will end up producing various combinations of S_k.

12.3.3 Explicit Projector Expansion

Now to evaluate the contour integral (12.23), we will need a generalization of the Cauchy integral formula (12.18), which we'll briefly review. Suppose we have a function $f(z)$, with a Laurent expansion of the form

$$f(z) = \sum_{k=-\infty}^{\infty} c_k (z - a)^k. \tag{12.31}$$

It is possible to project out any one of the expansion coefficients by a contour integral, as

$$c_k = \frac{1}{2\pi i} \oint_\gamma \frac{f(z)}{(z - a)^{k+1}}\, dz, \tag{12.32}$$

where the contour again encloses a once counterclockwise, and the Cauchy integral formula (12.18) corresponds to the case $k = 0$ here, so that $c_0 = f(a)$. In the case of $k = -1$, Eq. (12.32) reads

$$c_{-1} = \frac{1}{2\pi i} \oint_\gamma f(z)\, dz, \tag{12.33}$$

which is essentially the same statement that the residue theorem (12.19) makes, but divergences worse than simple poles are now allowed; c_{-1} is then a more general way to define the residue $\mathrm{Res}[f(a)]$, compared to Eq. (12.20).

In the case of Eq. (12.23), the integral has the form of Eq. (12.33), and by Eq. (12.31), the integral thus picks out the coefficient of $1/(z - E_0)$ in the Laurent series for $G_0(VG_0)^n$. Each factor of G_0 can have a factor of $1/(z - E_0)$, or other higher order terms of a given factor of G_0 can count if they are compensated by the $1/(z - E_0)$ contributions of other factors. In general the result of the contour integration may be written

$$\delta P_n = \quad - \sum_{\substack{k_1,\ldots,k_{n+1} \\ (k_1+\cdots+k_{n+1}=n)}} S_{k_1} V S_{k_2} V \cdots V S_{k_{n+1}}, \qquad \begin{matrix}(12.34)\\ (n\text{th projector correction})\end{matrix}$$

where the sum is over all $(n + 1)$-tuples $(k_1, k_2, \ldots, k_{n+1})$, under the constraint that the k_j's add up to exactly n. To justify this result, note that each factor S_k is associated with the factor $1/(z - E_0)^{k-1}$ in Eq. (12.29). The product in Eq. (12.34) involves a product of $(n + 1)$ of these factors, and thus the total power of $1/(z - E_0)$ in the product is

$$(k_1 - 1) + (k_2 - 1) + \cdots + (k_{n+1} - 1) = n - (n + 1) = -1 \tag{12.35}$$

after using $k_1 + \cdots k_{n+1} = n$. This is the desired result to give the result of the contour integral. The overall sign follows similarly, as again each factor S_k is associated with factor $(-1)^{k-1}$ in Eq. (12.29), and so the product has a total sign factor

$$(-1)^{k_1-1} \cdot (-1)^{k_2-1} + \cdots + (-1)^{k_{n+1}-1} = (-1)^n \cdot (-1)^{-(n+1)} = -1. \tag{12.36}$$

This explains the overall minus sign in Eq. (12.34).

To get a better idea of what the perturbation series (12.16) looks like with the expression (12.34) for the correction terms, let's write out the contributions up to order λ^2. First, in terms of the S_k operators, this is

$$\begin{aligned} P = -S_0 &- \lambda\Big(S_0 V S_1 + S_1 V S_0\Big) \\ &- \lambda^2\Big(S_0 V S_1 V S_1 + S_1 V S_0 V S_1 + S_1 V S_1 V S_0 \\ &\qquad + S_0 V S_0 V S_2 + S_0 V S_2 V S_0 + S_2 V S_0 V S_0\Big) \\ &+ \cdots, \end{aligned} \tag{12.37}$$

and translating this into projectors via Eq. (12.30),

$$\begin{aligned} P = P_0 &+ \lambda\Big(P_0 V G_Q + G_Q V P_0\Big) \\ &+ \lambda^2\Big(P_0 V G_Q V G_Q + G_Q V P_0 V G_Q + G_Q V G_Q V P_0 \\ &\qquad - P_0 V P_0 V G_Q^2 - P_0 V G_Q^2 V P_0 - G_Q^2 V P_0 V P_0\Big) \\ &+ \cdots. \end{aligned}$$

(projector perturbation expansion) (12.38)

Here, we are using

$$G_Q^k := Q_0 G_0^k(E_0) Q_0 = \frac{Q_0}{(E_0 - H_0)^k} = S_k \qquad (k > 0) \tag{12.39}$$

as a shorthand to keep the notation compact. Although this is a proper perturbation series for the eigenstate of H expressed as a density operator, it is more conventional to write the corresponding state-vector expression, which is where we're headed next.

12.4 Perturbation Series for the Eigenstate

Now to convert the projector series (12.16) or (12.38) into a perturbation series for the eigenket, we can note that since we are assuming $|\psi\rangle$ to be close to $|\psi_0\rangle$, that we can simply project the correct part of the original state:

$$|\psi\rangle \propto P|\psi_0\rangle. \tag{12.40}$$

This of course assumes that $\langle\psi|\psi_0\rangle \neq 0$, which is in line with the assumption of a weak perturbation. The result, in general, is not normalized, so the correct expression must include an explicit renormalization,

$$|\psi\rangle = \frac{P|\psi_0\rangle}{\sqrt{\langle\psi_0|P|\psi_0\rangle}}, \tag{12.41}$$
(perturbed eigenstate)

again with P given by Eqs. (12.16), (12.34), and (12.38). As an example, let's evaluate the perturbed state to order λ. Writing out Eq. (12.41), with P to order λ, and ignoring the normalization factor for the moment, we have

$$|\psi\rangle \approx \Big[P_0 + \lambda P_0 V G_Q + \lambda G_Q V P_0\Big]|\psi_0\rangle. \tag{12.42}$$

The second term in the projection factor vanishes, because $Q_0|\psi_0\rangle = 0$ by definition; also $P_0|\psi_0\rangle = |\psi_0\rangle$ in the remaining terms, and this expression simplifies to

$$|\psi\rangle \approx \Big(1 + \lambda Q_0 G_0(E_0) Q_0 V\Big)|\psi_0\rangle. \tag{12.43}$$

Writing out $Q_0 G_0(E_0) Q_0$ explicitly in the unperturbed basis, we have

$$|\psi\rangle \approx |\psi_0\rangle + \lambda \left(\sum_{\alpha\neq 0} \frac{|\alpha\rangle\langle\alpha|}{E_0 - E_\alpha}\right) V|\psi_0\rangle, \tag{12.44}$$

and after a bit of rearrangement, the result is

$$|\psi\rangle \approx |\psi_0\rangle + \lambda \sum_{\alpha\neq 0} |\alpha\rangle \frac{\langle\alpha|V|\psi_0\rangle}{E_0 - E_\alpha}. \tag{12.45}$$
(perturbed state, first order)

Remember that we ignored the normalization factor, so we should verify the normalization of the result (12.45). Technically, the left-hand side is just $P|\psi_0\rangle$, and computing the squared modulus of this vector, we find

$$\langle\psi_0|P|\psi_0\rangle \approx 1 + \lambda^2 \sum_{\alpha\neq 0} \frac{|\langle\alpha|V|\psi_0\rangle|^2}{(E_0 - E_\alpha)^2}. \tag{12.46}$$

Thus, the renormalization factor only matters at second order in the perturbed result. At second order, the λ^2 term would appear in the result with a factor of $-1/2$ from expanding the normalization factor to the same order.

The second-order expression for the perturbed state, including the normalization corrections, is

$$|\psi\rangle \approx |\psi_0\rangle + \lambda \sum_{\alpha\neq 0} |\alpha\rangle \frac{V_{\alpha 0}}{E_{0\alpha}} + \lambda^2 \sum_{\alpha\neq 0}\sum_{\beta\neq 0} |\alpha\rangle \frac{V_{\alpha\beta}V_{\beta 0}}{E_{0\alpha}E_{0\beta}} - \lambda^2 V_{00} \sum_{\alpha\neq 0} |\alpha\rangle \frac{V_{\alpha 0}}{(E_{0\alpha})^2} - \frac{\lambda^2}{2}|\psi_0\rangle \sum_{\alpha\neq 0} \frac{|V_{\alpha 0}|^2}{(E_{0\alpha})^2}, \tag{12.47}$$
(perturbed state, second order)

where we are using the shorthand notations

$$V_{\alpha\beta} := \langle\alpha|V|\beta\rangle, \qquad E_{\alpha\beta} := E_\alpha - E_\beta, \tag{12.48}$$

with a zero index referring to $|\psi_0\rangle$. The derivation of this expression is left as an exercise (Problem 12.2). Note that instead of incorporating the normalization correction (12.46) directly, it is easiest to compute $P|\psi_0\rangle$ to second order, and then normalize the entire expression.

12.5 Perturbation Series for the Eigenvalue

To obtain an expression for the perturbed energy, we must carry out a parallel development to the projector case. In this case we will go back to Eq. (12.21),

$$P = \frac{1}{2\pi i}\oint_\gamma G(z)\,dz, \tag{12.49}$$

and operate with the Hamiltonian to obtain

$$HP = \frac{1}{2\pi i}\oint_\gamma HG(z)\,dz. \tag{12.50}$$

Now since $G(z) = 1/(z-H)$, this means $HG = zG - 1$, and thus

$$HP = \frac{1}{2\pi i}\oint_\gamma \big[zG(z) - 1\big]\,dz. \tag{12.51}$$

However, the second term in the integrand vanishes because it is an analytic function [recall Eq. (12.17)]. Thus, we have the integral formula

$$HP = \frac{1}{2\pi i}\oint_\gamma zG(z)\,dz, \tag{12.52}$$

which is the basis for the perturbation series. The motivation for studying HP is that we have already established that $P|\psi_0\rangle$ is the desired eigenvector of H (up to normalization), and so computing $HP|\psi_0\rangle$ should yield the corresponding eigenvalue.

We will now proceed in essentially the same way as before, developing a series for HP in the form

$$\begin{aligned}(H-E_0)P &= \frac{1}{2\pi i}\oint_\gamma (z-E_0)G(z)\,dz \\ &= \sum_{n=1}^{\infty}\lambda^n\Delta_n,\end{aligned} \tag{12.53}$$

where after inserting the Born series (12.12) for $G(z)$ in the above expression and matching powers of λ, we have

$$\Delta_n := \frac{1}{2\pi i}\oint_\gamma (z-E_0)G_0(VG_0)^n\,dz. \tag{12.54}$$

Note that we didn't need to include the $n=0$ term in the above series, because $\Delta_0 = 0$; that's because $(z-E_0)G_0$ is analytic, and thus the contour integral vanishes. The quantities Δ_n are analogous to the δP_n in Eq. (12.23), and the idea is to carry out the contour integral in essentially the same way. The contour integral is in fact equivalent except for an extra factor of $(z-E_0)$, which modifies the counting of the indices a bit in getting to the same overall factor of $1/(z-E_0)$ when accounting for all the factors of G_0. The result, in analogy with Eq. (12.34), is

$$\Delta_n = \sum_{\substack{k_1,\ldots,k_{n+1}\\(k_1+\cdots+k_{n+1}=n-1)}} S_{k_1}VS_{k_2}V\cdots VS_{k_{n+1}}. \qquad (n\text{th } HP \text{ correction}) \tag{12.55}$$

That is, accounting for the extra factor of $(z - E_0)$ means that the indices should sum to $n-1$ rather than n, and the overall sign changes.

Now to convert Eq. (12.53) into a series for the energy, we can simply recognize P as the density operator corresponding to $|\psi\rangle$, and thus we can simply compute the trace,

$$E = \mathrm{Tr}[HP] = E_0 + \sum_{n=1}^{\infty} \lambda^n \mathrm{Tr}\Delta_n =: E_0 + \sum_{n=1}^{\infty} \delta E_n, \tag{12.56}$$

(energy perturbation series)

and thus the perturbed energy is determined in terms of corrections as trace of Δ_n in Eq. (12.55).

12.5.1 First-Order Energy Shift

To illustrate how all this works, let's again work out the first few corrections to the unperturbed energy. Starting at first order, Eq. (12.55) says that we are summing over combinations of two S_k where the indices sum to zero. There is only one possible contribution:

$$\Delta_1 = S_0 V S_0 = P_0 V P_0. \tag{12.57}$$

Then the first-order energy correction is given simply by

$$\delta E_1 = \lambda \mathrm{Tr}\Delta_1 = \lambda \langle \psi_0 | V | \psi_0 \rangle = \lambda V_{00}, \tag{12.58}$$

(first-order energy correction)

where we have used the invariance of the trace under cyclic permutation. It will generally be the case that the permutation of the projectors will give expectation values or matrix elements of the interaction potential. The expression (12.58) is just the expectation value of the perturbation potential with respect to the initial state.

12.5.2 Second-Order Energy Shift

At second order we should sum over combinations of three S_k where the indices sum to one, giving three terms:

$$\Delta_2 = S_0 V S_0 V S_1 + S_0 V S_1 V S_0 + S_1 V S_0 V S_0. \tag{12.59}$$

However, in the trace, remember that the ''edge'' operators will operate on each other due to the cyclic nature of the trace. Since S_0 and S_1 are effectively projectors on different spaces (P_0 and Q_0, respectively), only terms with the same operator on either end will survive. In this case, only the middle term survives the trace, and we have

$$\mathrm{Tr}\Delta_2 = \mathrm{Tr}\big[S_0 V S_1 V S_0\big] = \langle \psi_0 | V Q_0 G_0(E_0) Q_0 V | \psi_0 \rangle \tag{12.60}$$

after writing out S_1 explicitly. Writing out the Green tensor on the complementary space in the unperturbed basis, we have

$$\mathrm{Tr}\Delta_2 = \sum_{\alpha \neq 0} \langle \psi_0 | V \frac{|\alpha\rangle\langle\alpha|}{E_0 - E_\alpha} V | \psi_0 \rangle, \tag{12.61}$$

and with a bit of rearrangement we have a second-order energy shift of

$$\delta E_2 = \lambda^2 \mathrm{Tr}\Delta_2 = \lambda^2 \sum_{\alpha \neq 0} \frac{|\langle \psi_0 | V | \alpha \rangle|^2}{E_0 - E_\alpha} = \lambda^2 \sum_{\alpha \neq 0} \frac{|V_{0\alpha}|^2}{E_{0\alpha}}, \tag{12.62}$$

(second-order energy correction)

where in the second expression we are again using the shorthands

$$V_{\alpha\beta} := \langle \alpha | V | \beta \rangle, \qquad E_{\alpha\beta} := E_\alpha - E_\beta \tag{12.63}$$

for the matrix elements and energy differences, respectively, where a zero index refers to $|\psi_0\rangle$.

12.5.3 Third- and Fourth-Order Energy Shifts

At third order we sum over combinations of four S_k where the indices sum to two, giving ten terms in all:

$$\begin{aligned}\Delta_3 = {} & S_0VS_0VS_1VS_1 + S_0VS_1VS_0VS_1 + S_0VS_1VS_1VS_0 \\ & + S_1VS_0VS_1VS_0 + S_1VS_1VS_0VS_0 + S_1VS_0VS_0VS_1 \\ & + S_0VS_0VS_0VS_2 + S_0VS_0VS_2VS_0 + S_0VS_2VS_0VS_0 + S_2VS_0VS_0VS_0.\end{aligned} \tag{12.64}$$

In the trace, only the third, sixth, eighth, and ninth terms survive. After using the cyclic-permutation invariance, the sixth and eighth terms cancel with the observation that $S_1S_1 = S_2$, and thus we are left with

$$\begin{aligned}\mathrm{Tr}\Delta_3 &= \langle\psi_0|VS_1VS_1V|\psi_0\rangle - \langle\psi_0|V|\psi_0\rangle\langle\psi_0|VS_2V|\psi_0\rangle \\ &= \langle\psi_0|VQ_0G_0(E_0)Q_0VQ_0G_0(E_0)Q_0V|\psi_0\rangle - \langle\psi_0|V|\psi_0\rangle\langle\psi_0|VQ_0G_0^2(E_0)Q_0V|\psi_0\rangle.\end{aligned} \tag{12.65}$$

Expressing the resolvents in the unperturbed basis as usual, we obtain a third-order energy shift of

$$\delta E_3 = \lambda^3\mathrm{Tr}\Delta_3 = \lambda^3\sum_{\alpha,\beta\neq0}\frac{V_{0\alpha}V_{\alpha\beta}V_{\beta0}}{E_{0\alpha}E_{0\beta}} - \lambda^3V_{00}\sum_{\alpha\neq0}\frac{|V_{0\alpha}|^2}{(E_{0\alpha})^2}$$

(third-order energy correction) (12.66)

in the same compact notation defined in Eqs. (12.63). Note that if the first-order correction vanishes ($\mathrm{Tr}\Delta_1 = 0$), Eq. (12.66) simplifies in that the second term vanishes. Often, the high-order perturbation expressions are most useful when they are the leading, nonvanishing correction.

At fourth order, the idea is essentially the same. The resulting correction is

$$\begin{aligned}\delta E_4 &= \lambda^4\mathrm{Tr}\Delta_4 \\ &= \lambda^4\sum_{\alpha,\beta,\gamma\neq0}\frac{V_{0\alpha}V_{\alpha\beta}V_{\beta\gamma}V_{\gamma0}}{E_{0\alpha}E_{0\beta}E_{0\gamma}} - \lambda^4\sum_{\alpha,\beta\neq0}\frac{|V_{0\alpha}|^2|V_{0\beta}|^2}{(E_{0\alpha})^2E_{0\beta}} \\ &\qquad - \lambda^4V_{00}\sum_{\alpha,\beta\neq0}\left[\frac{V_{0\alpha}V_{\alpha\beta}V_{\beta0}}{(E_{0\alpha})^2E_{0\beta}} + \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta0}}{E_{0\alpha}(E_{0\beta})^2}\right] + \lambda^4V_{00}^2\sum_{\alpha\neq0}\frac{|V_{0\alpha}|^2}{(E_{0\alpha})^3},\end{aligned}$$

(fourth-order energy correction) (12.67)

and the derivation is left as an exercise.

Note that the higher-order corrections become rapidly more complicated. However, they simplify somewhat in the case of the nth order *leading* correction (i.e., when all the lower order corrections vanish). In terms of the correction operator (12.55), the only term that survives the trace is

$$\mathrm{Tr}\Delta_n = \langle\psi_0|V(S_1V)^{n-1}|\psi_0\rangle. \tag{12.68}$$

This is because all other terms will involve intermediate factors of P_0, which will belong to lower-order perturbation expansions. This doesn't change anything at first or second order, but the trace in the third-order expression (12.66) simplifies to

$$\mathrm{Tr}\Delta_3 = \sum_{\alpha,\beta\neq0}\frac{V_{0\alpha}V_{\alpha\beta}V_{\beta0}}{E_{0\alpha}E_{0\beta}}, \tag{12.69}$$

and the subsequent expressions continue in the reasonably obvious way.

12.6 Example Applications

12.6.1 Spectroscopic Notation for Hydrogen: Simplified

As good examples of perturbation theory in action, we'll look at some examples involving the hydrogen atom. First, however, it will help to bring our notation more in line with standard notation for atomic states. We haven't yet discussed spin in the context of an atom, but we will do so soon. In the meantime, we will only introduce part of the notation, deferring the rest until later.

We have been looking at hydrogen electronic states in the form $|n\ \ell\ m\rangle$. Standard notation dictates that we refer to such a state in the form $n\ell(m = m)$. However, the ℓ quantum number has a special notation, where the values are referred to by S, P, D, F, G, H, ...; the first four letters are based on a historic notation for spectral lines, standing for "sharp," "principal," "diffuse," "fine/fundamental," and then the rest continue alphabetically (skipping S, P, and J). These letters correspond to $\ell = 0, 1, 2, \ldots$; thus the $|1\ 0\ 0\rangle$ is the 1S state (no need to write the m value if only one is possible). The first excited states are the 2S and 2P states—$|2\ 0\ 0\rangle$ and $|2\ 1\ m\rangle$, respectively.

12.6.2 Nuclear-Size Correction in Hydrogen

A first and simple example of perturbation theory in action is the correction to the ground-state energy in hydrogen if we account for the nonzero radius of the nucleus—our calculation implicitly assumed a zero radius in employing a $-1/r$ potential at every $r > 0$. As a crude estimate of this effect, let's treat the nucleus as a sphere of uniform charge density of radius a_n. The Couloumb potential will still be

$$V_\mathrm{C}(r) = -\frac{\hbar c\alpha}{r} \qquad (r \geq a_\mathrm{n}) \tag{12.70}$$

outside the nucleus, but we should construct the modified potential *inside* the nucleus. In this case, Gauss' law says that the Coulomb force on the electron at radius r is due only to the nuclear charge enclosed by the sphere of the same radius. The enclosed nuclear charge is thus

$$q = e\frac{r^3}{a_\mathrm{n}^3}, \tag{12.71}$$

so we should tack this fraction onto the normal Coulomb force:

$$F_\mathrm{C} = -\frac{\hbar c\alpha}{r^2}\frac{r^3}{a_\mathrm{n}^3} = -\frac{\hbar c\alpha}{a_\mathrm{n}^3}r \qquad (r \leq a_\mathrm{n}). \tag{12.72}$$

Integrating to find the potential,

$$V_\mathrm{C}(r) = \frac{\hbar c\alpha}{2a_\mathrm{n}^3}r^2 + (\text{const}) \qquad (r \leq a_\mathrm{n}), \tag{12.73}$$

where the integration constant should be chosen so that V_C is continuous at $r = a_\mathrm{n}$. Doing this, we find the interior potential

$$V_\mathrm{C}(r) = \frac{\hbar c\alpha}{2a_\mathrm{n}}\left(\frac{r^2}{a_\mathrm{n}^2} - 3\right) \qquad (r \leq a_\mathrm{n}). \tag{12.74}$$

The perturbation potential is the difference between the original and this improved Coulomb potential,

$$V(r) = \frac{\hbar c\alpha}{2a_\mathrm{n}}\left(\frac{r^2}{a_\mathrm{n}^2} - 3\right) + \frac{\hbar c\alpha}{r} \qquad (r \leq a_\mathrm{n}), \tag{12.75}$$

while the perturbation vanishes for $r \geq a_\mathrm{n}$. The first-order correction (12.58) to the energy is just (setting $\lambda = 1$)

$$\delta E_1 = \langle\psi_0|V|\psi_0\rangle, \tag{12.76}$$

where $|\psi_0\rangle$ is the 1S eigenfunction, which is

$$\langle \mathbf{r}|\psi_0\rangle = R_{10}(r)\,Y_0^0(\Omega) = \frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}, \tag{12.77}$$

after combining the radial and angular parts [Eqs. (8.164) and (7.91), respectively] of the wave function. Thus, the perturbation integral is

$$\delta E_1 = \frac{4\pi}{\pi a_0^3}\int_0^{a_\mathrm{n}} dr\, r^2 \frac{\hbar c\alpha}{2a_\mathrm{n}}\left(\frac{r^2}{a_\mathrm{n}^2} - 3 + \frac{2a_\mathrm{n}}{r}\right) e^{-2r/a_0}. \tag{12.78}$$

In this expression, we can make the further approximation that $e^{-2r/a_0} \approx 1$, since r is of the order of the nucleus ($\sim$1 fm), and thus $r \ll a_0$, where a_0 is the Bohr radius ($\sim$1 Å). Then we have

$$\delta E_1 \approx \frac{2\hbar c\alpha}{a_0^3 a_\mathrm{n}}\int_0^{a_\mathrm{n}} dr\,\left(\frac{r^4}{a_\mathrm{n}^2} - 3r^2 + 2a_\mathrm{n} r\right), \tag{12.79}$$

in which case we just need to integrate a polynomial. The result is

$$\delta E_1 \approx \frac{2\hbar c\alpha a_\mathrm{n}^2}{5a_0^3}. \tag{12.80}$$

(nuclear-size correction, hydrogen 1S)

This is a small correction, and so let's put in some numbers to see how small. First, for a sense of scale, let's compute the 1S–2P transition energy, but translated into more atomic-friendly quantities. First, recall the hydrogen-atom eigenenergies (8.160)

$$E_n = -\frac{\alpha^2\mu c^2}{2n^2}, \tag{12.81}$$

and so the difference from 1S to 2P is $E_2 - E_1$, or

$$\Delta E = \frac{\alpha^2\mu c^2}{2}\left(1 - {}^1\!/_4\right) = \frac{3\alpha^2\mu c^2}{8}. \tag{12.82}$$

Expressed as a multiple of h, this translates into a transition frequency

$$\Delta E \approx h \cdot 2.4674\,\mathrm{PHz}, \tag{12.83}$$

where P = peta = 10^{15}. The corresponding wavelength is

$$\lambda = \frac{hc}{\Delta E} \approx 121.50\,\mathrm{nm} \tag{12.84}$$

which is well into the UV range (in fact it's in the "vacuum UV" range, meaning it doesn't propagate well in air due to absorption by oxygen). Now coming back to the shift (12.80), if we assume $a_\mathrm{n} \sim 1$ fm, then we obtain

$$\delta E_1 \approx h \cdot 1\,\mathrm{MHz}, \tag{12.85}$$

which is *way* smaller, by about 9 orders of magnitude. Nevertheless, a shift of this order is easily detectable by modern laser-spectroscopy methods. Also, this same argument applies to heavy ions with a nuclear charge Ze and a single electron, which is a less useful scenario, but the effect is much stronger. The energy shift in this case picks up an extra factor of Z^4, because the modification to this heavy-atom problem involves the replacements $a_0 \longrightarrow a_0/Z$ and $\alpha \sim e^2 \longrightarrow \alpha Z$. In addition, the nuclear radius will be larger in such heavy ions.

12.6.3 Quadratic Stark Effect

The **dc Stark effect** is the shift of atomic energy levels due to an applied, dc electric field. To set up the problem, the base Hamiltonian is the hydrogen Hamiltonian(8.66) from before:

$$H_0 = \frac{p^2}{2\mu} - \frac{\hbar c\alpha}{r}. \tag{12.86}$$

The interaction potential is the interaction energy of an electric dipole with an electric field:

$$V = -\mathbf{d}\cdot\boldsymbol{\mathscr{E}}. \tag{12.87}$$

Here, $\boldsymbol{\mathscr{E}}$ is the electric field seen by the atom, which we will assume has the form

$$\boldsymbol{\mathscr{E}} = \mathscr{E}\hat{z}, \tag{12.88}$$

and $\mathbf{d}$ is the atomic dipole moment, which we can write as

$$\mathbf{d} = -e\mathbf{r}, \tag{12.89}$$

where $\mathbf{r}$ is the same relative electron coordinate that appears in the Hamiltonian. Combining these parts, the dipole interaction Hamiltonian has the form

$$V = e\mathscr{E}z. \tag{12.90}$$

We will again treat this problem in time-independent perturbation theory, and for the moment we will only compute the energy change of the 1S state. (The other states will have energy shifts too, but for that we'll need *degenerate* perturbation theory, so we'll come back to that calculation later.) As in the previous example, the first-order energy shift is given by

$$\delta E_1 = \langle\psi_0|V|\psi_0\rangle, \tag{12.91}$$

where $|\psi_0\rangle$ is the 1S eigenstate. However, this expectation value vanishes for this perturbation: Since the state is spherically symmetric, and we have an integral of the form $\langle\psi_0|z|\psi_0\rangle$, which is odd and thus vanishes. Spherical symmetry also implies that $\langle z\rangle = 0$; another way to see that this matrix element vanishes is to remember that a dipole interaction couples states of opposite parity.

And so we must move on to second order. Recall that the second-order shift (12.62) is given (again with $\lambda = 1$) by

$$\delta E_2 = \sum_{\beta\neq 0}\frac{|V_{0\beta}|^2}{E_{0\beta}}, \tag{12.92}$$

which for the problem at hand is

$$\delta E_2 = e^2\mathscr{E}^2\sum_{\beta\neq 0}\frac{|z_{0\beta}|^2}{E_{0\beta}}. \tag{12.93}$$

It's apparent that the energy shift is second order in the electric field—hence, the *quadratic* Stark effect. Beyond that, it's a little complicated to proceed, because the perturbation expression involves a sum over all states and all energy differences. The energy differences we know, but a sum over all states—although we can generate any one of them in principle—is not so easy, in principle.

12.6.3.1 Sum Rule

For the hydrogen 1S state, there is a fortunate trick for computing this sum.[2] It works because it doesn't even involve the other wave functions. As a prelude, since we are looking at the matrix elements $z_{\beta 0} = \langle\beta|z|\psi_0\rangle$,

[2]Here we are following the calculation in Hans C. O'hanian, *Principles of Quantum Mechanics* (Prentice-Hall, 1990) (ISBN: 0137127952), Chapter 10. For another calculation using the perturbed wave function as an intermediate result, see Leonard L. Schiff, *Quantum Mechanics*, 3rd ed. (McGraw–Hill, 1968) (ISBN: 0070856435), Section 33, pp. 263–8.

where $|\psi_0\rangle$ is given again by Eq. (12.77), we will need to make use of the commutators

$$\begin{aligned}[p^2, z] &= -2\hbar^2\partial_z \\ [p^2, r] &= -2\hbar^2\left(\partial_r + \frac{1}{r}\right).\end{aligned} \tag{12.94}$$

The first commutator is relatively obvious, following from $[z, f(p_z)] = i\hbar f'(p_z)$. The second commutator is slightly more involved:

$$\begin{aligned}[p^2, r] &= -\hbar^2[\nabla^2, r] \\ &= -\hbar^2\nabla^2 r - 2\hbar^2(\nabla\mathbf{r})\cdot\nabla \\ &= -2\hbar^2\left(\frac{1}{r} + \hat{r}\cdot\nabla\right).\end{aligned} \tag{12.95}$$

In the second equality we expanded the commutator; remembering that the commutator is itself an operator that should operate on some test function, say $f(\mathbf{r})$, the forward-ordered term of the commutator involves $\nabla^2(rf) = (\nabla^2 r)f + 2(\nabla r)\cdot(\nabla f) + r\nabla^2 f$, where the last term here cancels the reverse-ordered part of the commutator. For the last equality in Eqs. (12.95), we used $\nabla r = \mathbf{r}/r = \hat{r}$ and $\nabla^2 r = \nabla\cdot(\mathbf{r}/r) = 3/r - r^2/r^3 = 2/r$.

Now on to the trick. We want to consider the action of the operator $(r + 2a_0)z$ on the 1S state $|\psi_0\rangle$, and in particular commuting it with H_0. Emphasizing that we are in the position representation, we can start by commuting H_0 through $(r + 2a_0)$ and then z, using the above two commutators:

$$\begin{aligned}\langle\mathbf{r}|H_0(r+2a_0)z|\psi_0\rangle &= \langle\mathbf{r}|(r+2a_0)H_0 z|\psi_0\rangle - \frac{\hbar^2}{\mu}\langle\mathbf{r}|\left(\partial_r + \frac{1}{r}\right)z|\psi_0\rangle \\ &= \langle\mathbf{r}|(r+2a_0)zH_0|\psi_0\rangle - \frac{\hbar^2}{\mu}\langle\mathbf{r}|\left(\partial_r + \frac{1}{r}\right)z|\psi_0\rangle - \frac{\hbar^2}{\mu}\langle\mathbf{r}|(r+2a_0)\partial_z|\psi_0\rangle,\end{aligned} \tag{12.96}$$

where we assumed that the state is of the form e^{-r/a_0}. Now evaluating the second term, we have

$$\langle\mathbf{r}|\left(\partial_r + \frac{1}{r}\right)z|\psi_0\rangle = \langle\mathbf{r}|\left(\partial_r + \frac{1}{r}\right)r\cos\theta|\psi_0\rangle = \langle\mathbf{r}|\left(\frac{1}{r} - \frac{1}{a_0} + \frac{1}{r}\right)r\cos\theta|\psi_0\rangle = \langle\mathbf{r}|\left(\frac{2}{r} - \frac{1}{a_0}\right)z|\psi_0\rangle. \tag{12.97}$$

In the third term, we again need to assume a state of the form e^{-r/a_0}, and so both of these calculations are specific to the 1S state:

$$\langle\mathbf{r}|(r+2a_0)\partial_z|\psi_0\rangle = \langle\mathbf{r}|(r+2a_0)\left(-\frac{z}{a_0 r}\right)\partial_r|\psi_0\rangle = \langle\mathbf{r}|\left(-\frac{2}{r} - \frac{1}{a_0}\right)z|\psi_0\rangle. \tag{12.98}$$

Putting these two results into Eq. (12.96) gives

$$\langle\mathbf{r}|H_0(r+2a_0)z|\psi_0\rangle = \langle\mathbf{r}|(r+2a_0)zH_0|\psi_0\rangle + \frac{2\hbar^2}{\mu a_0}\langle\mathbf{r}|z|\psi_0\rangle. \tag{12.99}$$

This result will be useful in treating the matrix element $z_{\beta 0}$. In particular,

$$\begin{aligned}z_{\beta 0} &= \langle\beta|z|\psi_0\rangle \\ &= \frac{\mu a_0}{2\hbar^2}\langle\beta|\Big[H_0(r+2a_0)z - (r+2a_0)zH_0\Big]|\psi_0\rangle \\ &= \frac{\mu a_0}{2\hbar^2}\big(E_\beta - E_0\big)\langle\beta|(r+2a_0)z|\psi_0\rangle.\end{aligned} \tag{12.100}$$

Now we can use this result in the energy shift (12.93) to write

$$\begin{aligned}\delta E_2 &= e^2\mathscr{E}^2\sum_{\beta\neq 0}\frac{z_{0\beta}z_{\beta 0}}{E_{0\beta}} \\ &= -\frac{e^2\mathscr{E}^2\mu a_0}{2\hbar^2}\sum_{\beta\neq 0}\langle\psi_0|z|\beta\rangle\langle\beta|(r+2a_0)z|\psi_0\rangle.\end{aligned} \tag{12.101}$$

Now look what has happened: Not only has the energy difference canceled, making the sum simpler, but now we can also remove the excited states, which only appear as the bulk of an identity operator:

$$\sum_{\beta\neq 0} |\beta\rangle\langle\beta| = 1 - |\psi_0\rangle\langle\psi_0|. \tag{12.102}$$

Thus,

$$\delta E_2 = -\frac{e^2\mu a_0 \mathscr{E}^2}{2\hbar^2}\Big[\langle\psi_0|z^2(r+2a_0)|\psi_0\rangle - \langle\psi_0|z|\psi_0\rangle\langle\psi_0|(r+2a_0)z|\psi_0\rangle\Big]. \tag{12.103}$$

The second term vanishes for the same reason that $\delta E_1 = 0$, and so

$$\delta E_2 = -\frac{e^2\mu a_0 \mathscr{E}^2}{6\hbar^2}\langle\psi_0|r^2(r+2a_0)|\psi_0\rangle. \tag{12.104}$$

(Note the replacement of z^2 by $r^2/3$. Why can we do this?) The matrix element is now a straightforward integral to evaluate in terms of the 1S wave function (12.77):

$$\langle\psi_0|r^2(r+2a_0)|\psi_0\rangle = 4\pi\frac{1}{\pi a_0^3}\int_0^\infty dr\, r^2\, e^{-2r/a_0} r^2(r+2a_0) = \frac{27a_0^3}{2}. \tag{12.105}$$

Putting this back into Eq. (12.104), the shift becomes

$$\delta E_2 = -\frac{9e^2\mu a_0^4 \mathscr{E}^2}{4\hbar^2} = -9\pi\epsilon_0 a_0^3 \mathscr{E}^2, \tag{12.106}$$

(quadratic Stark shift, hydrogen 1S)

after recalling the expression

$$a_0 := \frac{\hbar}{\alpha\mu c} = \frac{4\pi\epsilon_0\hbar^2}{\mu e^2}. \tag{12.107}$$

for the Bohr radius (8.138). This result, where we were able to carry out a weighted sum over all excited states in closed form, is called a **sum rule**.

12.6.3.2 Static Polarizability

The more conventional way to report the dc Stark effect is in terms of the **static polarizability** α_0, defined such that

$$\mathbf{d} = \alpha_0 \boldsymbol{\mathscr{E}}. \tag{12.108}$$

This is of course a general expression if α_0 depends on the electric field, but at second order in perturbation theory α_0 is constant, implying an induced dipole proportional to the applied field, which we will now justify. (That the direction is the same follows from spherical symmetry of the 1S state.) Recomputing the energy shift due to the dipole interaction, we can start with the interaction energy Eq. (12.87), indicating the field dependence of the induced dipole,

$$V = -\mathbf{d}(\boldsymbol{\mathscr{E}})\cdot\boldsymbol{\mathscr{E}}. \tag{12.109}$$

Then the energy shift due to a small field change $\delta\boldsymbol{\mathscr{E}}$ is

$$\delta V = -\mathbf{d}(\boldsymbol{\mathscr{E}})\cdot\delta\boldsymbol{\mathscr{E}} = -\alpha_0 \mathscr{E}\,\delta\mathscr{E}. \tag{12.110}$$

Integrating the field strength from 0 to $\mathscr{E}$, the energy change is

$$\Delta E = \int_0^{\mathscr{E}} \delta V(\mathscr{E}') = -\alpha_0 \int_0^{\mathscr{E}} \mathscr{E}'\,\delta\mathscr{E}', \tag{12.111}$$

or

$$\Delta E = -\frac{1}{2}\alpha_0 \mathscr{E}^2. \tag{12.112}$$

(Stark shift in terms of polarizability)

Thus, the 1/2 appears in the energy shift due to the fact that the dipole moment is induced by the electric field, and in doing the integration we computed the energy involved in setting up the induced dipole in the electric field.

Comparing this last expression to the shift (12.106), we can thus write

$$\alpha_0 = \frac{9}{2}\left(4\pi\epsilon_0 a_0^3\right) \tag{12.113}$$

(quadratic Stark shift, hydrogen 1S)

for the static polarizability.[3] This result is "exact" within the hydrogen atom model; better calculations based on the Dirac equation match this result to three decimal places.[4]

The Stark effect is detectable as a shift in the frequency of optical transitions. We've only computed one end of such shifts, since we have yet to compute the shift of any excited states. Another cool manifestation of the ground-state Stark effect is in creating **optical tweezers** for atoms. In this case, a focused laser beam creates a point of maximum intensity. Since the Stark shift is proportional to $\mathscr{E}^2$, it is proportional to the laser intensity, and since the shift is negative, the focused laser beam creates a potential well for atoms. Note that an optical field is an ac field, while we are considering the dc Stark effect here, but if the laser frequency is far below any of the atomic transition frequencies, it behaves to a good approximation as a dc field in creating this Stark shift (For example, a CO_2 laser at $\lambda = 10.6\,\mu$m, deep in the infrared, is basically static from the point of view of many relevant atoms.) This technique is often used with laser-cooled atoms (most often alkali or alkaline earth atoms, not with hydrogen), and can be used to trap atoms for minutes if they are held under sufficiently good vacuum.

12.6.3.3 Explicit Summation

Now in most cases, a sum rule won't exist, in which case we're left to fend for ourselves in dealing with the summation in the energy (12.93). So the question is, how well can we do by plowing through terms in the sum? The answer will obviously depend a lot on the specific problem, and even the formulation of the specific problem. Nevertheless, it's an instructive example to try this out on a problem where we already know the exact answer. In practice terms of the sum can be carried out by calculation with respect to numerically computed states (which are difficult to compute accurately in heavy atoms), or to infer the matrix elements from measurements (in atoms, they can be inferred from lifetime measurements of states). Here, we have access to the hydrogen states (at least in the spinless, nonrelativistic approximation), so we can compute the terms analytically.

As a really rough approximation to the sum, suppose that we only account for the $n = 2$ states in the sum. The candidate states are therefore, in $|n\ \ell\ m\rangle$ notation,

$$|2\ 0\ 0\rangle, \qquad |2\ 1\ 0\rangle, \qquad |2\ 1\ \pm 1\rangle. \tag{12.114}$$

However, only one of these states will give rise to a nonvanishing matrix element: $|2\ 0\ 0\rangle$ will still give rise to a spherically symmetric wave-function product, while $|2\ 1\ \pm 1\rangle$ will vanish under the azimuthal integral. Alternatively, referring back to the selection rules from the Wigner–Eckart theorem (Sections 7.4.4.8 and 7.4.4.9), we should note that ℓ must change by ± 1, and for the z matrix element (which is $m' = 0$ in the discussion there), m should not change.

Thus, the only transition we will account for is 1S–2P. We already computed the energy difference in Eq. (12.82),

$$E_{01} = -\frac{3\alpha^2\mu c^2}{8}, \tag{12.115}$$

where we'll use "1" to refer to the 2P state as the first (relevant) excited state, and note the minus sign, since we're computing the difference with respect to the ground (1S) state. The 2P wave function is, combining

[3] In "atomic units," $4\pi\epsilon_0 a_0^3 \approx 1.649 \times 10^{-41}\ \mathrm{J\cdot m^2/V^2}$ is the standard unit of electric polarizability. (See `https://physics.nist.gov/cgi-bin/cuu/Value?auepol`.)

[4] Peter Schwerdtfeger and Jeffrey K. Nagle, "2018 Table of static dipole polarizabilities of the neutral elements in the periodic table," *Molecular Physics* (2018) (doi: 10.1080/00268976.2018.1535143).

radial and angular parts [Eqs. (8.164) and (7.91), respectively],

$$\langle \mathbf{r}|1\rangle = R_{21}(r)\, Y_1^0(\Omega) = \frac{1}{\sqrt{\pi}(2a_0)^{3/2}}\, \frac{r}{2a_0}\, e^{-r/2a_0}\, \cos\theta, \tag{12.116}$$

and the 1S wave function is again given by Eq. (12.77). Then we can compute the matrix element

$$z_{01} = \frac{1}{2^{3/2}a_0^4} \int_0^\infty dr\, r^4 e^{-r/a_0} e^{-r/2a_0} \int_0^\pi d\theta\, \sin\theta\, \cos^2\theta, \tag{12.117}$$

and since the radial integral gives $256a_0^5/81$ and the angular integral gives $2/3$, we have

$$z_{10} = \frac{2^8 a_0}{3^5\sqrt{2}}. \tag{12.118}$$

Thus, carrying out the first term in the summation (12.93) gives

$$\delta E_2 \approx e^2\mathscr{E}^2 \frac{|z_{01}|^2}{E_{01}} = -\mathscr{E}^2 \frac{2^{18}e^2a_0^2}{3^{11}\alpha^2\mu c^2} = -\frac{2^{20}}{3^{11}}\pi\epsilon_0 a_0^3 \mathscr{E}^2, \tag{12.119}$$

or in terms of a polarizability, the shift (12.93) with the defining relation (12.113) give in general

$$\alpha_0 = -2e^2 \sum_{\beta\neq 0} \frac{|z_{0\beta}|^2}{E_{0\beta}} = \sum_{\beta\neq 0} \frac{2|d_{0\beta}|^2}{E_{\beta 0}}, \tag{12.120}$$

which in the present one-term approximation becomes

$$\alpha_0 \approx \frac{2^{19}}{3^{11}}\big(4\pi\epsilon_0 a_0^3\big) \approx 2.96\big(4\pi\epsilon_0 a_0^3\big). \tag{12.121}$$

Comparing this to the exact result of $9/2$, we see that this first term in the sum already accounts for about $2/3$ of the sum. Carrying out the first *two* terms of the sum (Problem 12.8) will account for about 75%.

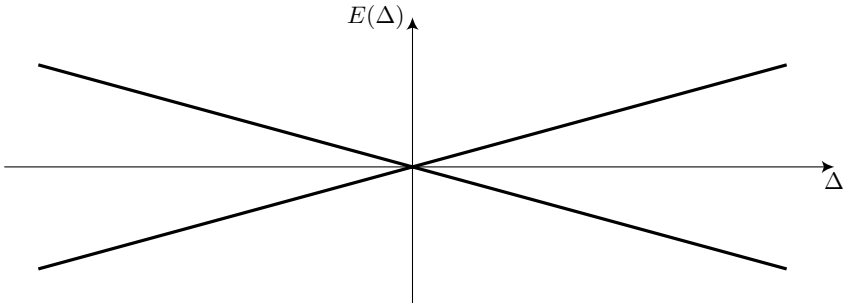
12.7 Validity of Perturbation Theory

At this point it is good to step back and take a look at how well and under what conditions can we expect perturbation theory to work. The main condition for perturbation theory to be valid is that for the contour integrals in Eqs. (12.21) and (12.22) to be obviously valid, the energies should not shift much. As we discussed before, the contour should enclose both the unperturbed and perturbed poles corresponding to the energy of interest, without enclosing any others. Thus, the shift in the pole should be small compared to the energy gap to any other level:

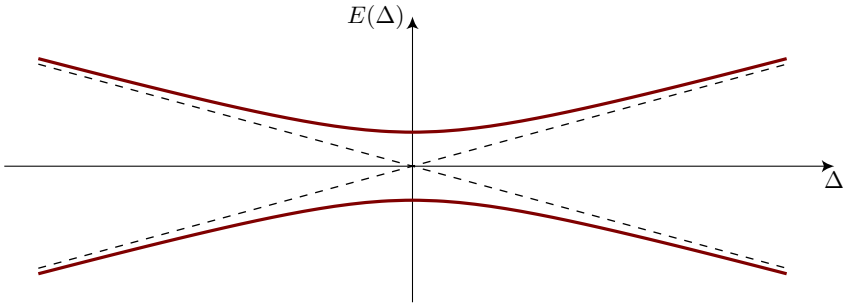
$$|E - E_0| \ll |E_{0\alpha}| \quad \forall_{\alpha\neq 0}. \tag{12.122}$$

Obviously, this also means that we are not considering states in the continuum, but only discrete states.

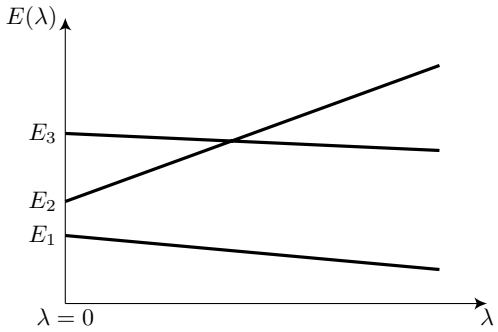
To discuss this point in a bit more depth, we can recall that in studying the double-well tunneling problem, we have already considered what happens when two levels come close to each other. To briefly review the discussion from Section 3.5, consider the case of two uncoupled levels that move through each other as a function of some parameter (here, Δ), as shown below.



In the case where we "turn on" a coupling, generically the energy levels will *not* cross through each other; rather, there is an **avoided level crossing**, as shown below, where the size of the energy gap is proportional to the coupling.



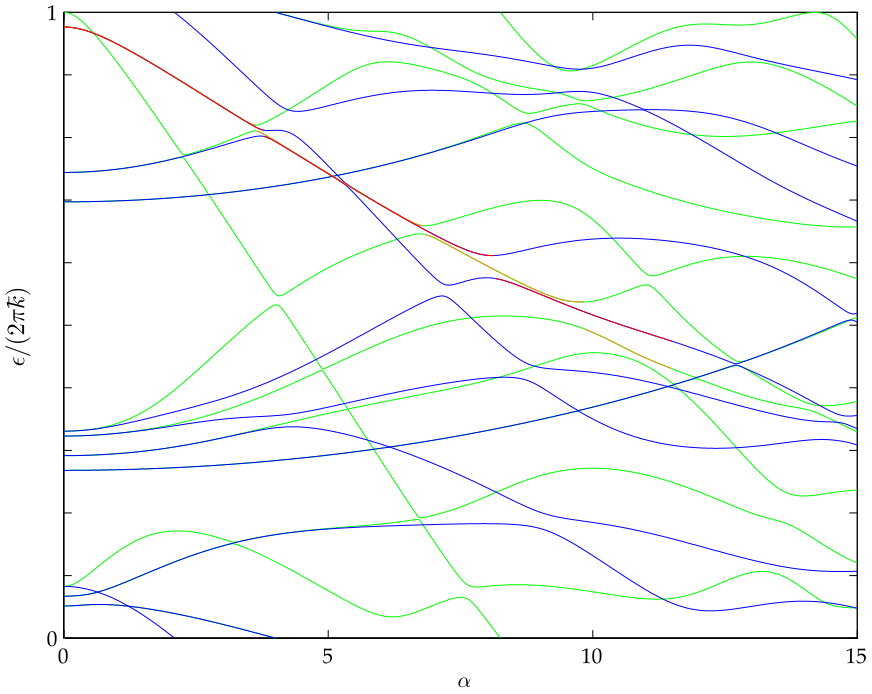
Now to translate this into perturbation theory, consider a perturbation operator λV, and consider what happens at first order in λ. As a function of λ, the energy shifts are straight lines, as plotted schematically below.



In this example, two levels cross at some value of λ. However, if there is any coupling via V (i.e., the matrix element $V_{23} \neq 0$), then this crossing shouldn't happen; there should instead be an avoided crossing as in the tunneling problem. This should show up at higher orders in perturbation theory. This behavior is called **level repulsion** in the perturbed spectrum. But this also means that first-order perturbation theory is only valid in the regime of λ well below the crossing, in line with our expectation above.

A good example of this avoided-crossing behavior is shown in the spaghetti-like plot below of the eigenvalues of a system that amounts to a pendulum with a periodic modulation of the gravitational acceleration g.[5]

[5] Daniel Adam Steck, *Quantum Chaos, Transport, and Decoherence in Atom Optics*, Ph.D. dissertation (The University of Texas at Austin, 2001), `http://steck.us/dissertation`, Fig. 6.24.



Here, α plays the role of the perturbation parameter λ, and the ϵ label the eigenvalues (which are **Floquet energies** rather than energies, because this is a time-periodic system). The states are labeled green or blue according to their parity, and states are only coupled to states of the same parity. Thus there are avoided crossings between green states, but green states may cross blue states. (The red and orange lines mark states that corresponded to a generalized form of double-well tunneling called **dynamical tunneling**.)

One final note about the convergence of the perturbation series. Clearly, for sufficiently small λ, the series should converge, because the high-order terms are rapidly becoming small. In general, though the series will not necessarily converge, but it should be viewed as an **asymptotic expansion**: while the series may diverge, a truncation to a finite number of terms still makes for a good approximation.

12.8 Degenerate Perturbation Theory

In developing the perturbation series before, the perturbation expressions that we have already derived [e.g., Eq. (12.45)] all involve energy differences $E_{0\alpha}$ in the denominator. However, if there are energy degeneracies, some of these will be zero, causing divergences in the perturbation expressions. It could happen that these divergences are tempered by some zero matrix element, say of the form $V_{0\alpha}$, but this doesn't generally happen. So we will need a more general formalism to handle this.

Also, in nondegenerate perturbation theory, the assumption underlying the projection (12.40) for the perturbed state was that the perturbed and unperturbed states should not be orthogonal: $\langle\psi|\psi_0\rangle \neq 0$. In the case where $|\psi_0\rangle$ is not degenerate, this assumption is fine. However, if there is degeneracy in the unperturbed states, we have to be more careful. The problem is that it can happen that $\langle\psi|\psi_0\rangle = 0$ (even at zero perturbation). More concretely, in the degenerate case, there are multiple unperturbed states $|\psi_0\rangle$ with the same energy E_0, and these states span a subspace where the basis may be chosen more or less arbitrarily. However, in general after the perturbation is incorporated, the perturbation selects some preferred basis for the corresponding perturbed states. It is not guaranteed without extra care that the unperturbed and perturbed states will be compatible in this sense.

So let's adapt the nondegenerate perturbation theory to the degenerate case.[6] Suppose that we have

[6] We are still following the treatment from Albert Messiah, *op. cit.*; however, some of the details omitted by Messiah are

degenerate, unperturbed states

$$|\psi_0, \gamma\rangle, \qquad \gamma = 1, \ldots, g, \tag{12.123}$$

indexed here by γ. There are then g total states with the same unperturbed energy E_0. Now we can redefine P_0 to be the projector for this whole unperturbed subspace:

$$P_0 := \sum_{\gamma=1}^{g} |\psi_0, \gamma\rangle\langle\psi_0, \gamma|. \tag{12.124}$$

As before, we can define the complementary projector

$$Q_0 := 1 - P_0. \tag{12.125}$$

We will also need the projector on the perturbed subspace, which is trickier to define, since the perturbed states are no longer degenerate, in general. However, we can define P as a projector on a subspace such that

$$P \longrightarrow P_0 \quad \text{as} \quad \lambda \longrightarrow 0. \tag{12.126}$$

The states in the subspace of P can then be written

$$|\psi, \gamma'\rangle, \qquad \gamma' = 1, \ldots, g, \tag{12.127}$$

since the dimension of P is the same as that of P_0. We are using a different (dummy) index γ' here to emphasize that the perturbed and unperturbed states cannot obviously be pairwise identified.

Nevertheless, to proceed, it is critical to identify the states in the two subspaces by some means, and the way to do this is by the projection operators, in analogy with the nondegenerate projection (12.40) to find the perturbed state. The idea is to first note that given a particular unperturbed state $|\psi_0, \gamma\rangle$, the projection $P|\psi_0, \gamma\rangle$ into the perturbed subspace is some *superposition* of the perturbed states $|\psi, \gamma'\rangle$; furthermore, each such projection maps to a unique superposition in the perturbed space. Recalling that the choice of the $|\psi_0, \gamma\rangle$ is somewhat arbitrary, if we make the *right* choice (or perhaps one of several correct choices), then $P|\psi_0, \gamma\rangle$ will map uniquely to a single counterpart $|\psi, \gamma'\rangle$. If none of this is obvious, remember that this must hold in the limit as $\lambda \longrightarrow 0$, and due to the adiabatic theorem the eigenvalues and eigenstates must change continuously with λ.

These statements more or less hold in the reverse direction, and things are maybe more clear this way. Given a particular perturbed state $|\psi, \gamma'\rangle$, the projection $P_0|\psi, \gamma'\rangle$ into the unperturbed space uniquely defines a linear combination of unperturbed states $|\psi_0, \gamma\rangle$. In fact, since the choice of unperturbed states is arbitrary within the subspace of P_0, it would be best to chose the unpertubed basis as the projection of the perturbed basis (although we don't in principle yet *know* the unperturbed basis, this still serves as a means for defining the states, and things will sort themselves out later).

The useful result of this discussion for the moment is that we can write a perturbed state $|\psi, \gamma'\rangle$ as a projection of the form $P|\psi_0, \gamma\rangle$. Thus, this form of the state satisfies the perturbed eigenvalue equation

$$HP|\psi_0, \gamma\rangle = E_\gamma P|\psi_0, \gamma\rangle, \tag{12.128}$$

remembering that the perturbed eigenvalues E_γ are no longer degenerate in general. This eigenvalue equation must still hold if we project back into the unperturbed space:

$$P_0HP|\psi_0, \gamma\rangle = E_\gamma P_0 P|\psi_0, \gamma\rangle. \tag{12.129}$$

The above discussion ensures that this is not a trivial statement of $0 = 0$. Now inserting projectors P_0 next to the unperturbed states doesn't change anything:

$$P_0HPP_0|\psi_0, \gamma\rangle = E_\gamma P_0 PP_0|\psi_0, \gamma\rangle. \tag{12.130}$$

from the original source of Claude Bloch, "Sur la théorie des perturbations des états liés," *Nuclear Physics* **6**, 329 (1958) (doi: 10.1016/0029-5582(58)90116-0).

The operator P_0HPP_0 on the left-hand side is Hermitian (why?), while the operator P_0PP_0 on the right-hand side is Hermitian and positive semidefinite (why?). This is a generalized eigenvalue equation that determines the appropriate eigenvalues and eigenvectors. In fact, since we have already developed perturbative expansions for P and HP [Eqs. (12.16) and (12.34) for P, and Eqs. (12.54) and (12.59) for HP], we can use this equation as the basis for a perturbative approximation. Unfortunately, while this gives the standard result at first order, at higher order the resulting expansions are more complicated than the standard results with no obvious benefit, so we will continue to develop a different method. The problem here is that there are *two* operators in the single equation that need expansions, whereas before we only expanded *one* operator to develop the energies and one other operator to develop the eigenvalues. The extra complication in the degenerate problem requires us to handle the eigenvalues and eigenvectors together. So we will need to develop a method that allows us to expand only a single operator to determine both the eigenvalues and eigenvectors *together*. This will come, of course, at the expense of a more complicated setup.

12.8.1 Perturbation-Mapping Operator

Let's now formalize the identification between the perturbed and unperturbed subspaces via the P and P_0 operators, as discussed above, by defining the perturbation operator $\mathscr{U}$ that maps unperturbed states to perturbed states,

$$\mathscr{U} : |\psi_0, \gamma\rangle \longrightarrow |\psi, \gamma\rangle. \tag{12.131}$$

In doing so, we are assuming that the ambiguity of the choice of unperturbed states has been resolved to make them compatible with the perturbed states, as we discussed. Then we can explicitly define

$$\mathscr{U} := \sum_\gamma |\psi, \gamma\rangle\langle\bar{\psi}_0, \gamma| \tag{12.132}$$
(perturbation map)

In this definition, the bar in the unperturbed state $|\bar{\psi}_0, \gamma\rangle$ denotes that this is an *unnormalized* form of the unperturbed state $|\psi_0, \gamma\rangle$, with norm defined such that its projection into the perturbed space is properly normalized:

$$P|\bar{\psi}_0, \gamma\rangle = |\psi, \gamma\rangle. \tag{12.133}$$

(That is, it's norm is *larger* than one.) With this definition of $\mathscr{U}$, we have the identities

$$\mathscr{U}P_0 = \mathscr{U}, \qquad P\mathscr{U} = \mathscr{U}, \qquad P_0\mathscr{U} = P_0, \qquad \mathscr{U}P = P. \tag{12.134}$$

The first two identities are straightforward applications of the perturbation-map operator; the second two follow from the projection relation (12.133), and that

$$\mathscr{U} = \sum_\gamma |\bar{\psi}, \gamma\rangle\langle\psi_0, \gamma|, \tag{12.135}$$

where $P_0|\bar{\psi}, \gamma\rangle = |\psi_0, \gamma\rangle$. This is just a geometric statement that the same normalization factor is lost in projecting from one space to the other, no matter in which direction.

Now the goal is to develop a perturbation series for $\mathscr{U}$. To this end, we will need the identity

$$\mathscr{U} = P_0 + \lambda Q_0 G_0(E_0) Q_0 \Big(V\mathscr{U} - \mathscr{U}V\mathscr{U} \Big), \tag{12.136}$$
(perturbation map)

which we will now prove. Starting with $H|\psi, \gamma\rangle = E_\gamma|\psi, \gamma\rangle$, and thus $(H - E_0)|\psi, \gamma\rangle = (E_\gamma - E_0)|\psi, \gamma\rangle$, along with

$$P_0(H - E_0) = P_0(H_0 - E_0 + \lambda V) = \lambda P_0 V, \tag{12.137}$$

we have

$$P_0\lambda V|\psi, \gamma\rangle = (E_\gamma - E_0)P_0|\psi, \gamma\rangle. \tag{12.138}$$

Operating on the left by $\mathscr{U}$, and using $\mathscr{U}P_0 = \mathscr{U}$,

$$\mathscr{U}\lambda V|\psi, \gamma\rangle = (E_\gamma - E_0)\mathscr{U}|\psi, \gamma\rangle = (E_\gamma - E_0)|\psi, \gamma\rangle, \tag{12.139}$$

where we used

$$\mathscr{U}|\psi,\gamma\rangle = |\bar{\psi},\gamma\rangle\langle\psi_0,\gamma|\psi,\gamma\rangle = |\psi,\gamma\rangle, \tag{12.140}$$

by definition of the unnormalized state $|\bar{\psi},\gamma\rangle$. Now rearranging Eq. (12.139), we have

$$\Big(H - E_0 - \mathscr{U}\lambda V\Big)|\psi,\gamma\rangle = 0. \tag{12.141}$$

Multiplying on the right by $\langle\bar{\psi}_0,\gamma|$ and summing over γ, we obtain another $\mathscr{U}$ to the right:

$$\Big(H - E_0 - \mathscr{U}\lambda V\Big)\mathscr{U} = 0. \tag{12.142}$$

Writing out $H = H_0 + \lambda V$ and rearranging,

$$\big(E_0 - H_0\big)\mathscr{U} = \lambda V\mathscr{U} - \mathscr{U}\lambda V\mathscr{U}. \tag{12.143}$$

Inserting $1 = P_0 + Q_0$ between $(E_0 - H_0)$ and $\mathscr{U}$,

$$\big(E_0 - H_0\big)Q_0\mathscr{U} = \lambda V\mathscr{U} - \mathscr{U}\lambda V\mathscr{U}, \tag{12.144}$$

and then we can multiply on the left by

$$Q_0 G_0(E_0)Q_0 = Q_0\frac{1}{E_0 - H_0}Q_0 \tag{12.145}$$

to find

$$Q_0\mathscr{U} = \lambda Q_0 G_0(E_0)Q_0\Big(V\mathscr{U} - \mathscr{U}V\mathscr{U}\Big). \tag{12.146}$$

Finally, using $Q_0 = 1 - P_0$ on the left with $P_0\mathscr{U} = P_0$, we obtain Eq. (12.136).

12.8.2 Expansion of the Perturbation Operator

Now to produce a series expansion for $\mathscr{U}$, we can define the expansion by

$$\mathscr{U} = \sum_{n=0}^{\infty}\lambda^n\mathscr{U}_n, \tag{12.147}$$

(perturbation-map expansion)

and plug this into the identity (12.136), matching orders of λ:

$$\begin{aligned}\mathscr{U}_0 &= P_0\\ \mathscr{U}_n &= Q_0 G_0(E_0)Q_0\left[V\mathscr{U}_{n-1} + \sum_{k=1}^{n-1}\mathscr{U}_k V\mathscr{U}_{n-k-1}\right].\end{aligned} \tag{12.148}$$

The form of $\mathscr{U}_0$ is reasonably obvious; the form for $\mathscr{U}_n$ comes from collecting all terms proportional to λ^n, accounting for the leading factor of λ in Eq. (12.136). There is, however, no $k = 0$ term in the sum because $Q_0P_0 = 0$. These relations determine all the $\mathscr{U}_n$ via recursion, and the solution to the recursion relation is

$$\mathscr{U}_n = \sum_{\substack{k_1,\ldots,k_n\\(k_1+\cdots+k_n=n)\\(k_1+\cdots+k_j\geq j,\ \forall_{0<j<n})}} S_{k_1}VS_{k_2}V\cdots VS_{k_n}VP_0, \tag{12.149}$$

(perturbation-map expansion terms)

in analogy to the expansions in the nondegenerate case. The conditions for the sum are somewhat more complicated than before, and bear some more explanation. Since $\mathscr{U}_n$ is associated with λ^n, clearly there should be n factors of V. However, the recursion (12.148) is asymmetric in having the G_0 always to the left, so that when the recursion is solved, the factors of G_0 tend to accumulate towards the left. There are n total

factors of G_0; due to the asymmetry the rightmost factor can't involve G_0, and so must be P_0. Similarly, due to the asymmetry, not only must the indices add up to n, but the lower partial sums $k_1 + \cdots + k_j$ must add up to at least j for every j from 1 to $n-1$. To illustrate the expansion the terms are

$$\begin{aligned}\mathscr{U} = \mathscr{U}_0 &+ \lambda G_Q V P_0 \\ &+ \lambda^2 \Big(G_Q V G_Q V P_0 - G_Q^2 V P_0 V P_0 \Big) \\ &+ \lambda^3 \Big(G_Q V G_Q V G_Q V P_0 \\ &\qquad - G_Q^2 V G_Q V P_0 V P_0 - G_Q V G_Q^2 V P_0 V P_0 - G_Q^2 V P_0 V G_Q V P_0 \\ &\qquad + G_Q^3 V P_0 V P_0 V P_0 \Big) \\ &+ \cdots\end{aligned}$$

(perturbation-map expansion) (12.150)

up through third order.

To convert this series into a perturbation series for the eigenvalues and eigenstates, we can return to Eq. (12.129):

$$P_0 H P |\psi_0, \gamma\rangle = E_\gamma P_0 P |\psi_0, \gamma\rangle. \tag{12.151}$$

Now using

$$\mathscr{U} P_0 P = \mathscr{U} P = P, \tag{12.152}$$

which follows from the identities (12.134), we can use this equation (replacing P on the left-hand side) to rewrite Eq. (12.151) as

$$\Big(P_0 H \mathscr{U} - E_\gamma \Big) P_0 P |\psi_0, \gamma\rangle = 0, \tag{12.153}$$

which is an eigenvalue problem of the form

$$\Big(P_0 H \mathscr{U} - E \Big) |\psi_0\rangle = 0. \tag{12.154}$$

(perturbation eigenvalue problem)

The idea is to expand the operator $P_0 H \mathscr{U}$ in a perturbation series using the series for $\mathscr{U}$ in Eqs. (12.147), (12.149), and (12.150). Explicitly through third order, this series is

$$\begin{aligned}P_0 H \mathscr{U} &= P_0 \big(H_0 + \lambda V \big) \mathscr{U} \\ &= E_0 P_0 + \lambda P_0 V \mathscr{U} \\ &= E_0 P_0 + \lambda P_0 V P_0 \\ &\qquad + \lambda^2 P_0 V G_Q V P_0 \\ &\qquad + \lambda^3 \Big(P_0 V G_Q V G_Q V P_0 - P_0 V G_Q^2 V P_0 V P_0 \Big) \\ &\qquad + \cdots .\end{aligned}$$

(eigenvalue-operator expansion) (12.155)

Now we should set up the series (12.154) for the various powers of λ to obtain the perturbation corrections at the various orders.

12.8.2.1 First Degenerate Order

Starting now with Eq. (12.154) and putting in the expansion (12.155) up through order λ, we have

$$\Big(E_0 + \lambda P_0 V P_0 \Big) |\psi_0\rangle = E |\psi_0\rangle, \tag{12.156}$$

keeping in mind that $P_0|\psi_0\rangle = |\psi_0\rangle$. Writing $\delta E_1 = E - E_0$,

$$\lambda P_0 V P_0 |\psi_0\rangle = \delta E_1 |\psi_0\rangle. \tag{12.157}$$

Expanding the second P_0 via Eq. (12.124),

$$P_0 = \sum_{\gamma'} |\psi_0, \gamma'\rangle\langle\psi_0, \gamma'|, \tag{12.158}$$

and operating from the left with $\langle\psi_0, \gamma|$,

$$\sum_{\gamma'} \lambda \langle\psi_0, \gamma|V|\psi_0, \gamma'\rangle\langle\psi_0, \gamma'|\psi_0\rangle = \delta E_1 \langle\psi_0, \gamma|\psi_0\rangle. \tag{12.159}$$

This equation is maybe a bit more clear if we switch to more compact notation,

$$\sum_{\gamma'} \lambda V_{\gamma\gamma'} \psi_{0,\gamma'} = \delta E_1 \psi_{0,\gamma}. \tag{12.160}$$

(first-order eigenvalue equation)

where the new notation should be reasonably obvious. This is an eigenvalue equation for the $g \times g$ matrix $\lambda V_{\gamma\gamma'}$, which is the perturbation operator expressed as matrix elements in the degenerate unperturbed subspace. The vector $\psi_{0,\gamma}$ gives the coefficients of the first-order eigenvectors in the unperturbed bases. Of course, in the nondegenerate ($g = 1$) case, this equation is simple to solve, and gives the previous first-order expression (12.58).

We have already worked through an example of this type of solution in the problem of double-well tunneling in Section 3.2. The degenerate states $|\mathrm{L}\rangle$ and $|\mathrm{R}\rangle$ are coupled by a matrix element $\langle\mathrm{R}|V|\mathrm{L}\rangle$; this lifts the degeneracy by splitting the eigenvalues about the unperturbed energy, and the new eigenvectors are even and odd superpositions of the unperturbed states. This calculation fits into the first-order perturbation scheme here, because the first-order eigenvalue problem involves only the degenerate states, and ignores the influence of any other states (say, the unbound continuum in the double-delta well).

In the unperturbed case, we have already made great fanfare about the ambiguity in choosing the basis in the space of P_0. If $V_{\gamma\gamma'}$ has all distinct eigenvalues, then the ''appropriate'' set of unperturbed eigenvectors is completely determined. If $V_{\gamma\gamma'}$ has some degenerate eigenvalues, then the adapted set of unperturbed eigenvectors is not determined until some higher order in perturbation theory. Note that, if $[H_0, V] = 0$ on some subspace of P_0's subspace, then the degeneracy will never be broken on the subspace at any order—the unperturbed Hamiltonian and perturbation respect some common symmetry that gives rise to the degeneracy.

12.8.2.2 Second Degenerate Order

At second order, we return to Eq. (12.154) and put in the expansion (12.155) up through order λ^2 to find

$$\Big(E_0 + \lambda P_0 V P_0 + \lambda^2 P_0 V G_Q V P_0\Big)|\psi_0\rangle = E|\psi_0\rangle. \tag{12.161}$$

Now writing $E = E_0 + \delta E_1 + \delta E_2$, we can cancel the E_0 and δE_1 components to write

$$\lambda^2 P_0 V G_Q V P_0 |\psi_0\rangle = \delta E_2 |\psi_0\rangle. \tag{12.162}$$

Expanding this out in the usual way, going directly to compact notation,

$$\sum_{\gamma', \alpha \neq 0} \lambda^2 \frac{V_{\gamma\alpha} V_{\alpha\gamma'}}{E_{0\alpha}} \psi_{0,\gamma'} = \delta E_2 \, \psi_{0,\gamma}. \tag{12.163}$$

(second-order eigenvalue equation)

Since the notation here is a bit more subtle, we'll explicitly note that

$$V_{\gamma\alpha} := \langle\psi_0, \gamma|V|\alpha\rangle, \qquad V_{\alpha\gamma'} := \langle\alpha|V|\psi_0, \gamma'\rangle. \tag{12.164}$$

We thus have again an eigenvalue equation for a $g \times g$ matrix; though the calculation of the matrix is more complicated than in first order, the diagonalization is in principle the same. Again, this reduces to the second-order shift (12.62) when $g = 1$.

12.8.3 Near-Degeneracy

Before moving on to calculations, it's worth noting that we can generalize the degenerate method somewhat. The underlying assumption is that there are g unperturbed states of energy E_0, and that for perturbation theory to be valid, the energy shifts should be small compared to the energy gaps to any other level. Now suppose there is a set of g *quasi*-degenerate states $|\psi_0, \gamma\rangle$ with energies $E_{0,\gamma}$, where the $E_{0,\gamma}$ span an energy range δE_g that is small compared to the gaps to any other level outside this group. (There may or may not be truly degenerate states among this group.) In principle, perturbation theory fails when the shifts become of the order δE_g, but this may be a limiting requirement. The way to handle this is to treat the group of nearly degenerate states as being degenerate; that is, P_0 is the projector for all of these states. Let E_0 be any energy in the range of the $E_{0,\gamma}$; this can be assigned as the degenerate energy of the group. Then the perturbation operator V is replaced by

$$V \longrightarrow V + \sum_{\gamma=1}^{g} (E_{0,\gamma} - E_0)\, |\psi_0, \gamma\rangle\langle\psi_0, \gamma|. \tag{12.165}$$

That is, we lump the small energy differences from the ''center energy'' E_0 into the perturbation operator. Then we can proceed with ordinary degenerate perturbation theory as before.

12.9 More Example Applications

12.9.1 Spectroscopic Notation for Hydrogen

As a first example of degenerate perturbation theory in action, let's look at the fine structure of hydrogen. So far, we have ignored the spin ($S = 1/2$) of the electron in hydrogen. But now, let's add it in. Also, since we are going more into the realm of atomic physics, it is time to introduce some new notation and modify some old notation. First, we have been referring to the eigenvalue of L^2 by the quantum number ℓ, which is conventional in basic treatments of the hydrogen atom. But more generally in atomic physics it is conventional to label this quantum number by L, so the eigenvalue of L^2 is $\hbar^2 L(L+1)$. There is a reason for this; in the case of multielectron atoms, L would refer to the *total* electronic orbital angular momentum, while ℓ would refer to the orbital angular momentum of a *single* electron. In hydrogen, there is no distinction made by these notation options, but we'll now adopt the prevailing notation. The same will go for spin; we'll use S for the spin quantum number, but s would be the quantum number for a single spin.

Now in adding the electron spin, we have states of the form $|n\ L\ m_L\ m_S\rangle$. We will also be defining the total electronic angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S}, \tag{12.166}$$
(total electronic angular momentum)

in which case it will be useful to refer to the eigenvalues of J^2 and J_z. We will see why shortly, but it is good to keep in mind that we will use the quantum numbers J and m_J for the eigenvalues of these respective operators. With this in mind, we can introduce the remainder of atomic-state notation (for very simple atoms, like hydrogen); the notation is $n\,{}^{(2S+1)}L_J(m_J = m_J)$. The $(2S+1)$ is called the **spin multiplet**, and denotes the number of states at fixed L and J. In hydrogen, this is always 2, but the point is that the notation can apply to more complicated atoms as well, with multiple valence electrons. Thus, the former 1S state is now $1\,{}^2\mathrm{S}_{1/2}$; the 2S state becomes $2\,{}^2\mathrm{S}_{1/2}$; the former P states are now $2\,{}^2\mathrm{P}_{1/2}$ and $2\,{}^2\mathrm{P}_{3/2}$. Remember from the addition rules of angular momentum, J can range in integer steps from $|L-S|$ to $L+S$, which explains the different J values here. So far, the $2\,{}^2\mathrm{S}_{1/2}$, $2\,{}^2\mathrm{P}_{1/2}$, and $2\,{}^2\mathrm{P}_{3/2}$ states are all degenerate. Additionally, the states are degenerate thus far with respect to the two electron-spin states.

12.9.2 Fine Structure of Hydrogen

Now let's look at the effect of the electron spin. The hydrogen atom mostly involved electric fields, but the electron spin results in a magnetic dipole, so we expect the interaction energy to be small. Thus we will treat it as a perturbation to the ''vanilla'' hydrogen atom, using first-order degenerate perturbation theory.

Since the states are $|n\ L\ m_L\ m_S\rangle$ after including electron spin (this is an eigenstate of S^2 as well, but the quantum number is fixed at $1/2$ so we won't bother to write it), we'll reiterate that these unperturbed states are at least doubly degenerate with respect to m_S, plus the $n = 2$ and higher degeneracies as noted in the notation discussion above.

Now to discuss the spin coupling quantitatively, the electron has a magnetic moment

$$\boldsymbol{\mu}_S = -g_S \mu_{\mathrm{B}} \frac{\mathbf{S}}{\hbar}, \tag{12.167}$$

where $\mu_{\mathrm{B}} = e\hbar/2m_{\mathrm{e}}$ is the **Bohr magneton** (which gives the expected magnetic moment per unit orbital angular momentum for an electron, to be derived shortly), and g_S is the electron g-factor, which is a fudge factor to account for the fact that spin is not equivalent to angular momentum. The g-factor isn't derivable in nonrelativistic theory, comes out to $g_S = 2$ in Dirac theory, and is just a smidge more in reality and in more sophisticated relativistic theory. (We saw all this before in Section section:spinhalf when we discussed spin-$1/2$, but we didn't justify these things very well there since we only needed the basic interaction.)

The magnetic moment should couple to a *magnetic* field, but the proton provides an *electric* field. Via the Lorentz transformations, the movement of the electron through the electric field causes it to see an effective magnetic field

$$\boldsymbol{\mathscr{B}} = -\frac{\mathbf{v}}{c^2} \times \boldsymbol{\mathscr{E}} = -\frac{\mathbf{p}}{m_{\mathrm{e}} c^2} \times \boldsymbol{\mathscr{E}}, \tag{12.168}$$

where $\mathbf{p}$ is the kinematic momentum ($m_{\mathrm{e}}\mathbf{v}$, not the canonical momentum, which involves the vector potential), and m_{e} is the electron mass. Now we'll reiterate another issue of notation, which starts with the fact that we used the reduced electron mass $\mu = m_{\mathrm{e}} m_{\mathrm{n}}/(m_{\mathrm{e}} + m_{\mathrm{n}})$ in the derivation of the hydrogen-atom eigenstates and eigenenergies. However, the prevailing convention (as mentioned before) is to write everything in terms of the *full electron mass*, and then switch to the reduced mass at the last second before plugging in numbers. This is evident in the constants μ_{B} and a_0, which are defined in terms of m_{e}, not μ (although they should be evaluated in terms of μ). Because of these standard definitions we will follow the convention, and switch back to m_{e} instead of μ, keeping in mind that it's necessary to switch back at the end of any calculation.

Now the Coulomb force on the electron is

$$\mathbf{F} = -e\boldsymbol{\mathscr{E}} = -\nabla V(r) = -\hat{r}\partial_r V(r), \tag{12.169}$$

since we are dealing with a central potential, and thus

$$\boldsymbol{\mathscr{E}} = \frac{\hat{r}}{e}\partial_r V(r). \tag{12.170}$$

Putting this into the above expression for $\boldsymbol{\mathscr{B}}$,

$$\boldsymbol{\mathscr{B}} = -\frac{\partial_r V(r)}{e m_{\mathrm{e}} c^2} \mathbf{p} \times \hat{r}, \tag{12.171}$$

and with

$$\mathbf{p} \times \hat{r} = \mathbf{p} \times \mathbf{r}\frac{1}{r} = -\mathbf{L}\frac{1}{r} = -\frac{\mathbf{L}}{r}, \tag{12.172}$$

keeping in mind $\mathbf{L}$ commutes with any function of r, so that

$$\boldsymbol{\mathscr{B}} = \frac{\partial_r V(r)}{e m_{\mathrm{e}} c^2 r}\mathbf{L}. \tag{12.173}$$

So the magnetic-dipole interaction (which we'll call the **fine-structure interaction**) is

$$H_{\mathrm{fs}} = -\boldsymbol{\mu}_S \cdot \boldsymbol{\mathscr{B}} = \frac{g_S \mu_{\mathrm{B}} \partial_r V(r)}{e m_{\mathrm{e}} c^2 \hbar r}\mathbf{L} \cdot \mathbf{S}. \tag{12.174}$$

This is a perturbation potential (like λV from the development of perturbation theory), but here we are using the also-common notation of calling this a "perturbation Hamiltonian." With the hydrogen-atom binding potential

$$V(r) = -\frac{\hbar c\alpha}{r}, \tag{12.175}$$

then

$$\partial_r V(r) = \frac{\hbar c\alpha}{r^2}, \tag{12.176}$$

and so

$$H_{\text{fs}} = \frac{g_S \mu_{\text{B}} \alpha}{e m_{\text{e}} c r^3} \mathbf{L}\cdot\mathbf{S}. \tag{12.177}$$

The $1/r^3$ dependence is characteristic of a dipole–dipole interaction, here between the spin and orbital magnetic-dipole moments of the electron. Using $\alpha = \hbar/m_{\text{e}}ca_0$ and $\mu_{\text{B}} = e\hbar/2m_{\text{e}}$, we can clean up the expression somewhat to read

$$H_{\text{fs}} = \frac{g_S \alpha^2 a_0}{2 m_{\text{e}} r^3} \mathbf{L}\cdot\mathbf{S}. \tag{12.178}$$

After doing a lot of manipulation of constants, it's always a good idea to do a dimension check: here $\mathbf{L}\cdot\mathbf{S}$ has the dimensions of squared action, where (action) = (energy)$\cdot$(time) = (length)$\cdot$(momentum). Thus, the expression is (action)^2/(mass)$\cdot$(length)^2, which is (energy)$\cdot$(time)$\cdot$(length)$\cdot$(momentum)/(mass)$\cdot$(length)^2, which in turn is just an energy, so the units check out.

There is one more important issue in the above derivation. Up to the point where we started worrying about what else $\mathbf{L}$ commutes with, the derivation was entirely classical, as it assumed a well-defined position (not to mention momentum) for the electron, so that the electric field seen by the electron had a well-defined value. Nonetheless, we got a result that is A-okay for a quantum electron bound to the hydrogen atom. Why does this work out?

Now we glossed over one point, which is that we computed the fine-structure interaction in the rest frame of the electron, but this is a *noninertial* frame, and so we should transform back into the laboratory frame. Essentially, the calculation imagined a magnetic field due to a proton orbiting an electron. The magnetic field causes precession (rotation)—called **Larmor precession**—of the spin about the field axis, in the same direction as the proton rotation. (We saw this before in our discussion of spin-$^1/_2$ dynamics in Section 9.2.2.) This amounts to overcounting the precession rate, since it includes this orbital frequency. The correction for transforming back into the lab frame, called **Thomas precession** amounts to the same expression, but with g_S replaced by 1;[7] adding in this correction gives

$$H_{\text{fs}} = \frac{(g_S - 1)\alpha^2 a_0}{2 m_{\text{e}} r^3} \mathbf{L}\cdot\mathbf{S}, \tag{12.179}$$
(fine-structure interaction)

where $g_S - 1 \approx 1$, but we will keep this more explicit form for numerical evaluation later.

Now in degenerate perturbation theory, we should treat the degenerate states together. As noted above, these correspond to the states of fixed n, L, and S, but different m_L and m_S. Recall from Eq. (12.160) that perturbation theory gives an eigenvalue problem; however, if we can find a basis to diagonalize the interaction operator, then solving the eigenvalue problem amounts to computing expectation values in this basis. The operator $\mathbf{L}\cdot\mathbf{S}$ is not diagonal in the basis $|n\ L\ m_L\ S\ m_S\rangle$, so we must find another basis. Fortunately it is easy to do so. Let's define the total angular momentum

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{12.180}$$
(total electronic angular momentum)

for the electron, as mentioned before. Remembering the rules for adding angular momentum (Section 7.3.1), in terms of the composite angular momentum we can replace the uncoupled simultaneous eigenstates of L^2,

[7] Roger R. Haar and Lorenzo J. Curtis, "The Thomas precession gives g_e-1, not $g_e/2$," *American Journal of Physics* **55**, 1044 (1987) (doi: 10.1119/1.14884).

L_z, S^2, and S_z with the simultaneous eigenstates of L^2, S^2, J^2, and J_z. Then squaring the total angular momentum,

$$J^2 = (\mathbf{L}+\mathbf{S})^2 = L^2 + S^2 + 2\mathbf{L}\cdot\mathbf{S}, \tag{12.181}$$

and solving for the dot product, we find

$$\mathbf{L}\cdot\mathbf{S} = \frac{1}{2}\Big(J^2 - L^2 - S^2\Big). \tag{12.182}$$

This expression is clearly diagonal in the coupled basis,

$$\langle L\ S\ J\ m_J|\mathbf{L}\cdot\mathbf{S}|L'\ S'\ J'\ m'_J\rangle = \delta_{LL'}\delta_{SS'}\delta_{JJ'}\delta_{m_J m'_J}\frac{\hbar^2}{2}\Big[J(J+1) - L(L+1) - S(S+1)\Big], \tag{12.183}$$

where the term $S(S+1)$ is always $3/4$ for hydrogen. So now that we have found the diagonalizing basis, it remains just to compute expectation values of the Hamiltonian (12.179). We will also need the radial expectation value Problem (12.9)

$$\left\langle r^{-3}\right\rangle = \frac{1}{L(L+1/2)(L+1)n^3a_0^3}, \tag{12.184}$$

which is divergent for $L = 0$, which is something we will ignore, because it will be accompanied by a corresponding zero in the numerator of the energy shift. The divergence here is a spurious side effect of the assumption of a $1/r$ potential, which should be cut off for the S states by the finite nuclear radius (Section 12.6.2). Then the zero in the numerator always "wins," and there is no fine-structure shift for S states.

Putting together Eqs. (12.183) and (12.184) to compute the expectation value of $H_{\rm fs}$ in Eq. (12.179), we have the **fine-structure shift**

$$\begin{aligned}\Delta E_{\rm fs} &= \frac{(g_S-1)\alpha^2 a_0\hbar^2}{4m_{\rm e}a_0^3n^3}\,\frac{J(J+1)-L(L+1)-S(S+1)}{L(L+1/2)(L+1)}\\ &= \frac{(g_S-1)m_{\rm e}c^2\alpha^4}{4n^3}\,\frac{J(J+1)-L(L+1)-S(S+1)}{L(L+1/2)(L+1)}\\ &= \frac{(g_S-1)(E_n)^2 n}{m_{\rm e}c^2}\,\frac{J(J+1)-L(L+1)-S(S+1)}{L(L+1/2)(L+1)}.\end{aligned} \tag{12.185}$$

(fine-structure shift)

The last two forms here show that this is a small effect, of order α^4 as compared to the eigenenergies E_n of order α^2.

An unrelated perturbation is the relativistic correction to the hydrogen energies, and it turns out to be of the same order in α. If this correction is computed and added to Eq. (12.185), in the approximation $g_S - 1 \approx 1$, the result is simpler, and only depends on J (Problem 12.10):

$$\Delta E_{\rm fs} + \Delta E_{\rm rel} = \frac{(E_n)^2}{2m_{\rm e}c^2}\left(3 - \frac{4n}{J+1/2}\right). \tag{12.186}$$

(fine-structure shift with relativistic correction)

In this expression, we can see that the states $2\,^2{\rm S}_{1/2}$, $2\,^2{\rm P}_{1/2}$, and $2\,^2{\rm P}_{3/2}$, which were all degenerate, have *some* of the degeneracy broken by the fine-structure shift: the $2\,^2{\rm P}_{3/2}$ is now at a different (higher) energy than the others. In the expression (12.185), there was no shift of S states, so evidently it is the relativistic correction that shifts the 1S and 2S states. In the real hydrogen atom, the $2\,^2{\rm S}_{1/2}$ and $2\,^2{\rm P}_{1/2}$ are not, in fact, degenerate. This is because of the **Lamb shift**,[8] which is basically a Stark shift of the energy levels due to the vacuum electromagnetic field. This is a tricky calculation and involves quantizing the electromagnetic field, so we won't discuss this effect further.

[8] This was measured in hydrogen by Willis E. Lamb, Jr. and Robert C. Retherford, "Fine Structure of the Hydrogen Atom by a Microwave Method," *Physical Review* **72**, 241 (1947) (doi: 10.1103/PhysRev.72.241); and then numerically calculated by H. A. Bethe, "The Electromagnetic Shift of Energy Levels," *Physical Review* **72**, 339 (1947) (doi: 10.1103/PhysRev.72.339); H. A. Bethe, L. M. Brown, and J. R. Stehn, "Numerical Value of the Lamb Shift," *Physical Review* **77**, 370 (1950) (doi: 10.1103/PhysRev.77.370). See also Edwin A. Power, "Zero-Point Energy and the Lamb Shift," *American Journal of Physics* **34**, 516 (1966) (doi: 10.1119/1.1973082).

12.9.2.1 Numerical Evaluation

To get a sense of scale for the fine-structure shift, let's put in some numerical values, and we'll also see that the calculation we've done is pretty accurate. Returning to the plain fine-structure shift (12.185) (that is, we'll ignore the relativistic correction, which will drop out of transition energies between levels with common L values), we can compute the difference in shifts[9] (Problem 12.187)

$$\Delta E_{\rm fs}(n, J = L + S) - \Delta E_{\rm fs}(n, J = L - S) = \frac{1 + \alpha/\pi}{1 + m_{\rm e}/m_{\rm p}} \frac{hcR\alpha^2}{n^3 L(L+1)}(2S). \tag{12.187}$$

This expression assumes $g_S \approx 2 + \alpha/\pi$ (which includes the leading correction from QED), has restored the reduced-mass correction, and uses the Rydberg constant R (dimensions of 1/length), defined such that the hydrogen-atom energies are (note the electron mass, not the reduced mass)

$$E_n = -\frac{\alpha^2 m_{\rm e} c^2}{2n^2} = -\frac{hcR}{n^2}. \tag{12.188}$$

The Rydberg in this conventional form is a funny thing, but defined such that one can compute wavelengths directly from $\lambda^{-1} = R(n^{-2} - n'^{-2})$. Using $L = 1$, $n = 2$, and $S = 1/2$, the numerical energy difference comes out to

$$\Delta E_{\rm fs}(2{\rm P}_{3/2}) - \Delta E_{\rm fs}(2{\rm P}_{1/2}) = h \cdot 10.96874\,{\rm GHz}. \tag{12.189}$$

This is in impressive agreement with the experimental value $h \cdot 10.969127(87)\,{\rm GHz}$.

Note that the fine-structure splitting is fairly small in hydrogen, but it is much larger in heavier, hydrogen-like atoms. For example, in sodium (^{23}Na), this corresponds to the famous ''D-line doublet,'' the yellowish 589-nm transition ($3^2{\rm S}_{1/2} \longrightarrow 3^2{\rm P}_{1/2,3/2}$) that gives sodium street lights their characteristic color. The two lines here are split by about 0.58 nm, and the splitting is visible by eye with a sufficiently good spectrometer.[10] The fine-structure splitting in the corresponding near-infrared transition in cesium (^{133}Cs) is much larger, amounting to 42 nm (between $6^2{\rm S}_{1/2} \longrightarrow 6^2{\rm P}_{1/2}$, or the D_1 line, at 894 nm, and $6^2{\rm S}_{1/2} \longrightarrow 6^2{\rm P}_{3/2}$, or the D_2 line, at 852 nm).

12.9.2.2 Bohr Magneton: Derivation

We've been referring to the Bohr magneton $\mu_{\rm B}$ for a while now, so it's time to define it more carefully and derive it, since we'll need it again soon. This is a quantity that defines the magnetic moment due to an electron's orbital angular momentum. We'll do this calculation classically. The magnetic dipole moment due to a current loop is the current times the enclosed area.[11] Let's assume a circular orbit of radius r and period T. Then the current is the charge flow per unit time, or

$$I = \frac{\Delta q}{\Delta t} = -\frac{e}{T}, \tag{12.190}$$

while the loop area is

$$A = \pi r^2. \tag{12.191}$$

Then the magnetic moment is

$$\mu_{_L} = IA = -\frac{e\pi r^2}{T} \tag{12.192}$$

in magnitude. Now the angular momentum for a circular orbit is

$$L = rp = m_{\rm e} r v = m_{\rm e} r \left(\frac{2\pi r}{T}\right), \tag{12.193}$$

[9] Roger R. Haar and Lorenzo J. Curtis, *op. cit.*; this reference also quotes the experimental value for the fine-structure splitting.

[10] Nice demonstration: `https://www.youtube.com/watch?v=49K9WUmuInQ`

[11] David J. Griffiths, *Introduction to Electrodynamics*, 4th ed. (2013), p. 253 (ISBN: 9788120347762).

and thus

$$\frac{\mu_{L}}{L} = -\frac{e}{2m_{\mathrm{e}}}. \tag{12.194}$$

Since the area normal vector is in the same direction as the moment (actually, in the opposite direction, but we've accounted for this in the sign), we can then write

$$\boldsymbol{\mu}_{L} = -\frac{e}{2m_{\mathrm{e}}}\mathbf{L}. \tag{12.195}$$

Since it's handy to have a coefficient with the same dimensions as the magnetic moment, and the $\mathbf{L}$ has an $\hbar$ effectively built-in, we can write

$$\boldsymbol{\mu}_{L} = -\frac{e\hbar}{2m_{\mathrm{e}}}\frac{\mathbf{L}}{\hbar}, \tag{12.196}$$

and then define

$$\mu_{\mathrm{B}} := \frac{e\hbar}{2m_{\mathrm{e}}}, \tag{12.197}$$

(Bohr magneton)

so that the orbital magnetic moment is

$$\boldsymbol{\mu}_{L} = -\mu_{\mathrm{B}}\frac{\mathbf{L}}{\hbar}. \tag{12.198}$$

(orbital magnetic moment)

Note again that the Bohr magneton is defined with respect to the full electron mass m_{e}, not the reduced mass μ, so in principle this should still be corrected. In particular, from Eq. (12.194), the ratio $L/\mu_{L} \propto m_{\mathrm{e}}$ (note that both $\mathbf{L}$ and μ_{L} depend on the mass), so we should correct this ratio by multiplying by μ/m_{e}. This amounts to inserting the same factor in front of $\mathbf{L}$ in Eq. (12.198).

Again, we are getting away with doing a classical calculation for a quantum-mechanical system; why can we do this? The idea is essentially the same as in the derivation for the fine-structure Hamiltonian. The electron in reality has some charge distribution. Rather than using classical orbits, we can split up the distribution into a bunch of thin rings of different radii r; all of these pieces have the same moment in terms of the angular momentum, and the result is linear in the angular momentum, so we can simply sum over all the different rings to obtain the full result. The key here is the *linearity* of the quantity of interest in the charge; this is the fundamental reason that the classical treatment works (with some care).

12.9.3 Hyperfine Structure of Hydrogen

The last missing piece in our treatment of the hydrogen-atom level structure is the magnetic moment of the nucleus, which we have so far been neglecting. Recalling that the orbital and spin magnetic moments are both on the order of the Bohr magneton $\mu_{\mathrm{B}} = e\hbar/2m_{\mathrm{e}}$, the nuclear magnetic moment should be on the order of the **nuclear magneton** $\mu_{\mathrm{N}} := e\hbar/2m_{\mathrm{p}}$, where m_{p} is the proton mass. The nuclear magnetic moment should thus be smaller by a factor of order $m_{\mathrm{e}}/m_{\mathrm{p}} \approx 1/1836$ than the electronic magnetic moments, and its effect on the level structure should be correspondingly smaller as well.

12.9.3.1 Schematic Treatment

To develop the hyperfine structure, the idea is basically the same as for the fine structure. The nuclear magnetic moment is

$$\boldsymbol{\mu}_{I} = -\mu_{\mathrm{B}} g_{I}\frac{\mathbf{I}}{\hbar}, \tag{12.199}$$

where $\mathbf{I}$ is the nuclear spin operator and g_{I} is the nuclear spin g-factor.[12,13] With the convention here, $g_{I} \approx -0.00304$ for a single proton, showing the correspondingly small magnitude (for comparison, a single

[12] Note that we are defining g_{I} in the same way as g_{S}, in terms of the Bohr magneton and the sign for a negative charge. This is appropriate for atomic-structure theory when it is useful to compare electron and nuclear spin effects on a similar footing. However, it is also common to define g_{I} in other contexts in terms of the nuclear magneton, without the minus sign.

[13] Experimentally measured values for g_{I} for the alkali atoms are given by E. Arimondo, M. Inguscio, and P. Violino, "Experimental determinations of the hyperfine structure in the alkali atoms," *Reviews of Modern Physics* **49**, 31 (1977) (doi: 10.1103/RevModPhys.49.31).

neutron has $g_n \approx 0.00208$). Via its spin and orbital angular momenta, the electron generates a magnetic field $\mathbf{B}$; as a toy model to show how the hyperfine structure arises, we will assume for the moment that the magnetic field has the form

$$\mathbf{B} = -b\mathbf{J}, \tag{12.200}$$

where b is some positive constant, since $\mathbf{B}$ and $\mathbf{J}$ should be antiparallel for an electron where the charge is negative. (We will return later to treat the form of this field with more care.) The interaction is then given by

$$H_{\text{hfs}} = -\boldsymbol{\mu}_I \cdot \mathbf{B} = -\frac{\mu_B g_I b}{\hbar}\,\mathbf{I}\cdot\mathbf{J} =: A_{\text{hfs}}\,\frac{\mathbf{I}\cdot\mathbf{J}}{\hbar^2}, \tag{12.201}$$

where, since we have considered the interaction of the nuclear and electron magnetic dipoles, A_{hfs} is called the **magnetic dipole hyperfine constant** and has units of energy. The form of this interaction ($\mathbf{I}\cdot\mathbf{J}$) is very similar to the fine-structure ($\mathbf{L}\cdot\mathbf{S}$) interaction.

As in the fine-structure case, we can add the angular momenta to obtain the total atomic angular momentum

$$\mathbf{F} = \mathbf{J} + \mathbf{I}. \tag{12.202}$$
(hyperfine-structure angular momentum)

Under this interaction, we can use the new **hyperfine** quantum number F to label the new eigenstates; as in the fine-structure case, we square Eq. (12.202) to obtain the operator equation

$$\mathbf{F}^2 = \mathbf{J}^2 + \mathbf{I}^2 + 2\mathbf{I}\cdot\mathbf{J}, \tag{12.203}$$

and so when the operator $\mathbf{I}\cdot\mathbf{J}$ acts on a hyperfine state $|J\ I\ F\ m_F\rangle$ we find that it is an eigenstate,

$$(\mathbf{I}\cdot\mathbf{J})|J\ I\ F\ m_F\rangle = \frac{\hbar^2 K}{2}|J\ I\ F\ m_F\rangle, \tag{12.204}$$

where the eigenvalue is written in terms of the combination

$$K = F(F+1) - I(I+1) - J(J+1) \tag{12.205}$$

of angular-momentum quantum numbers. Thus, the energy shift due to this interaction is simply

$$\Delta E_{\text{hfs}} = \frac{1}{2}A_{\text{hfs}}K, \tag{12.206}$$

in terms of the dipole hyperfine constant.

12.9.3.2 The 1S State of Hydrogen

In the case of hydrogen, we can go on to compute the constant A_{hfs}. We already showed that the orbiting electron gives rise to a magnetic field, from Eqs. (12.173) and (12.176). However, we should reverse the sign here compared to the previous calculation because we need the field due to an orbiting electron, but before we computed the field *seen* by the electron moving through the nucleus' electric field:

$$\mathbf{B}_L = -\frac{\hbar\alpha}{em_e cr^3}\mathbf{L} = -\frac{\alpha^2 a_0}{er^3}\mathbf{L}. \tag{12.207}$$

On the other hand, the (classical) magnetic field due to a dipole moment $\boldsymbol{\mu}_S$ is[14]

$$\mathbf{B}_S = \frac{\mu_0}{4\pi r^3}\Big[3(\boldsymbol{\mu}_S\cdot\hat{r})\hat{r} - \boldsymbol{\mu}_S\Big] + \frac{2\mu_0}{3}\boldsymbol{\mu}_S\delta^3(\mathbf{r}), \tag{12.208}$$

[14]The first term here can be found in any standard book on electromagnetism, but the delta-function term is much less commonly discussed. There doesn't seem to be a great intuitive explanation for it, but if you integrate the magnetic field of a dipole over the volume of a sphere of some radius R, you find that the result is proportional to the magnetic moment and independent of R, necessitating the delta function. See John David Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, 1999) (ISBN: 8126510943) pp. 187-8.

which is the sum of an r^{-3} dipole-field term and a "contact" term. Using

$$\mu_0 \mu_{\text{B}}^2 = \frac{e^2\hbar^2}{4m_{\text{e}}^2\epsilon_0 c^2} = \frac{\pi\alpha\hbar^3}{m_{\text{e}}^2 c} = \frac{\pi\alpha^2 a_0 \hbar^2}{m_{\text{e}}} \tag{12.209}$$

and the magnetic moments (12.167) and (12.199), the Hamiltonian $H_{\text{hfs}} = -\boldsymbol{\mu}_I \cdot \mathbf{B} = -\boldsymbol{\mu}_I \cdot (\mathbf{B}_L + \mathbf{B}_S)$ becomes

$$H_{\text{hfs}} = -\frac{g_I \alpha^2 a_0}{2m_{\text{e}} r^3}\mathbf{L}\cdot\mathbf{I} - \frac{g_I g_S \alpha^2 a_0}{4m_{\text{e}} r^3}\Big[3(\mathbf{S}\cdot\hat{r})(\mathbf{I}\cdot\hat{r}) - \mathbf{S}\cdot\mathbf{I}\Big] - \frac{2\pi g_I g_S \alpha^2 a_0}{3m_{\text{e}}}\mathbf{S}\cdot\mathbf{I}\,\delta^3(\mathbf{r}),$$

(hydrogen magnetic-dipole hyperfine interaction Hamiltonian) (12.210)

which is relatively complicated compared to the electronic spin-orbit interaction.

At this point, to simplify things, we can specialize to the hydrogen 1S state. Since this is a spherically symmetric state, the $\mathbf{L}\cdot\mathbf{I}$ term will not contribute in the 1S state. This can be seen by imagining $\mathbf{I}$ to be in a fixed direction, and a 1S expectation value will involve an orientation average over $\mathbf{L}\cdot\mathbf{I}$, which will vanish. Another way to see this is to define $\mathbf{G} = \mathbf{L} + \mathbf{I}$, in which case

$$\mathbf{L}\cdot\mathbf{I} = \frac{1}{2}\big(G^2 - L^2 - I^2\big). \tag{12.211}$$

But since we have the quantum number $L = 0$, then the quantum numbers G and I must match, and so the expectation value of $\mathbf{L}\cdot\mathbf{I}$ will vanish.

Furthermore, in the 1S state, the second term of Eq. (12.210) will also not contribute, again because the expectation value will amount to a spherical average. In this case the average will not be changed by taking $\hat{r} = \hat{x}$, $\hat{y}$, or $\hat{z}$; averaging over these three cases in the expectation value takes $3(\mathbf{S}\cdot\hat{r})(\mathbf{I}\cdot\hat{r})$ to $3(S_x I_x + S_y I_y + S_z I_z)/3 = \mathbf{S}\cdot\mathbf{I}$, which cancels the other component of the same term.

Thus, we are left with

$$H_{\text{hfs}}(1\text{S}) = -\frac{2\pi g_I g_S \alpha^2 a_0}{3m_{\text{e}}}\mathbf{S}\cdot\mathbf{I}\,\delta^3(\mathbf{r}) \tag{12.212}$$

as the effective interaction Hamiltonian for the 1S state. The corresponding energy shift at first order in degenerate perturbation theory is just given by the expectation value

$$\Delta E_{\text{hfs}}(1\text{S}) = -\frac{2\pi g_I g_S \alpha^2 a_0}{3m_{\text{e}}}\Big\langle \mathbf{S}\cdot\mathbf{I}\Big\rangle |\psi_{100}(\mathbf{r}=0)|^2 \tag{12.213}$$

on the degenerate subspace of $|F\ m_F\rangle$. From Eq. (12.77) we have $|\psi_{100}(\mathbf{r}=0)|^2 = 1/\pi a_0^3$, and we have already shown in Eq. (12.204) that $\mathbf{S}\cdot\mathbf{I}$ (which here is equivalent to $\mathbf{J}\cdot\mathbf{I}$) is diagonal in the $|F\ m_F\rangle$ basis, so we are basically done. Since $L = 0$ and $S = 1/2$, we have $J = 1/2$; also with $I = 1/2$, F can take on the values 1 or 0, with corresponding values of $K = 1/2$ or $K = -3/2$, with K as defined in Eq. (12.205). Putting everything together, with $\langle \mathbf{J}\cdot\mathbf{I}\rangle = \hbar^2 K/2$,

$$\Delta E_{\text{hfs}}(1\text{S}, F) = -\frac{g_I g_S \alpha^2 \hbar^2}{6m_{\text{e}} a_0^2}\begin{cases} \times 1 & \text{if } F = 1 \text{ (triplet)} \\ \times(-3) & \text{if } F = 0 \text{ (singlet).}\end{cases}$$

(hydrogen 1S hyperfine shift) (12.214)

Remember that the $F = 1$ state has three-fold degeneracy, while the $F = 0$ is nondegenerate; the single state is shifted by an energy three times in magnitude of the shift of the triplet state. The hyperfine splitting of the 1S state is then the difference of the two shifts (remembering $g_I g_S < 0$ here):

$$\Delta E_{\text{hfs}}(1\text{S}, F=1) - \Delta E_{\text{hfs}}(1\text{S}, F=0) = -\frac{2 g_I g_S \alpha^2 \hbar^2}{3m_{\text{e}} a_0^2} \approx h \cdot 1.42\,\text{GHz}.$$

(hydrogen 1S hyperfine splitting) (12.215)

The corresponding wavelength is $\lambda = hc/\Delta E \approx 21.1\,\text{cm}$, which is the famous "21-cm line." This is, for example, included in the search range of the SETI project, in case extraterrestrials who did their quantum-mechanics homework want to contact us (it's also in a quiet window of the electromagnetic spectrum).[15] The hyperfine splitting is an order of magnitude smaller than the fine-structure splitting, justifying the name.

[15] https://www.seti.org/seti-institute/project/details/seti-observations

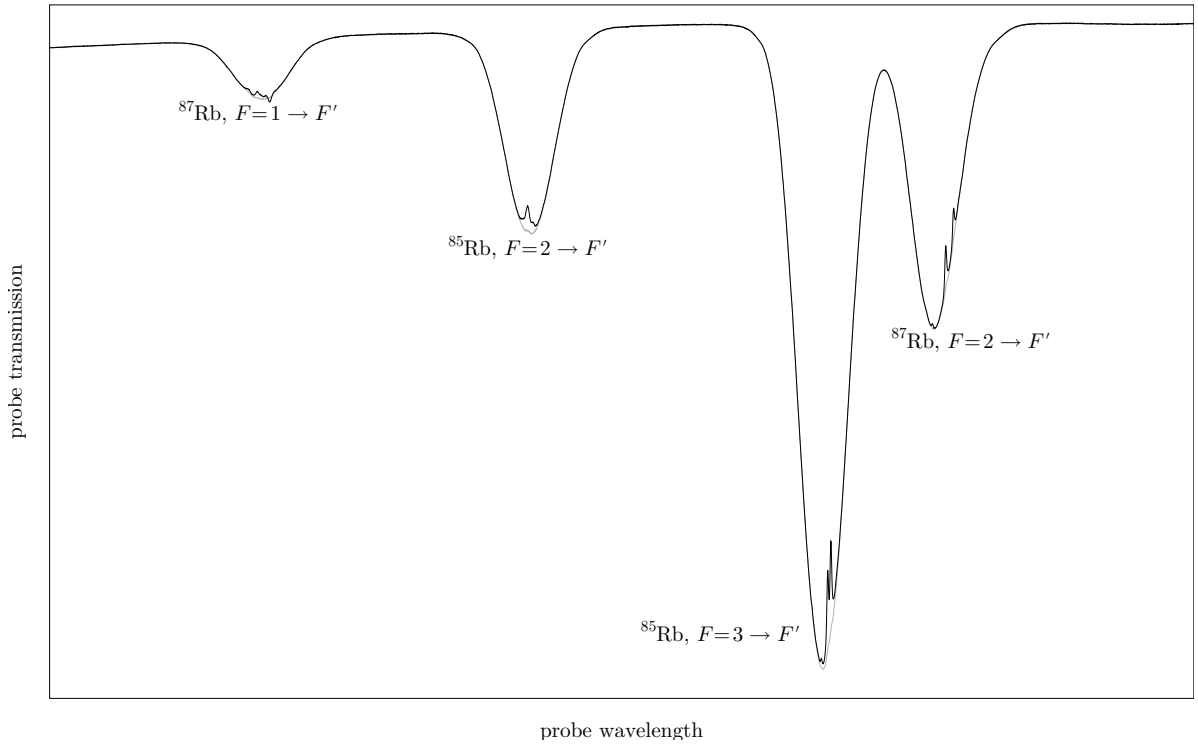
12.9.3.3 Other Hyperfine Splittings

In hydrogen, the same kind of calculation carries through for the $2P_{1/2}$ state, except now the detailed calculation of A_{hfs} will be more complicated. For larger-J states like $2P_{3/2}$ in hydrogen, it turns out that the same theory will carry through because $I = 1/2$. For more complicated nuclei (with larger I), the theory as presented so far is relatively crude—in these cases it is also important to consider higher-order multipole effects to get the shifts right. Nevertheless, the qualitative idea will still be correct: for example, for a $J = 3/2$ state, in general F will take on four different values, which will split into four distinct hyperfine levels, though the spacing will not be accurately predicted by a theory involving only A_{hfs} but not other hyperfine coefficients.

The hyperfine splitting of course shows up in other atoms too, with the hydrogen-like alkali atoms making for the simplest comparisons. We mentioned sodium before, and in ^{23}Na (the only stable isotope), $I = 3/2$ and the splitting of the ground (3S) state is about 1.7 GHz. This splitting is comparable to hydrogen, and thus it is far smaller relative to the fine-structure splitting in sodium than in hydrogen. For ^{133}Cs (the only stable isotope of cesium), $I = 7/2$, and the ground-state (6S) splitting is about 9.2 GHz. This is, in fact, at present the definition of the second (i.e., the second is defined such that the hyperfine splitting is *exactly* 9.192 631 77 GHz), though this definition will probably change to an optical transition in the coming years.

Another nice example of hyperfine splitting is shown in the plot below, where the wavelength of a laser is varied near the 780-nm D_2 transition ($5S_{1/2} \longrightarrow 5P_{3/2}$) of rubidium. The plot shows the transmission of the laser through a vapor cell of rubidium. There are two stable isotopes of rubidium, ^{85}Rb ($I = 5/2$, 3.0 GHz 5S splitting) and ^{87}Rb ($I = 3/2$, 6.8 GHz 5S splitting, technically unstable but long-lived). There are four dips in the transmission spectrum, corresponding to the two hyperfine-split ground-state levels in the two isotopes. Note how the splitting is asymmetric about the "center of gravity," with the lower-F level being shifted farther than the upper-F level. There is some extra structure in each of the dips, which reflects excited-state hyperfine structure (with much smaller splittings). In this example, ^{87}Rb has the larger hyperfine splitting owing to a larger g_I value (more than three times larger than in ^{85}Rb). The ^{87}Rb hyperfine splitting illustrated here is also a common basis for "secondary-standard" atomic clocks, since they are capable of high stability but are cheaper to produce than primary-standard cesium atomic clocks.[16]

[16] Here is a good example of a commercial rubidium-based clock: `https://www.thinksrs.com/products/perf10.html`. It seems a bit of overkill for audio applications, but whatever. Speaking of overkill, check out this cesium primary standard worn as a wristwatch: `http://leapsecond.com/pages/atomic-bill/`.



Besides time and frequency standards, hyperfine structure is important in the development of quantum information processing. The nucleus of a trapped atom or ion is a good realization of a qubit, because it is a discrete quantum system (being a spin), and because it only interacts via its (weak) magnetic moment, it is relatively insensitive to environmental perturbations and its states are long-lived. Although it is difficult to interact with, precision stabilized lasers that can resolve the hyperfine structure can be used to initialize and readout the nuclear qubit.

12.9.4 Zeeman Effect: Interaction with Static Magnetic Fields

Another nice example of degenerate perturbation theory in action is the **Zeeman effect**, or the energy-level shift due to interaction with an externally applied, dc magnetic field. First, let's consider the case of hydrogen with fine structure, and then later return to what happens when we add the hyperfine structure back in. In practice, this will apply when the applied field causes shifts large compared to the hyperfine splitting, but weak compared to the fine-structure splitting.

Again, each of the fine-structure (J) energy levels contains $2J+1$ sublevels labeled by m_J that determine the angular distribution of the electron wave function. In the absence of external fields, these sublevels are degenerate: as we saw above, the fine-structure shift only depends on J, not m_J.

However, when an external magnetic field is applied, their degeneracy is broken. Both the magnetic moments due to the electron spin and orbit couple to the field, and the Hamiltonian describing the atomic interaction with the magnetic field is simply the Hamiltonian for a magnetic-dipole interaction ,

$$\begin{aligned} H_B^{(\mathrm{fs})} &= -\boldsymbol{\mu}_S \cdot \mathbf{B} - \boldsymbol{\mu}_L \cdot \mathbf{B} \\ &= \frac{\mu_\mathrm{B}}{\hbar}(g_S \mathbf{S} + g_L \mathbf{L}) \cdot \mathbf{B} \\ &= \frac{\mu_\mathrm{B}}{\hbar}(g_S S_z + g_L L_z) B, \end{aligned} \tag{12.216}$$

if we take the magnetic field to be along the z-direction (i.e., along the atomic quantization axis), $\mathbf{B} = B\hat{z}$. Again, the quantities g_S and g_L are respectively the electron spin and orbital "g-factors" or fudge-factors that account for various modifications to the corresponding magnetic dipole moments. We already saw g_S in

Section 12.9.2, but g_L is new. The Bohr magneton μ_B, as derived in Section 12.9.2.2, is defined in terms of the electron mass m_e, although the relevant mass is the reduced mass $\mu = m_e m_p/(m_e + m_p)$. This reflects the prevailing convention of performing calculations in the infinite-nuclear-mass approximation, and then correcting the result later. The reduced-mass correction is a factor of μ/m_e multiplying $\mathbf{L}$ [see Eq. (12.198) and the following discussion], and thus

$$g_L = \frac{\mu}{m_e} = \frac{1}{1 + m_e/m_p} \approx 1 - \frac{m_e}{m_p}, \tag{12.217}$$

where again m_p is the proton mass (which would be replaced by the nuclear mass in the more general case).

12.9.4.1 Weak-Field Calculation

If we work in the low-magnetic-field regime, the magnetic-interaction Hamiltonian $H_B^{(fs)}$ is a perturbation to to the fine-structure Hamiltonian H_{fs} [which at this point we can define such that it produces the energy shift (12.186)]. Then in first-order degenerate perturbation theory we ignore any mixing of fine-structure states of different J, and the energy shift is

$$\begin{aligned}
\Delta E_B^{(fs)}(J, m_J) &= \langle J\, m_J | H_B^{(fs)} | J\, m_J \rangle \\
&= \frac{\mu_B B}{\hbar} \langle J\, m_J | (g_S S_z + g_L L_z) | J\, m_J \rangle \\
&= \frac{\mu_B B g_L}{\hbar} \langle J\, m_J | J_z | J\, m_J \rangle + \frac{\mu_B B (g_S - g_L)}{\hbar} \langle J\, m_J | S_z | J\, m_J \rangle \\
&= \mu_B B g_L m_J + \frac{\mu_B B (g_S - g_L)}{\hbar} \langle J\, m_J | S_z | J\, m_J \rangle,
\end{aligned} \tag{12.218}$$

where we used $J_z = L_z + S_z$ and of course $J_z |J\, m_J\rangle = \hbar m_J |J\, m_J\rangle$. To evaluate the second term, we first note that since $\mathbf{J} = \mathbf{L} + \mathbf{S}$, squaring this relation gives

$$\mathbf{S} \cdot \mathbf{J} = \frac{1}{2} \left(\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2 \right). \tag{12.219}$$

Using the projection theorem (7.208), we can write

$$\begin{aligned}
\langle J\, m_J | S_z | J\, m_J \rangle &= \frac{m_J}{\hbar J(J+1)} \langle J\, m_J | \mathbf{S} \cdot \mathbf{J} | J\, m_J \rangle \\
&= \frac{m_J}{2\hbar J(J+1)} \langle J\, m_J | \left(\mathbf{J}^2 + \mathbf{S}^2 - \mathbf{L}^2 \right) | J\, m_J \rangle \\
&= \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \hbar m_J,
\end{aligned} \tag{12.220}$$

where we used Eq. (12.219) for the dot product, and we recall that $|J\, m_J\rangle \equiv |L\, S\, J\, m_J\rangle$. Putting this expectation value into Eq. (12.218), we obtain the perturbative shift

$$\Delta E_B^{(fs)} = \mu_B g_J m_J B, \tag{12.221}$$

(fine-structure Zeeman shift, small B)

where the **Landé g_J factor**[17] is

$$g_J := g_L + (g_S - g_L) \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \tag{12.222}$$

(Landé g_J factor)

[17] S. Goudsmit, "Nuclear Magnetic Moments," *Physical Review* **43**, 636 (1933) (doi: 10.1103/PhysRev.43.636); Alfred Landé, "The Magnetic Moment of the Proton," *Physical Review* **44**, 1028 (1933) (doi: 10.1103/PhysRev.44.1028); Alfred Landé, "Nuclear Magnetic Moments and Their Origin," *Physical Review* **46**, 477 (1934) (doi: 10.1103/PhysRev.46.477); Paul Forman, "Alfred Landé and the anomalous Zeeman Effect, 1919-1921," *Historical Studies in the Physical Sciences* **2**, 153 (1970).

Note that since $g_L \approx 1$ and $g_S \approx 2$, the g_J factor is commonly written as

$$g_J \approx 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \tag{12.223}$$

The shift in this regime is proportional to both the m_J quantum number and the magnetic field. Recall that this is *only* valid when the magnetic field is along the $\hat{z}$ direction; otherwise, you must compute the energy shifts according to this method for the states quantized along the magnetic field, and then effect a coordinate rotation to obtain the states with the desired quantization axis, which will no longer be eigenstates of the system. Thus, with other quantization axes, a given state will ''remix'' with the others due to precession along the magnetic-field axis. It was a fortunate choice of the atomic orientation that allowed us to diagonalize the interaction Hamiltonian relatively easily.

For the hyperfine case, if the energy shift due to the magnetic field is small compared to the fine-structure splitting, then as we just argued J is a good quantum number. Then the interaction Hamiltonian can be written as the fine-structure interaction plus the magnetic-dipole interaction of the *nuclear* magnetic moment with the magnetic field:

$$H_B^{(\text{hfs})} = H_B^{(\text{fs})} - \boldsymbol{\mu}_I \cdot \mathbf{B} = \frac{\mu_\text{B}}{\hbar}(g_J J_z + g_I I_z)B_z. \tag{12.224}$$

Again, if the energy shift due to the magnetic field is small compared to the hyperfine splittings, then the fine-structure treatment carries through with $J \longrightarrow F$, $S \longrightarrow I$, and $L \longrightarrow J$, so that

$$\Delta E_\text{B}^{(\text{hfs})} = \mu_\text{B} g_F m_F B, \tag{12.225}$$

(hyperfine Zeeman shift, small B)

where the g_F factor is

$$g_F := g_J + (g_I - g_J)\frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)}, \tag{12.226}$$

or in a more symmetric form,

$$g_F := g_J \frac{F(F+1) - I(I+1) + J(J+1)}{2F(F+1)} + g_I \frac{F(F+1) + I(I+1) - J(J+1)}{2F(F+1)}.$$

(Landé g_F factor) (12.227)

Recalling that g_I is much smaller than g_J, this is commonly written

$$g_F \approx g_J \frac{F(F+1) - I(I+1) + J(J+1)}{2F(F+1)}, \tag{12.228}$$

which is correct at the 0.1% level.

The shifts proportional to the magnetic fields in this weak-field regime were historically referred to as the **anomalous Zeeman effect**, after Zeeman's observation of the splitting of spectral lines.[18] The ''normal'' case was based on the predicted splittings due only to orbital angular momentum. In this case, for something like the 1S⟶2P hydrogen transition, the spectrum should split into three components with an applied magnetic field. However, the ''anomalous'' case due to the inclusion of spin, leads to splitting into an even number of components, something that can't be explained by orbital angular momentum alone. The anomalous Zeeman effect was observed before spin was known, laying the foundation for the Stern–Gerlach experiment to confirm the existence of electron spin.

[18] P. Zeeman, ''The Effect of Magnetisation on the Nature of Light Emitted by a Substance,'' *Nature* **55**, 347 (1897) (doi: 10.1038/055347a0); P. Zeeman, ''On the influence of Magnetism on the Nature of the Light emitted by a Substance,'' *Philosophical Magazine* **43**, 226 (1897); P. Zeeman, ''Doubles and triplets in the spectrum produced by external magnetic forces,'' *Philosophical Magazine* **44** 55 (1897).

12.9.4.2 Strong-Field Calculation

Let's review for a second what we just did in the above Zeeman-shift calculation. In the hyperfine-structure case, we worked with the magnetic-dipole interaction Hamiltonian (12.224) for the external magnetic field

$$H_B^{(\mathrm{hfs})} = -\boldsymbol{\mu}_J \cdot \mathbf{B} - \boldsymbol{\mu}_I \cdot \mathbf{B} = \frac{\mu_\mathrm{B}}{\hbar}(g_J J_z + g_I I_z)B_z, \tag{12.229}$$

and we treated this as a perturbation to the hyperfine-structure Hamiltonian (12.201)

$$H_\mathrm{hfs} = \frac{A_\mathrm{hfs}}{\hbar^2}\,\mathbf{I}\cdot\mathbf{J}. \tag{12.230}$$

This treatment is appropriate for small magnetic fields such that the Zeeman shifts are small compared to the hyperfine splitting. In this case, first-order degenerate perturbation theory amounts to diagonalizing $H_B^{(\mathrm{hfs})}$ on subspaces of constant F.

This system is a nice example, because we can also do perturbation theory in *reverse*: in the case of a strong magnetic field, such that the field-induced energy shifts are large compared to the hyperfine splitting, we should instead treat the hyperfine-structure Hamiltonian H_hfs as a perturbation to the external-field Hamiltonian $H_B^{(\mathrm{hfs})}$. In this regime the effect is called the **Paschen–Back effect**[19] (or more properly, the **hyperfine Paschen–Back effect**). We will focus on the hyperfine Paschen–Back effect rather than the fine-structure version, because it is generally easier to enter this regime for hyperfine structure with fields that aren't too extreme.

At zeroth order, ignoring the hyperfine-structure Hamiltonian, the eigenstates of the interaction are the uncoupled, or ''high-field'' fine-structure states $|J\,m_J; I\,m_I\rangle$, and F is no longer a good quantum number. The energy shifts are just given by the expectation value of the interaction Hamiltonian in this basis, or

$$\Delta E(J\,m_J; I\,m_I) = \left\langle H_B^{(\mathrm{hfs})} \right\rangle = \frac{\mu_\mathrm{B}}{\hbar}\langle g_J J_z + g_I I_z\rangle\, B = \mu_\mathrm{B}(g_J m_J + g_I m_I)B. \tag{12.231}$$

The energies again shift linearly with the applied field amplitude in this regime, but now the shifts have contributions proportional to m_J and m_I rather than simply being proportional to m_F. Because g_I is relatively small, the dependence on m_J will be the strongest effect.

Now at first order in perturbation theory, we can include the effect of H_hfs by diagonalizing it and including the expectation values in the diagonal basis. For this treatment to hold, the energy perturbations must still be small compared to the fine-structure splitting, otherwise we need to include the fine-structure Hamiltonian as well. To proceed, we will now show that the Hamiltonian is diagonal in the strong-field basis $|J\,m_J; I\,m_I\rangle$. To do this, we first invert the defining relations (7.8) for the angular-momentum ladder operators to find $J_x = (J_+ + J_-)/2$ and $J_y = (J_+ - J_-)/2i$, so that

$$\begin{aligned}
\mathbf{I}\cdot\mathbf{J} &= I_z J_z + I_x J_x + I_y J_y \\
&= I_z J_z + \frac{(I_+ + I_-)(J_+ + J_-)}{4} - \frac{(I_+ - I_-)(J_+ - J_-)}{4} \\
&= I_z J_z + \frac{I_+ J_- + I_- J_+}{2}.
\end{aligned} \tag{12.232}$$

In an expectation value with respect to $|J\,m_J; I\,m_I\rangle$, the second term vanishes, leaving

$$\langle J\,m_J; I\,m_I|\mathbf{I}\cdot\mathbf{J}|J\,m_J; I\,m_I\rangle = \hbar^2 m_I m_J, \tag{12.233}$$

and thus the strong-field eigenstates diagonalize the hyperfine-structure Hamiltonian. Then adding the expectation value of the hyperfine-structure Hamiltonian (12.230) to the zeroth-order energy (12.231), we obtain the shift

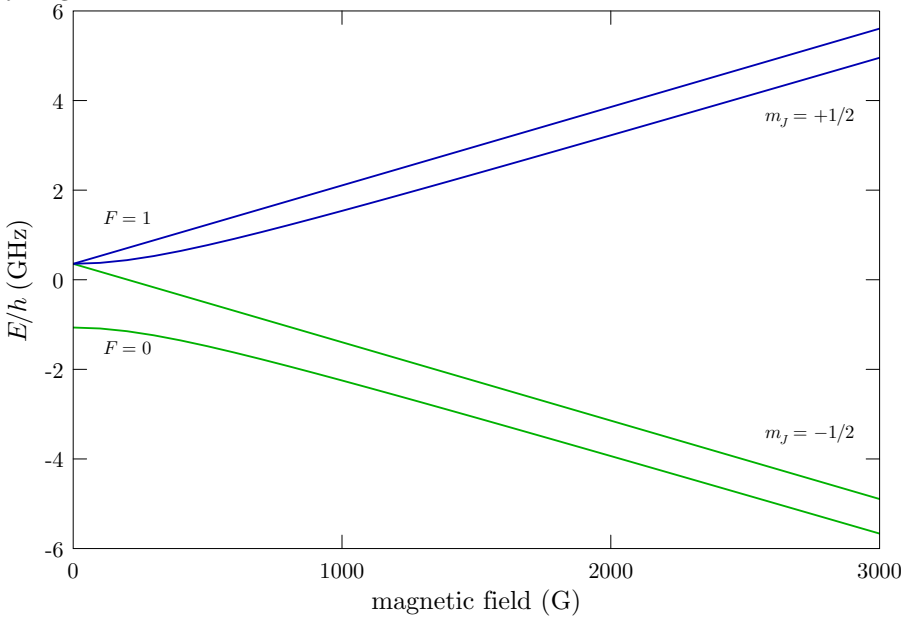
$$\Delta E(J\,m_J; I\,m_I) \approx A_\mathrm{hfs} m_I m_J + \mu_\mathrm{B}(g_J\,m_J + g_I\,m_I)B. \tag{12.234}$$

(hyperfine Paschen–Back effect)

[19] F. Paschen and E. Back, ''Normale und anomale Zeemaneffekte,'' *Annalen der Physik* **344**, 897 (1912) (doi: 10.1002/andp.19123441502).

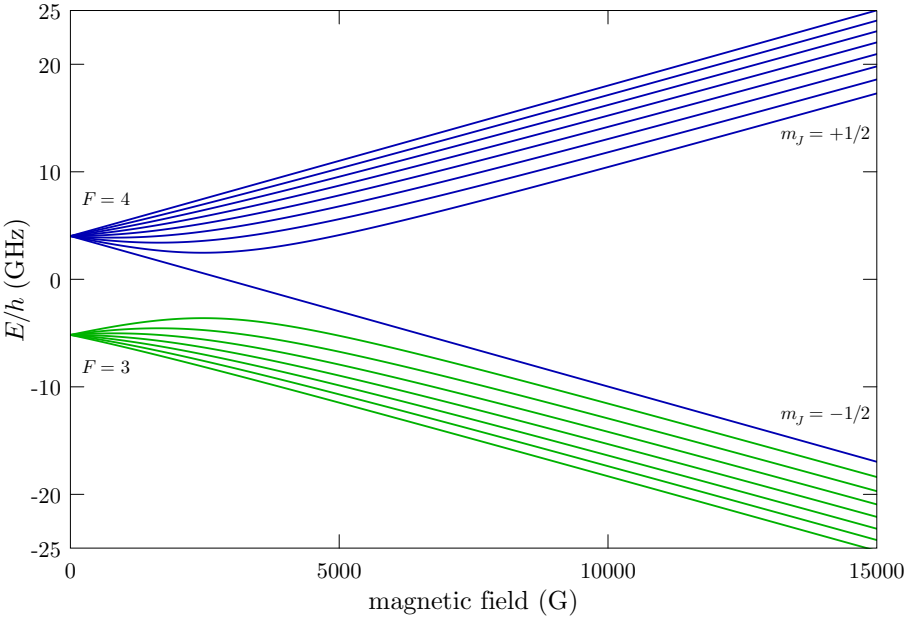
For magnetic fields intermediate between the Zeeman and Paschen–Back regimes, perturbation theory doesn't work well anymore. This regime is called the **incomplete Paschen–Back effect**. Generally, the combined Hamiltonian on a subspace of fixed J and L must be diagonalized numerically, although if either $J = 1/2$ or $I = 1/2$ it turns out that the Hamiltonian can be diagonalized analytically (Problem 12.15).

To illustrate the Zeeman, Paschen–Back, and intermediate regimes, the magnetic field shift is plotted below for the hydrogen 1S state.



For small fields, the levels split with a shift proportional to m_F, and in fact the $m_F = \pm 1$ levels always shift linearly for this problem. For large fields, the levels reorganize into two groups corresponding to $m_J = \pm 1/2$, with smaller splittings in each group corresponding to $m_I = \pm 1/2$. Notice that there is an avoided crossing between the $m_F = 0$ states at $B = 0$.

The structure here is a bit more dramatically illustrated in atoms with larger angular momenta. For example, in the ^{133}Cs ground ($6S_{1/2}$) state, where $I = 7/2$, the magnetic-field shifts are shown below.

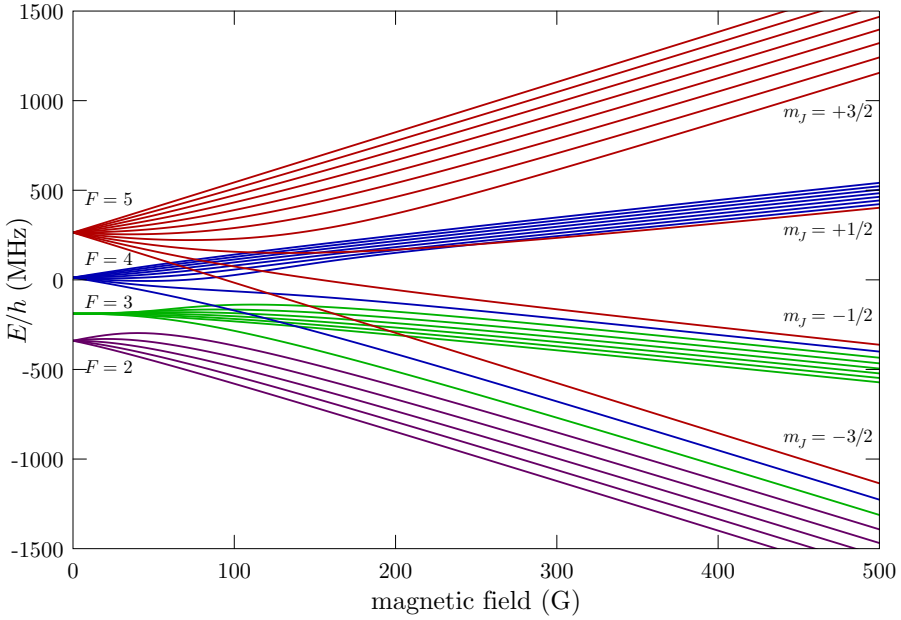


At small B-field values, the levels fall into the two groups $F = 7/2 \pm 1/2$ and split linearly according to m_F. For large fields the levels again separate into two other groups corresponding to $m_J = \pm 1/2$, with smaller

splittings in each group corresponding to m_I between $-7/2$ and $+7/2$. But notice also how the spacing in the high-field regime is not quite uniform, owing to the perturbative influence of the hyperfine-structure Hamiltonion.

Recall that the above cesium transition is the basis for the second (at zero magnetic field). When used for metrology purposes, the $m_F = 0$ states are used because they are insensitive to magnetic-field shifts to first order in B. For other non-metrology but noise-sensitive purposes, there are other options available. For example, notice how the $|F = 3, m_F = +3\rangle$ and $|F = 4, m_F = -3\rangle$ states undergo an avoided crossing around 2.5 kG. These two states could be used as a qubit realization in a bias field; then the transition frequency is first-order insensitive to changes in B, *and* any perturbation would have a hard time changing the *orientation* of the field (remember that the magnetic-field orientation breaks the degeneracy of the hyperfine sublevels m_F, and staying near $B = 0$ means that it is easy for the magnetic-field *direction* to drift, the effect being that the different m_F levels slowly mix together, causing uncontrolled perturbations of the nuclear qubit).

As a slightly more complicated example, consider the $6P_{3/2}$ excited state of ^{133}Cs. Since $J = 3/2$ (and still $I = 7/2$), F can range from 2 to 5, with correspondingly more m_F states. These break apart and group into four different m_J groups. Note that the spacings are different in different m_J groups, a more clear manifestation of the hyperfine-structure Hamiltonian in the Paschen–Back regime.



12.9.5 Linear Stark Effect in Hydrogen

Now we return to the dc Stark effect that we considered in Section 12.6.3. There we found a quadratic Stark shift for the hydrogen 1S state. Now we can calculate the shift of the first set of excited states (2S, $2P_{1/2}$ singlet, $2P_{3/2}$ triplet) in hydrogen. Due to fine-structure splitting, not all of these states are degenerate. However, as discussed in Section 12.8.3, degenerate perturbation theory can still apply, since the other states are far away in energy. In fact, we will simplify things by ignoring the fine-structure splittings, which means that we are considering Stark shifts much larger than the fine-structure splitting. In this case we only need to consider four states: 2S and $2P(m_L = 0, \pm 1)$.

We are back to considering the dipole interaction with a static electric field (12.90)

$$V = e\mathscr{E}z. \tag{12.235}$$

At first order in perturbation theory, we just need to diagonalize this Hamiltonian to compute the energy shifts. From the dipole selection rules, remember that a matrix element of z between two states vanishes unless L changes by 1 and m_L doesn't change. Thus, the only nonvanishing matrix element is

$$\langle 2\,0\,0|z|2\,1\,0\rangle = 3a_0, \tag{12.236}$$

where by now you know how to set up and carry out the integral to compute the result. This means we need to diagonalize the matrix

$$[V] = \begin{bmatrix} 0 & 3a_0e\mathscr{E} \\ 3a_0e\mathscr{E} & 0 \end{bmatrix}, \tag{12.237}$$

for which the eigenvalues are

$$\Delta E_1 = \pm 3a_0e\mathscr{E}. \tag{12.238}$$

That is, the electric field mixes the 2S and 2P($m_{\scriptscriptstyle L} = 0$) states to produce a doublet with a splitting linear in $\mathscr{E}$. This is something of an oddity in hydrogen, due to the (near) degeneracy of these two levels (in heavier alkali atoms the nS and nP states don't generally match up).

In the spirit of Section 12.8.3, let's consider for a bit how the calculation would go through if we account for fine-structure splitting. In this case the dipole interaction couples the 2S($m_{\scriptscriptstyle J}$) states to various 2P$_{1/2}$($m_{\scriptscriptstyle J}$) and 2P$_{3/2}$($m_{\scriptscriptstyle J}$) states. Thus we should employ the above matrix element $\langle 2\,0\,0|z|2\,1\,0\rangle$, in the form of an expansion in Clebsch–Gordan coefficients to compute the various matrix elements between the fine-structure states. This gives the off-diagonal elements of the matrix $[V]$, while the diagonal elements are the fine-structure shifts. Then diagonalize!

12.10 Wigner–Brillouin Perturbation Theory

Returning to the nondegenerate case, the traditional time-independent perturbation theory that we developed starting in Section 12.1 is called **Rayleigh–Schrödinger perturbation theory**.[20] An alternate to the usual formulation of is called **Brillouin–Wigner perturbation theory**.[21] It has a simpler structure, and provides some insight into the more common formulation.

12.10.1 Perturbed State

We can define the perturbed Hamiltonian as before,

$$H = H_0 + \lambda V, \tag{12.239}$$

in terms of the unperturbed Hamiltonian H_0 and perturbation λV. The perturbed eigenenergy and eigenstate, along with their unperturbed counterparts, are given in terms of the respective eigenvalue conditions as

$$H|\psi\rangle = E|\psi\rangle, \qquad H_0|\psi_0\rangle = E_0|\psi_0\rangle. \tag{12.240}$$

Beginning with the eigenvalue condition for H, we want to develop an expression for the perturbed state $|\psi\rangle$ in terms of the unperturbed resolvent $G_0(E) = 1/(E - H_0)$. Thus, we want to rearrange the perturbed eigenvalue condition to isolate the combination $(E - H_0)$, and so writing H in terms of H_0 and V and rearranging, we find

$$(E - H_0)|\psi\rangle = \lambda V|\psi\rangle. \tag{12.241}$$

Now multiplying through by $G_0(z) = 1/(z - H_0)$, we have

$$|\psi\rangle = \lambda G_0(E)V|\psi\rangle. \tag{12.242}$$

[20] Named after Lord Rayleigh's method, which he applied to analyzing the shift in frequency and nodal point of a string loaded by a small perturbing mass (see Problem 12.7); in John William Strutt, Baron Rayleigh, *Theory of Sound, vol. I* (Macmillan, 1877), pp. 87–93 (ISBN: 9781152060234). Schrödinger then applied the method to quantum mechanics: E. Schrödinger, "Quantisierung als Eigenwertproblem [Quantization as an Eigenvalue Problem]," Annalen der Physik **80**, 437 (1926) (doi: 10.1002/andp.19263851302).

[21] L. Brillouin, "Les problèmes de perturbations et les champs self-consistents," *Journal de Physique et Le Radium* **3**, 373 (1932) (doi: 10.1051/jphysrad:0193200309037300); E. P. Wigner, "On a Modification of the Rayleigh-Schrödinger Perturbation Theory," *Magyar Tudományos Akadémia Matematikai és Természettudományi Ertesitöje* **53**, 477 (1935), reprinted as in *The Collected Works of Eugene Paul Wigner, Part A: The Scientific Papers, Volume IV, Part I: Physical Chemistry* (Springer-Verlag, 1997), p. 132. For a nice comparison to Rayleigh–Schrödinger perturbation theory, see William Silvert, "Comparison of Rayleigh-Schrödinger and Brillouin-Wigner Perturbation Theories," *American Journal of Physics* **40**, 557 (1972) (doi: 10.1119/1.1988048).

Now with the unperturbed-state and complementary projectors

$$P_0 := |\psi_0\rangle\langle\psi_0|, \qquad Q_0 := 1 - P_0 = \sum_{\alpha\neq 0} |\alpha\rangle\langle\alpha|, \tag{12.243}$$

respectively, we can multiply by $1 - P_0$ on the left-hand side and Q_0 on the right-hand side to obtain

$$(1 - P_0)|\psi\rangle = \lambda G_Q V|\psi\rangle. \tag{12.244}$$

Here we used $Q_0 G_0(E) = Q_0 G_0(E) Q_0$ since Q_0 is a projector that commutes with H_0, and of course the shorthand

$$G_Q := Q_0 G_0(E) Q_0 = \sum_{\alpha\neq 0} \frac{|\alpha\rangle\langle\alpha|}{E - E_\alpha} \tag{12.245}$$

for the part of the resolvent on the complementary space. Rearranging gives

$$|\psi\rangle = P_0|\psi\rangle + \lambda G_Q V|\psi\rangle. \tag{12.246}$$

This relation (still exact) gives an equation that implicitly relates the perturbed state $|\psi\rangle$ to the unperturbed state in $P_0|\psi\rangle$ and, upon iteration, yields a perturbation series for $|\psi\rangle$.

For the purposes developing the expansion, it is best to think of E as a free parameter, ignoring any dependence on λ. Iterating Eq. (12.246) by plugging in the whole right-hand side in for rightmost $|\psi\rangle$ to give iterated to give

$$|\psi\rangle = P_0|\psi\rangle + \lambda G_Q V P_0|\psi\rangle + \lambda^2 G_Q V G_Q V P_0|\psi\rangle + \cdots. \tag{12.247}$$

An alternate method comes from solving Eq. (12.246) for $|\psi\rangle$ in terms of $P_0|\psi\rangle$ (which is the only part that contains $|\psi_0\rangle$) to obtain

$$|\psi\rangle = \frac{1}{1 - \lambda G_Q V} P_0|\psi\rangle. \tag{12.248}$$

The Taylor expansion of the right-hand side in powers of λ gives the same series. Also writing out

$$P_0|\psi\rangle = |\psi_0\rangle\langle\psi_0|\psi\rangle \tag{12.249}$$

to make the dependence on $|\psi_0\rangle$ explicit, the full series becomes

$$|\psi\rangle = \langle\psi_0|\psi\rangle \sum_{n=0}^{\infty} \lambda^n (G_Q V)^n |\psi_0\rangle.$$

(Wigner–Brillouin perturbation series for $|\psi\rangle$) (12.250)

We can take $\langle\psi_0|\psi\rangle$ to be real, in which case $\langle\psi_0|\psi\rangle \leq 1$. Then this is a normalization factor, which indicates that the perturbation series results in a perturbed vector that has a norm that exceeds unity for a nontrivial perturbation.

12.10.2 Perturbed Energy

To obtain a perturbation series for the energy, we can start with the eigenvalue condition (12.241) and operate with $\langle\psi_0|$ on the left to find

$$\langle\psi_0|(E - H_0)|\psi\rangle = \lambda\langle\psi_0|V|\psi\rangle. \tag{12.251}$$

Replacing H_0 by its eigenvalue and using Eq. (12.250) on the right-hand side,

$$\langle\psi_0|\psi\rangle(E - E_0) = \langle\psi_0|\psi\rangle\lambda\langle\psi_0|V \sum_{n=0}^{\infty} \lambda^n (G_Q V)^n |\psi_0\rangle. \tag{12.252}$$

Canceling the common inner product and rearranging a bit, we obtain the desired perturbation series

$$E = E_0 + \sum_{n=1}^{\infty} \lambda^n \langle\psi_0|V(G_Q V)^{n-1}|\psi_0\rangle.$$

(Wigner–Brillouin perturbation series for E) (12.253)

Note that the perturbation corrections involve G_Q in terms of E, not E_0, so this is an implicit perturbation series.

12.10.3 Equivalence to the Rayleigh–Schrödinger Series

The perturbation series (12.250) and (12.253) are *much* simpler at high orders than the Rayleigh–Schrödinger perturbation series (12.41) and (12.56), when expanded out. However, they specify the perturbed energy only *implicitly*, because the energy perturbation series involves E at all orders beyond the zeroth. The truncated series is a nonlinear equation that must then be solved for E. One approach to dealing with these implicit equations is to iterate the perturbation series for E, replacing E's in the various correction terms by the entire series, and expanding the whole result to obtain an explicit series for E in terms of only E_0. The result of this procedure agrees with the Rayleigh–Schrödinger series. To see this equivalence at first order for $|\psi\rangle$, we can write out the terms in the series (12.250) through order λ:

$$|\psi\rangle = \langle\psi_0|\psi\rangle\Big(1 + \lambda G_Q V\Big)|\psi_0\rangle. \tag{12.254}$$

As in the standard perturbation series, we can drop the normalization factor $\langle\psi_0|\psi\rangle$ for now and show afterwards that it only matters at second order. Writing out G_Q, we have

$$|\psi\rangle = |\psi_0\rangle + \lambda \sum_{\alpha\neq 0} |\alpha\rangle \frac{\langle\alpha|V|\psi_0\rangle}{E - E_\alpha}. \tag{12.255}$$

Since E differs from E_0 at first order in λ, and E only appears in the first-order term, we can simply replace E by E_0 to obtain

$$|\psi\rangle = |\psi_0\rangle + \lambda \sum_{\alpha\neq 0} |\alpha\rangle \frac{V_{\alpha 0}}{E_{0\alpha}}, \tag{12.256}$$

after switching to standard abbreviations, matching the standard first-order result. To see the equivalence in the energy to third order, we can write out the terms in the series (12.253) through order λ^2:

$$E = E_0 + \lambda\langle\psi_0|V|\psi_0\rangle + \lambda^2\langle\psi_0|VG_QV|\psi_0\rangle + \lambda^3\langle\psi_0|VG_QVG_QV|\psi_0\rangle \tag{12.257}$$

Writing out G_Q,

$$E = E_0 + \lambda V_{00} + \lambda^2 \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{E - E_\alpha} + \lambda^3 \sum_{\alpha,\beta\neq 0} \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{(E - E_\alpha)(E - E_\beta)}. \tag{12.258}$$

Now E only begins to appear at order λ^2, and since we only ultimately need terms at order λ^3, we can be content to iterate using $E = E_0 + \lambda V_{00}$ in the λ^2 term and $E = E_0$ in the λ^3 term. Thus,

$$\begin{aligned} E &= E_0 + \lambda V_{00} + \lambda^2 \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{E_{0\alpha} + \lambda V_{00}} + \lambda^3 \sum_{\alpha,\beta\neq 0} \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{E_{0\alpha}E_{0\beta}} \\ &= E_0 + \lambda V_{00} + \lambda^2 \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{E_{0\alpha}} + \lambda^3 V_{00} \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{(E_{0\alpha})^2} + \lambda^3 \sum_{\alpha,\beta\neq 0} \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{E_{0\alpha}E_{0\beta}} \end{aligned} \tag{12.259}$$

after expanding the λ^2 term and switching to the abbreviated energy differences. This result agrees with the Rayleigh–Schrödinger perturbation result to third order.

12.10.4 Advantages of the Brillouin–Wigner Series

The obvious advantage of the Brillouin–Wigner series is the relative simplicity of the terms. For example, at fourth order, the Rayleigh–Schrödinger shift (12.67) is

$$\begin{aligned}\delta E_4 = \lambda^4 \sum_{\alpha,\beta,\gamma\neq 0} \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta\gamma}V_{\gamma 0}}{E_{0\alpha}E_{0\beta}E_{0\gamma}} - \lambda^4 \sum_{\alpha,\beta\neq 0} \frac{|V_{0\alpha}|^2|V_{0\beta}|^2}{(E_{0\alpha})^2 E_{0\beta}} \\ - \lambda^4 V_{00} \sum_{\alpha,\beta\neq 0} \left[\frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{(E_{0\alpha})^2 E_{0\beta}} + \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{E_{0\alpha}(E_{0\beta})^2}\right] + \lambda^4 V_{00}^2 \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{(E_{0\alpha})^3},\end{aligned} \tag{12.260}$$

while the Brillouin–Wigner counterpart is

$$\delta E_4 = \lambda^4 \sum_{\alpha,\beta,\gamma\neq 0} \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta\gamma}V_{\gamma 0}}{(E-E_\alpha)(E-E_\beta)(E-E_\gamma)}. \tag{12.261}$$

The latter is obviously simpler, and has the advantage of an interpretation of the term as a multi-transition process $|\psi_0\rangle \longrightarrow |\gamma\rangle \longrightarrow |\beta\rangle \longrightarrow |\alpha\rangle \longrightarrow |\psi_0\rangle$. Setting $E = E_0$ in the Brillouin–Wigner shift matches it up with the first Rayleigh–Schrödinger term. This makes it clear that the rest of the Rayleigh–Schrödinger terms are from expanding E in terms of E_0 from lower-order terms in the series.

The implicit dependence on E can be considered a disadvantage of the Brillouin–Wigner formulation of perturbation theory. However, it can be an asset too, in the sense that once the series is truncated at a given order, the implicit equation for E may give a more accurate result than the explicit version of the same order. A simple example is for a two-state system with eigenstates $|\psi_0\rangle$ and $|1\rangle$, under the assumption $\langle\psi_0|V|\psi_0\rangle = \langle 1|V|1\rangle = 0$ (note that if these matrix elements are not zero, they can be effectively set to zero by absorbing them into H_0). Writing down the (implicit) perturbation series for the energy, truncated to order λ^2,

$$E = E_0 + \lambda V_{00} + \lambda^2 \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{E - E_\alpha}, \tag{12.262}$$

and for this specific problem, this becomes

$$E = E_0 + \lambda^2 \frac{|V_{01}|^2}{E - E_1}. \tag{12.263}$$

We can rearrange this to read

$$E - E_0 = \lambda^2 \frac{|V_{01}|^2}{(E - E_0) - E_{10}}, \tag{12.264}$$

and it is easier to solve the simpler equation

$$E = \lambda^2 \frac{|V_{01}|^2}{E - E_{10}}, \tag{12.265}$$

if we interpret E as being relative to E_0 (i.e., we let $E \longrightarrow E - E_0$ at the end of the calculation. Them multiplying this out, we obtain the quadratic equation

$$E^2 - EE_{10} - \lambda^2|V_{01}|^2 = 0, \tag{12.266}$$

and the solutions from the quadratic formula are

$$E = \frac{E_{10} \pm \sqrt{(E_{10})^2 + 4\lambda^2|V_{01}|^2}}{2}. \tag{12.267}$$

Putting back the E_0 offset, the solution becomes

$$E = \frac{E_0 + E_1}{2} \pm \frac{1}{2}\sqrt{(E_{10})^2 + 4\lambda^2|V_{01}|^2}. \tag{12.268}$$

This is the *exact* solution for the eigenenergies. To see this, the perturbed Hamiltonian in the unperturbed representation is

$$(H) = \begin{bmatrix} E_0 & \lambda V_{01} \\ \lambda V_{10} & E_1 \end{bmatrix}, \tag{12.269}$$

and the eigenvalues follow from the characteristic equation

$$\det(E - H) = \det \begin{bmatrix} E - E_0 & -\lambda V_{01} \\ -\lambda V_{10} & E - E_1 \end{bmatrix} = 0, \tag{12.270}$$

which is exactly the quadratic equation (12.266) after shifting E up by E_0.

The Rayleigh–Schrödinger perturbation expression to the same order is

$$E = E_0 + \lambda^2 \frac{|V_{01}|^2}{E_{01}}. \tag{12.271}$$

This is the same as the expansion of the exact solution to order λ^2, after choosing the appropriate solution (e.g., the + solution in the case that $E_0 \geq E_1$).

12.11 Exercises

Problem 12.1

First, to get into the proper mood for this problem, please read the story ''Feynman vs. The Abacus.''[22]

In the story, Feynman was basically computing the solution to

$$x^3 = 12^3 + \lambda \tag{12.272}$$

where $\lambda = 1.03$ is (relatively) small. He was doing this using the lowest-order correction in the Taylor series for $\sqrt[3]{12^3 + \lambda}$, but this also makes for a nice toy model for understanding how perturbation theory works. Setting

$$x(\lambda) = x_0 + x_1\lambda + x_2\lambda^2 + \cdots, \tag{12.273}$$

we can solve for the solution order by order. This will rederive the Taylor series, of course, but without ever computing a derivative. (And the technique works for finding perturbative solutions to more complicated polynomials, provided a ''nearby'' polynomial is exactly soluble.)

(a) First, the zeroth-order solution is given by setting $\lambda = 0$, so $x_0 = 12$. Now take

$$x(\lambda) = x_0 + x_1\lambda \tag{12.274}$$

substitute it into Eq. (12.272), match terms proportional to λ, and derive an expression for x_1 in terms of x_0. What is the approximate value for x so far?

(b) Now repeat the process using

$$x(\lambda) = x_0 + x_1\lambda + x_2\lambda^2, \tag{12.275}$$

require consistency of the λ^2 terms, and derive an expression for x_2 in terms of x_0. What is the approximate value for x at this stage?

Problem 12.2

Show that, keeping terms up to λ^2, that the perturbed state in time-independent perturbation theory (for a nondegenerate level) is

$$|\psi\rangle \approx |\psi_0\rangle + \lambda \sum_{\alpha\neq 0} |\alpha\rangle \frac{V_{\alpha 0}}{E_{0\alpha}} + \lambda^2 \sum_{\alpha,\beta\neq 0} |\alpha\rangle \frac{V_{\alpha\beta}V_{\beta 0}}{E_{0\alpha}E_{0\beta}} - \lambda^2 V_{00} \sum_{\alpha\neq 0} |\alpha\rangle \frac{V_{\alpha 0}}{(E_{0\alpha})^2} - \frac{\lambda^2}{2}|\psi_0\rangle \sum_{\alpha\neq 0} \frac{|V_{\alpha 0}|^2}{(E_{0\alpha})^2}. \tag{12.276}$$

Problem 12.3

Show that the fourth-order correction to the perturbed energy in time-independent perturbation theory (for a nondegenerate level) is λ^4 times

$$\mathrm{Tr}\Delta_4 = \sum_{\alpha,\beta,\gamma\neq 0} \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta\gamma}V_{\gamma 0}}{E_{0\alpha}E_{0\beta}E_{0\gamma}} - \sum_{\alpha\beta\neq 0} \frac{|V_{0\alpha}|^2|V_{0\beta}|^2}{(E_{0\alpha})^2 E_{0\beta}} - V_{00} \sum_{\alpha,\beta\neq 0} \left[\frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{E_{0\alpha}(E_{0\beta})^2} + \frac{V_{0\alpha}V_{\alpha\beta}V_{\beta 0}}{(E_{0\alpha})^2 E_{0\beta}}\right] + V_{00}^2 \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{(E_{0\alpha})^3}. \tag{12.277}$$

How does this expression simplify if all lower-order corrections vanish ($\mathrm{Tr}\Delta_1 = \mathrm{Tr}\Delta_2 = \mathrm{Tr}\Delta_3 = 0$)?

Problem 12.4

The traditional approach to (nondegenerate) perturbation theory is to start with the perturbed Hamiltonian,

$$H = H_0 + \lambda V, \tag{12.278}$$

[22] in the book by Richard P. Feynman, *Surely, You're Joking, Mr. Feynman!* (Norton, 1985), p. 196 (ISBN: 0393316041); excerpt available, for example, at `https://www.ecb.torontomu.ca/~elf/abacus/feynman.html`. One nitpick, though: it's *raizes cúbicas*, not *raios cúbicos* (which would mean ''cubic radii'').

write a perturbation series for the energy

$$E = E_0 + \lambda\,\Delta E_1 + \lambda^2\,\Delta E_2 + \cdots \tag{12.279}$$

and state

$$|\psi\rangle = |\psi_0\rangle + \lambda\,\Delta|\psi\rangle_1 + \lambda^2\,\Delta|\psi\rangle_2 + \cdots, \tag{12.280}$$

put all these into the eigenvalue equation

$$H|\psi\rangle = E|\psi\rangle, \tag{12.281}$$

and require consistency of the eigenvalue condition, going up order by order in λ. The point of this problem is to get a taste of this procedure at the lowest order or so.

(a) Write out the eigenvalue equation with terms up to order λ. Solve for ΔE_1 to show that

$$\Delta E_1 = \langle\psi_0|V|\psi_0\rangle = V_{00}. \tag{12.282}$$

(b) Now use the consistency condition you obtained in (a) and solve it for $\Delta|\psi\rangle_1$. You will need to multiply through by Q_0 first to avoid a division by zero. This will leave one component of $\Delta|\psi\rangle_1$ undetermined, which you should fix by normalization (and choice of phase), with the result

$$\Delta|\psi\rangle_1 = \sum_{\alpha\neq 0} |\alpha\rangle \frac{V_{\alpha 0}}{E_{0\alpha}}. \tag{12.283}$$

(c) Now write out the eigenvalue equation with terms up to order λ^2, and use it to show that

$$\Delta E_2 = \sum_{\alpha\neq 0} \frac{|V_{0\alpha}|^2}{E_{0\alpha}}. \tag{12.284}$$

Problem 12.5

Consider a particle in an infinite square well of width L. Recall that the energies are [from Eq. (2.30)]

$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}, \qquad n \in \mathbb{Z}^+, \tag{12.285}$$

with corresponding eigenfunctions

$$\psi_n(x) = \sqrt{\frac{2}{L}}\,\sin\frac{n\pi x}{L}, \qquad x \in [0, L]. \tag{12.286}$$

Now suppose we introduce a perturbation of the form

$$V(x) = \lambda\,\delta(x - L/2), \tag{12.287}$$

with $\lambda \geq 0$.

(a) At first order in perturbation theory, intuitively, which levels shift, and which states are unaffected? Compute explicitly the first-order shift.

(b) To *all* orders in perturbation theory, intuitively, which levels shift, and which states are unaffected?

(c) Consider the limit $\lambda \longrightarrow \infty$. What can you say about the eigenenergies in this limit? Is your result consistent with your answer in (b)?

(d) Derive an inequality involving λ for the validity of first-order perturbation theory in this particular problem.

Problem 12.6

Consider a harmonic oscillator

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{12.288}$$

with perturbation potential

$$V = -bx. \tag{12.289}$$

(a) Compute the first-order shift to for every eigenstate.

(b) Compute the *exact* energy shift for every eigenstate.

(c) From (b), what is the relevant order in perturbation theory?

(d) Verify that you can obtain the exact energy shift from the relevant order in perturbation theory.

Problem 12.7

Rayleigh originally developed perturbation theory and applied it to the vibrations of a guitar string. This problem works through his original calculation. [23]

Consider a guitar string stretched along the x direction, with transverse displacement $y(x,t)$. If the string vibrates at frequency ω, $y(x,t) = y(x)\cos\omega t$, then the string's wave function satisfies the time-independent wave equation

$$\left(\partial_x^2 + \frac{\mu}{T}\omega^2\right) y(x) = 0, \tag{12.290}$$

where μ is the linear mass density of the string (ordinarily a constant along the string's length), and T is the tension of the wire.

(a) Find the eigenmodes $y_n(x)$ and eigenfrequencies ω_n for the string according to Eq. (12.290), assuming the endpoints are fixed at $x = 0$ and $x = L$.

(b) Suppose a small, point mass m is attached to the string at $x = \ell$. Compute the relative shifts $\delta\omega_n/\omega_n$ for the eigenfrequencies ω_n to first order in m.

(c) Derive an expression for the change $\delta y_n(x)$ in the nth eigenfunction due to the point mass, again to first order in m.

(d) Compute the shift in the nodal point x_0 for the second mode $y_2(x)$ due to the point mass placed at $\ell = L/4$, again to first order in m. The nodal point is defined here by the condition $y_2(x_0) = 0$, so that $x_0 = {}^L/_2$. Note that you should begin by writing down the perturbed $y_2(x)$ near the nodal point, $x = x_0 + \delta x$, working to linear order in δx; forcing the perturbed $y_2(x)$ to be zero gives the shift δx in the nodal point. You may also find the following sum useful:

$$\frac{1}{1-4} - \frac{1}{3^2-4} - \frac{1}{5^2-4} + \frac{1}{7^2-4} + \frac{1}{9^2-4} + \cdots = -\frac{\pi}{4\sqrt{2}}. \tag{12.291}$$

Problem 12.8

Compute the contribution to the Stark shift for the hydrogen 1S state due to the $n = 3$ states. (We already computed the contribution due to the $n = 2$ states in Section 12.6.3.3.) Add up the contributions from the $n = 2$ and $n = 3$ states; how does it compare to the exact solution?

Problem 12.9

For the hydrogen atom, it is useful for other calculations to have the expecation values $\langle r^{-1}\rangle$, $\langle r^{-2}\rangle$, and $\langle r^{-3}\rangle$ for all eigenstates. Getting these will require some degree of cleverness, so we'll go through some tricks for getting these here.

[23] John William Strutt, Baron Rayleigh, *Theory of Sound, vol. I* (Macmillan, 1877), pp. 87–93 (ISBN: 9781152060234).

(a) Before in Problem 6.1, you showed that

$$2\langle T\rangle = \eta\langle V\rangle \tag{12.292}$$

for a particle in a central potential $V(\mathbf{r}) = \lambda r^\eta$. This is a case of the **quantum virial theorem**.

Use this form of the quantum virial theorem to show that

$$\left\langle r^{-1}\right\rangle = \frac{1}{a_0 n^2}. \tag{12.293}$$

for the hydrogen atom.

(b) Here is another handy trick that we'll use to rederive the above result for $\left\langle r^{-1}\right\rangle$. The idea is to go back to the hydrogen-atom Hamiltonian (8.69),

$$H = \frac{p_r^2}{2m_\mathrm{e}} + \frac{\hbar^2 L(L+1)}{2m_\mathrm{e} r^2} - \frac{\hbar c\alpha}{r}, \tag{12.294}$$

when restricted to a subspace of constant L (and writing this in terms of the electron mass m_e instead of the reduced mass). Suppose we make a small change in α to $\alpha + \delta\alpha$. We could separate out the change into a perturbation term, $-\hbar c\delta\alpha/r$. According to first-order perturbation theory, the energy shift associated with this perturbation is just the expectation value with respect to the unperturbed states:

$$\delta E_1 = \left\langle -\frac{\hbar c\,\delta\alpha}{r}\right\rangle. \tag{12.295}$$

Now divide by $\delta\alpha$ and take the limit as $\delta\alpha \longrightarrow 0$. Then the first-order perturbation result is exact in this limit, and

$$\frac{\delta E_1}{\delta\alpha} = \frac{\partial E}{\partial\alpha} = \left\langle -\frac{\hbar c}{r}\right\rangle = \left\langle \frac{\partial H}{\partial\alpha}\right\rangle. \tag{12.296}$$

This is, in fact, an example of a more general result, called the **Hellmann–Feynman theorem**.[24] If $H(\lambda)$ is a Hamiltonian that depends on some parameter λ, then in essentially the same way that we just showed,

$$\frac{\partial E}{\partial\lambda} = \left\langle \frac{\partial H}{\partial\lambda}\right\rangle \tag{12.297}$$

for any eigenvalue E of H, where the expectation value is taken with respect to the corresponding eigenstate. (The proof goes through in the same way, it's just that you expand $H(\lambda+\delta\lambda)$ to first order in $\delta\lambda$, which yields the general partial derivative).

Use the Hellmann–Feynman theorem with $\lambda = \alpha$ to verify the result from part (a).

(c) Now use the Hellmann–Feynman theorem with $\lambda = \ell$ to derive the expectation value

$$\left\langle r^{-2}\right\rangle = \frac{1}{a_0^2(L+1/2)n^3}. \tag{12.298}$$

(d) Unfortunately the same theorem won't directly get us to $\left\langle r^{-3}\right\rangle$, but there is another trick that will get us there. First, note that

$$\left\langle [H, p_r]\right\rangle = 0 \tag{12.299}$$

in any eigenstate of the Hamiltonian H in Eq. (12.294). (Why is this? Note that this is true for any operator, not just p_r.) Now work out this commutator, which will get you an expression that connects $\left\langle r^{-2}\right\rangle$ to $\left\langle r^{-3}\right\rangle$. Combining this with Eq. (12.298) should then give you

$$\left\langle r^{-3}\right\rangle = \frac{1}{L(L+1/2)(L+1)n^3 a_0^3}. \tag{12.300}$$

[24] For a history of this theorem, see David Wallace, *An Introduction To Hellmann–Feynman Theory*, Master's thesis (University of Central Florida, 2005), available at `http://stars.library.ucf.edu/cgi/viewcontent.cgi?article=1412&context=etd`.

Problem 12.10

A correction in addition to the spin–orbit interaction is the relativistic correction. Heuristically, we can account for relativistic effects by replacing the kinetic energy $p^2/2m_\mathrm{e}$ with the relativistic energy $\sqrt{p^2c^2 + m_\mathrm{e}^2c^4}$. For small momenta, this becomes

$$\sqrt{p^2c^2 + m_\mathrm{e}^2c^4} = m_\mathrm{e}c^2\sqrt{1 + \frac{p^2}{m_\mathrm{e}^2c^2}} \approx m_\mathrm{e}c^2\left(1 + \frac{p^2}{2m_\mathrm{e}^2c^2} - \frac{p^4}{8m_\mathrm{e}^4c^4}\right) = m_\mathrm{e}c^2 + \frac{p^2}{2m_\mathrm{e}} - \frac{p^4}{8m_\mathrm{e}^3c^2}. \quad (12.301)$$

The first term is the electron rest energy (an ignorable energy offset), the second is the nonrelativistic kinetic energy, and the third we can take to be a perturbative correction to the Hamiltonian:

$$H_\mathrm{rel} := -\frac{p^4}{8m_\mathrm{e}^3c^2}. \quad (12.302)$$

(More properly, this correction is justified by a small-momentum expansion within a Dirac-equation treatment of the hydrogen atom.)

(a) Derive the energy shifts in first-order (degenerate) perturbation theory due to this correction. You can start by noting that the hydrogen-atom Hamiltonian can be written in terms of p^2, so that H_rel can be written in terms of the vanilla hydrogen Hamiltonian. At that point you'll need the expectation values from Problem 12.9. The result you should get is

$$\Delta E_\mathrm{rel} = \frac{(E_n)^2}{2m_\mathrm{e}c^2}\left(3 - \frac{4n}{L + 1/2}\right). \quad (12.303)$$

(b) Show that, combined with the fine-structure shift, the total shift reads

$$\Delta E_\mathrm{fs} + \Delta E_\mathrm{rel} = \frac{(E_n)^2}{2m_\mathrm{e}c^2}\left(3 - \frac{4n}{J + 1/2}\right). \quad (12.304)$$

Problem 12.11

Besides spin–orbit coupling and the relativistic correction, there is one more correction to come out of the low-energy limit of the Dirac-equation treatment of the hydrogen atom. Roughly speaking, the electron velocity is bounded above by c, and thus the uncertainty principle says that the electron position has some intrinsic uncertainty on the scale of the Compton wavelength $\lambda_\mathrm{C} = h/m_\mathrm{e}c$. This means the potential seen by the hydrogen atom should be blurred on this scale. The correction can be written as the interaction Hamiltonian

$$H_\mathrm{D} = \frac{\hbar^2\pi}{2m_\mathrm{e}^2c^2}\frac{e^2}{4\pi\epsilon_0}\,\delta^3(\mathbf{r}), \quad (12.305)$$

and this is called the **Darwin term** (yes, named after Charles Darwin,[25] but no, not *that* Charles Darwin, *this* one is his grandson). The delta function here can be understood as follows: the potential $V(r)$ has to be smeared over a small length scale, so expanding to lowest nonvanishing order gives a correction like $\nabla^2 V$. Then the delta function comes from $V(r) \sim 1/r$ and $\nabla^2(1/r) = 4\pi\delta^3(\mathbf{r})$ (recognize this from electrostatics?).

(a) Show that the Darwin term leads to a shift of the hydrogen states of

$$\Delta E_\mathrm{D} = \frac{m_\mathrm{e}c^2\alpha^4}{2n^3}\,\delta_{L0} \quad (12.306)$$

[25] Charles Galton Darwin, "The wave equations of the electron," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **188**, 654 (1928) (doi: 10.1098/rspa.1928.0076).

(ignoring the reduced-mass correction). For this, you'll need a general expression for the value of the wave function at $\mathbf{r} = 0$; use the general expression (8.168) for the radial hydrogen-atom wave functions. Also: you should argue the Kronecker delta part separately (argue physically why if a continuous field is circulating about the origin, its density must vanish there).

(b) The Darwin term also patches up some flaws of our previous treatment of the fine-structure energy levels. Namely, Eq. (12.300) is invalid for $L = 0$, and although the algebra magically worked out in getting to Eq. (12.304), it really shouldn't have for the problematic case. To wit: Eqs. (12.303) and (12.304) should be equivalent for $L = 0$, because $\Delta E_{\text{fs}} = 0$ for $L = 0$, but they aren't. However, show that the Darwin term saves the day: adding Eq. (12.306) to (12.303) gives the correct result (12.304) for $L = 0$.

Problem 12.12

Derive the energy difference (12.187)

$$\Delta E_{\text{fs}}(n, J = L + S) - \Delta E_{\text{fs}}(n, J = L - S) = \frac{1 + \alpha/\pi}{1 + m_{\text{e}}/m_{\text{p}}} \frac{hcR\alpha^2}{n^3 L(L+1)}(2S), \tag{12.307}$$

using $g_S \approx 2 + \alpha/\pi$ and including the reduced-mass correction.

Problem 12.13

Consider a Hamiltonian

$$H_\lambda = H_0 + \lambda V, \tag{12.308}$$

which is parameterized by λ, satisfying $0 \leq \lambda \leq 1$. The eigenvalues are similarly parameterized:

$$H_\lambda |E_\lambda\rangle = E_\lambda |E_\lambda\rangle. \tag{12.309}$$

Recall that the **Hellmann–Feynman theorem**, which we saw in Problem 12.9, says that

$$\frac{\partial E_\lambda}{\partial \lambda} = \left\langle \frac{\partial H_\lambda}{\partial \lambda} \right\rangle = \langle E_\lambda | V | E_\lambda \rangle. \tag{12.310}$$

We argued before that this relation holds in first-order perturbation theory, which is exact in the limit that yields the first derivative of the energy.

(a) Starting with the expression

$$\frac{\partial E_\lambda}{\partial \lambda} = \frac{\partial}{\partial \lambda} \langle E_\lambda | H_\lambda | E_\lambda \rangle, \tag{12.311}$$

note that there are effectively *three* factors that depend on λ, but the Hellmann–Feynman theorem says that only the effect of the derivative on H_λ matters—the variation of the eigenstates drops out. Can you come up with an intuitive explanation for this? *Hint:* you can think of the states $|E_\lambda\rangle$ at different λ as being connected by a unitary transformation.

(b) Starting with the expression in (a), go through the explicit proof of the theorem.

Problem 12.14

The spectrum of helium can't be computed exactly in closed form, but perturbation theory is a good place to start. Let's take

$$H_0 = \frac{p_1^2}{2m_{\text{e}}} + \frac{p_2^2}{2m_{\text{e}}} - \frac{2\hbar c\alpha}{r_1} - \frac{2\hbar c\alpha}{r_2} \tag{12.312}$$

as the base Hamiltonian, which is the sum of two hydrogen Hamiltonians with $\alpha \longrightarrow 2\alpha$ since the nucleus is doubly charged (we are also not implementing any reduced-mass correction). That is, at

zeroth order the helium energies are just double the hydrogen atoms after the $\alpha \longrightarrow 2\alpha$ substitution. The extra complication is the Coulomb repulsion of the electrons, which we can treat as a perturbation:

$$V = \frac{\hbar c \alpha}{|\mathbf{r}_1 - \mathbf{r}_2|}. \tag{12.313}$$

Using first-order perturbation theory, compute the ground-state energy of helium (for comparison, the double-ionization energy of helium is 79.0 eV).

For this problem, you can ignore any exchange-symmetry effects (though it is worth thinking through why this is the case.) Also, in this calculation, it will be handy to use the Legendre-polynomial expansion

$$\frac{1}{|\mathbf{r}_1 - \mathbf{r_2}|} = \frac{1}{r_>} \sum_{\ell=0}^{\infty} P_\ell(\cos\theta) \left(\frac{r_<}{r_>}\right)^\ell, \tag{12.314}$$

where $r_<$ and $r_>$ are the smaller and larger of r_1 and r_2, respectively, and θ is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$.

Problem 12.15

In the case of hyperfine structure, the Zeeman shift can be written down as a shift proportional to the m_F quantum number, provided the shifts are small enough that the states of different m_F don't interact. If the shifts are large, then in general it's not possible to write down any reasonable closed-form expression for the energy shifts.

A notable exception occurs if $J = 1/2$ or $I = 1/2$, however. For concreteness we'll assume $J = 1/2$ (as for the $1S_{1/2}$ state of hydrogen). In this case the hyperfine-structure Hamiltonian has the form

$$H_{\text{hfs}} = A_{\text{hfs}} \frac{\mathbf{I} \cdot \mathbf{J}}{\hbar^2}, \tag{12.315}$$

and the magnetic-field interaction still has the form

$$H_B^{(\text{hfs})} = \frac{\mu_{\text{B}}}{\hbar}(g_J J_z + g_I I_z) B_z. \tag{12.316}$$

Working in the "strong-field basis" $|J\, m_J; I\, m_I\rangle$, in first-order degenerate perturbation theory we only need to set up an eigenvalue problem for definite J (and I, L, and S). Thus, show that the combined Hamiltonian $H_{\text{hfs}} + H_B^{(\text{hfs})}$ is block-diagonal, with blocks of the form

$$\begin{bmatrix} A_{\text{hfs}} \dfrac{m_I}{2} + \mu_{\text{B}} \left(\dfrac{g_J}{2} + g_I m_I\right) B & \dfrac{A_{\text{hfs}}}{2} \sqrt{(I + m_I + 1)(I - m_I)} \\ \dfrac{A_{\text{hfs}}}{2} \sqrt{(I + m_I + 1)(I - m_I)} & -A_{\text{hfs}} \dfrac{(m_I + 1)}{2} + \mu_{\text{B}} \left(-\dfrac{g_J}{2} + g_I (m_I + 1)\right) B \end{bmatrix}. \tag{12.317}$$

Then diagonalize the matrix to derive the energy shifts

$$\Delta E(J = 1/2\, m_J; I\, m_I) = -\frac{\Delta E_{\text{hfs}}}{2(2I+1)} + g_I \mu_{\text{B}} m B \pm \frac{\Delta E_{\text{hfs}}}{2} \left(1 + \frac{4mx}{2I+1} + x^2\right)^{1/2}, \tag{12.318}$$

where

$$\begin{aligned} \Delta E_{\text{hfs}} &= A_{\text{hfs}} \left(I + \frac{1}{2}\right) \\ x &= \frac{\mu_{\text{B}}(g_J - g_I) B}{\Delta E_{\text{hfs}}} \\ m &= m_I \pm m_J. \end{aligned} \tag{12.319}$$

This formula is called the **Breit–Rabi formula**,[26] and it is valid for arbitrary B provided the energy shifts are small compared to any fine-structure splitting or the energy gaps to other electronic levels.

[26] G. Breit and I. I. Rabi, "Measurement of Nuclear Spin," *Physical Review* **38**, 2082 (1931) (doi: 10.1103/PhysRev.38.2082.2).

Chapter 13

Perturbed Time Evolution

13.1 Expansion of the Evolution Operator

Recall that, way back in Section 1.8, we introduced the unitary time-evolution operator, which acts as a mapping between state vectors at different times:

$$|\psi(t)\rangle = U(t,t_0)\,|\psi(t_0)\rangle. \tag{13.1}$$

There we showed that the time-evolution operator satisfies the Schrödinger equation [Eq. (1.179)]:

$$\partial_t U(t,t_0) = -\frac{i}{\hbar} H(t)\,U(t,t_0). \tag{13.2}$$

In this case, the Hamiltonian can depend on time, and in fact we will take $H(t)$ to be a combination of a static Hamiltonian H_0 (with known solutions) and a possibly time-dependent interaction (perturbation) potential:

$$H(t) = H_0 + V(t). \tag{13.3}$$

To simplify notation, we'll discard the bookkeeping parameter λ that we used in time-independent perturbation theory.

Now since we have the equation of motion

$$\partial_t U(t,t_0) = -\frac{i}{\hbar}\big[H_0 + V(t)\big]U(t,t_0) \tag{13.4}$$

for the evolution operator, we can define the evolution of the "base" evolution operator U_0 under H_0:

$$\partial_t U_0(t,t_0) = -\frac{i}{\hbar} H_0\,U_0(t,t_0), \tag{13.5}$$

Recall that since H_0 is time-independent, the base evolution operator has the explicit form

$$U_0(t,t_0) = \exp\left[-\frac{i}{\hbar}H_0(t-t_0)\right]. \tag{13.6}$$

In the case of the full evolution operator U, we can write the solution of Eq. (13.4) in terms of an integral as

$$U(t,t_0) = U_0(t,t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt_1\,U_0(t,t_1)\,V(t_1)\,U(t_1,t_0). \tag{13.7}$$

(evolution operator, integral solution)

That this is indeed the solution can be verified by checking the initial condition $U(t_0,t_0) = 1$ and then differentiating this expression (Problem 13.1).

To develop a perturbation series, we can simply iterate the solution (13.7), with the result

$$\begin{aligned} U(t,t_0) = U_0(t,t_0) &- \frac{i}{\hbar}\int_{t_0}^{t} dt_1\, U_0(t,t_1)\, V(t_1)\, U_0(t_1,t_0) \\ &- \frac{1}{\hbar^2}\int_{t_0}^{t} dt_2 \int_{t_0}^{t_2} dt_1\, U_0(t,t_2)\, V(t_2)\, U_0(t_2,t_1)\, V(t_1)\, U_0(t_1,t_0) \\ &+ \frac{i}{\hbar^3}\int_{t_0}^{t} dt_3 \int_{t_0}^{t_3} dt_2 \int_{t_0}^{t_2} dt_1\, U_0(t,t_3)\, V(t_3)\, U_0(t_3,t_2)\, V(t_2)\, U_0(t_2,t_1)\, V(t_1)\, U_0(t_1,t_0) \\ &+ \cdots . \end{aligned} \tag{13.8}$$

Note that in obtaining each of the successive terms from the previous one, we have renamed $t_k \longrightarrow t_{k+1}$ in order to maintain the ordering of the time variables (that is, t_1 is always the newest time variable from the iteration procedure). More formally, we can write the perturbation series for U as

$$U(t,t_0) = U_0(t,t_0) + \sum_{n=1}^{\infty} U_n(t,t_0),$$

(evolution-operator perturbation series) (13.9)

where the terms in the series are defined by

$$U_n(t,t_0) := \frac{1}{(i\hbar)^n} \int\limits_{t_0 \le t_1 \le \cdots \le t_n \le t} dt_n \cdots dt_1\, U_0(t,t_n)\, V(t_n)\, U_0(t_n,t_{n-1})\, V(t_{n-1}) \cdots V(t_2)\, U_0(t_2,t_1)\, V(t_1)\, U_0(t_1,t_0).$$

(evolution-operator expansion terms) (13.10)

This process looks a lot like the procedure we used from the resolvent operator in Section 12.2.1, where we started with the expression

$$G(z) = G_0(z) + G_0(z)VG(z) \tag{13.11}$$

and iterated it to generate the Born expansion

$$G = G_0 + G_0VG_0 + G_0VG_0VG_0 + G_0VG_0VG_0VG_0 + \cdots . \tag{13.12}$$

Of course, this resemblance is not superficial, although the result here is more general (and correspondingly a bit more complex due to the iterated integrations involved). However, this connection will require some more development of the resolvent operator. We'll come back to this shortly; for the moment let's put the series (13.9) into a simpler and more standard form.

13.1.1 Interaction Picture

Before in Sections 1.8.4 and 1.8.5, we introduced the Schrödinger picture, where states carry the time dependence, and the Heisenberg picture, where the time dependence is associated with operators. Explicitly, the Schrödinger-picture state evolves as

$$|\dot{\psi}\rangle_{\text{S}} = -\frac{i}{\hbar} H |\psi\rangle_{\text{S}}, \tag{13.13}$$

while the operator A_{S} is static. The Heisenberg-picture state $|\psi\rangle_{\text{H}}$ is static, but the

$$\dot{A}_{\text{H}} = -\frac{i}{\hbar}\left[A_{\text{H}}, H\right], \tag{13.14}$$

in the case where the evolution operator commutes with the Hamiltonian.

There is one more useful picture, the **interaction picture**, which is a hybrid of the Schrödinger and Heisenberg pictures. Again staying with the notation

$$H(t) = H_0 + V(t), \tag{13.15}$$

where V is the "interaction Hamiltonian," then the interaction picture is essentially the Schrödinger picture with respect to V, but the Heisenberg picture with respect to H_0. That is, the state vector carries the time dependence due to V, while the operators carry the time dependence due to H_0. The point is that the free time dependence due to H_0 should be relatively trivial, so it's handy to get it out of the way by burying it in the operators.

The transformation of the state vector to the interaction picture is

$$|\psi\rangle_{\text{I}} = U_0(0,t)|\psi\rangle_{\text{S}} = e^{iH_0t/\hbar}|\psi\rangle_{\text{S}}. \tag{13.16}$$
(interaction-picture state)

The operator transforms according to

$$A_{\text{I}}(t) = U_0(0,t)A_{\text{S}}U_0(t,0) = e^{iH_0t/\hbar}A_{\text{S}}e^{-iH_0t/\hbar}, \tag{13.17}$$
(interaction-picture operator)

in order to produce the correct matrix elements with respect to the interaction-picture states. Then the background Hamiltonian causes the operator to evolve,

$$\dot{A}_{\text{I}} = -\frac{i}{\hbar}\left[A_{\text{I}}, H_0\right], \tag{13.18}$$
(interaction-picture evolution)

while the state evolves according to the interaction potential

$$|\dot{\psi}\rangle_{\text{I}} = -\frac{i}{\hbar}V_{\text{I}}(t)|\psi\rangle_{\text{I}}, \tag{13.19}$$
(interaction-picture evolution)

noting that the V_{I} here is the potential $V(t)$ transformed into the interaction picture as in Eq. (13.17). The derivation of these equations of motion is a good exercise (Problem 13.2). The interaction picture is useful in perturbation theory, where the evolution due to H_0 should already be known. It is thus convenient to bury this evolution in the operators, so that it is possible to focus on the perturbation operator V.

Finally, note that we can think of the evolution operator $U_{\text{I}}(t,t_0)$ in the interaction picture, where the "free" evolution due to H_0 has been removed. Explicitly,

$$\begin{aligned}|\psi(t)\rangle_{\text{I}} &= U_0(0,t)|\psi(t)\rangle_{\text{S}} \\ &= U_0(0,t)\,U_{\text{S}}(t,t_0)|\psi(t_0)\rangle_{\text{S}} \\ &= U_0(0,t)\,U_{\text{S}}(t,t_0)\,U_0(t_0,0)|\psi(t_0)\rangle_{\text{I}},\end{aligned} \tag{13.20}$$

and thus we can identify the total operator acting on $|\psi(t_0)\rangle_{\text{I}}$ as $U_{\text{I}}(t,t_0)$,

$$U_{\text{I}}(t,t_0) := U_0(0,t)\,U_{\text{S}}(t,t_0)\,U_0(t_0,0), \tag{13.21}$$
(interaction-picture evolution operator)

so that

$$|\psi(t)\rangle_{\text{I}} = U_{\text{I}}(t,t_0)|\psi(t_0)\rangle_{\text{I}}. \tag{13.22}$$

Here, $U_{\text{S}}(t,t_0)$ is the Schrödinger-picture evolution operator.

13.1.2 Dyson Series

Now let's reconsider the perturbation series (13.9) in the interaction picture. We will also use tildes to denote operators in the interaction picture ($A_{\text{I}} \equiv \tilde{A}$), while operators with no tilde are by default in the Schrödinger picture ($A_{\text{S}} \equiv A$). Then we can transform the evolution operator as

$$\tilde{U}(t,t_0) = U_0(0,t)\,U(t,t_0)\,U_0(t_0,0), \tag{13.23}$$

while the base evolution operator obviously does nothing:

$$\tilde{U}_0(t,t_0) = U_0(0,t)\,U_0(t,t_0)\,U_0(t_0,0) = 1. \tag{13.24}$$

Transforming the entire series (13.9), using

$$\tilde{V}(t_k) = U_0(0,t_k)\,V(t_k)\,U_0(t_k,0) \tag{13.25}$$

and remembering $U_0(t_k,t_{k-1}) = U_0(t_k,0)\,U_0(0,t_{k-1})$, thus leads to

$$\tilde{U}(t,t_0) = 1 + \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int\limits_{t_0 \le t_1 \le \cdots \le t_n \le t} dt_n \cdots dt_1\, \tilde{V}(t_n) \cdots \tilde{V}(t_1). \tag{13.26}$$

(Dyson series)

This interaction-representation series is called the **Dyson series**,[1] and this is obviously a more compact form than the Schrödinger-picture counterpart.

Going on to introduce some formal notation, we can introduce the **chronological operator** $\mathscr{T}$ to write

$$\tilde{U}_n(t,t_0) = \frac{1}{(i\hbar)^n n!} \int_{t_0}^{t} dt_n \cdots dt_1\, \mathscr{T}\big[\tilde{V}(t_n) \cdots \tilde{V}(t_1)\big] \tag{13.27}$$

for the nth term in the Dyson series. That is, the chronological operator reorders its argument such that the times are in increasing order from right to left. Because of the action of the chronological operator, we don't need the time-ordering restriction on the integration limits. But then we are summing over redundant parts of the integrand, corresponding to the $n!$ different orderings of the potential—hence, the new factor of $1/n!$. Writing out the series explicitly as

$$\tilde{U}(t,t_0) = \mathscr{T} \sum_{n=0}^{\infty} \frac{1}{(i\hbar)^n n!} \int_{t_0}^{t} dt_n \cdots dt_1\, \tilde{V}(t_n) \cdots \tilde{V}(t_1), \tag{13.28}$$

the sum has the form of the series expansion of the exponential function. Recognizing that the n integrations in each term are independent, we can rewrite this series formally as

$$\tilde{U}(t,t_0) = \mathscr{T} \exp\left[-\frac{i}{\hbar} \int_{t_0}^{t} dt'\, \tilde{V}(t')\right].$$

(evolution operator, interaction picture) (13.29)

This is the general form of the evolution operator in the interaction picture, and the counterpart to the Schrödinger-picture version (1.185). Though common, this expression should be understood to be a shorthand for the full Dyson series, as the proper interpretation of $\mathscr{T}$ acting on the exponential function.

13.2 Connection to the Resolvent Operator

Now let's return to the development of the perturbation series for $U(t,t_0)$ in Eqs. (13.9) and (13.10), and how its structure parallels the Born series

$$G = G_0 + G_0VG_0 + G_0VG_0VG_0 + G_0VG_0VG_0VG_0 + \cdots. \tag{13.30}$$

These series are equivalent in the correct light, and we'll learn quite a bit in the process of exploring this connection.

13.2.1 Energy-Space Green Functions

Given a time-independent Hamiltonian H, consider the following function, defined by the integral expression

$$G^+(E) := -\lim_{\delta \to 0^+} \frac{i}{\hbar} \int_0^{\infty} d\tau\, e^{i(E-H)\tau/\hbar} e^{-\tau\delta/\hbar}, \tag{13.31}$$

[1] F. J. Dyson, "The Radiation Theories of Tomonaga, Schwinger, and Feynman," *Physical Review* **75**, 486 (1949) (doi: 10.1103/PhysRev.75.486)

where the δ exponential factor guarantees the convergence of the integral. Carrying out the integral,

$$\begin{aligned} G^+(E) &= -\lim_{\delta\to 0^+} \frac{i}{\hbar}\int_0^\infty d\tau\, e^{i(E-H+i\delta)\tau/\hbar} \\ &= -\lim_{\delta\to 0^+} \frac{e^{i(E-H+i\delta)\tau/\hbar}}{E-H+i\delta}\bigg|_0^\infty \\ &= \lim_{\delta\to 0^+} \frac{1}{E-H+i\delta} \\ &= \frac{1}{E-H+i0^+} \\ &= G(E+i0^+), \end{aligned} \tag{13.32}$$

where in the last step we recognize the resolvent $G(z) = 1/(z-H)$. Similarly, we can define the function

$$G^-(E) := \lim_{\delta\to 0^+} \frac{i}{\hbar}\int_{-\infty}^0 d\tau\, e^{i(E-H)\tau/\hbar} e^{+\tau\delta/\hbar}, \tag{13.33}$$

which becomes

$$\begin{aligned} G^-(E) &= \lim_{\delta\to 0^+} \frac{i}{\hbar}\int_{-\infty}^0 d\tau\, e^{i(E-H-i\delta)\tau/\hbar} \\ &= \frac{1}{E-H-i0^+} \\ &= G(E-i0^+). \end{aligned} \tag{13.34}$$

For reasons we will see, $G^+(E)$ is called the **retarded Green operator**, in energy (frequency) space, while $G^-(E)$ is called the **advanced Green operator** in energy space. We have thus shown that both Green functions are related to the resolvent via

$$G^\pm(E) = G(E\pm i0^+) = \frac{1}{E-H\pm i0^+}. \tag{13.35}$$

(retarded and advanced Green operators)

That is, they are essentially the resolvent along the line displaced infinitesimally above and below the real axis—a location riddled with poles and maybe a branch cut, if you recall. Note that $G^\pm(E)$ are indeed operators, although it is also common to call them Green *functions*; however, it's a little more appropriate to reserve the term "Green function" for matrix elements of the corresponding operator, such as $G^\pm(x,x';E) = \langle x|G^\pm(E)|x'\rangle$ in the position representation.

13.2.2 Time-Dependent Green Functions and Propagators

Now note that the definition (13.31) can be rewritten

$$G^+(E) = \frac{1}{i\hbar}\int_{-\infty}^\infty d\tau\, e^{i(E+i0^+)\tau/\hbar}\, U(\tau,0)\,\Theta(\tau), \tag{13.36}$$

where $\Theta(\tau)$ is the Heaviside step function and $U(\tau,0) = e^{-iH\tau/\hbar}$ is the unitary time-evolution operator from time 0 to τ for evolution under (the time-independent) Hamiltonian H. That is, $G^+(E)$ is (within a specific normalization convention) the Fourier transform of "half" of the time-evolution operator, $U(\tau,0)\,\Theta(\tau)$. Similarly, from the definition (13.33), we see that

$$G^-(E) = \frac{1}{i\hbar}\int_{-\infty}^\infty d\tau\, e^{i(E-i0^+)\tau/\hbar}\,[-U(\tau,0)\,\Theta(-\tau)], \tag{13.37}$$

so that up to a minus sign, $G^-(E)$ is the Fourier transform of the "other half" of the time-evolution operator, $U(\tau,0)\,\Theta(-\tau)$. Thus, defining the time-dependent retarded and advanced Green operators (+ for retarded, − for advanced)

$$G^\pm(t,t_0) := \pm U(t,t_0)\,\Theta[\pm(t-t_0)],$$

(retarded and advanced Green operators) (13.38)

these are related by the above Green operators by a Fourier transform:

$$G^\pm(E) = \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau\, e^{i[E+(\mathrm{sgn}\tau)i0^+]\tau/\hbar}\, G^\pm(\tau,0).$$

(Green-operator Fourier transform) (13.39)

In the notation we use here, we'll just use the argument of the Green operator to determine whether it is a time-dependent or energy-space Green operator. Note that since we are dealing with time-independent systems, $G^\pm(t,t_0)$ only depends on $t-t_0$.

Now to explain the terminology of advanced and retarded Green operators. First, recall [Eq. (1.179)] that the time-evolution operator satisfies the Schrödinger equation,

$$i\hbar\partial_t U(t,t_0) = HU(t,t_0). \tag{13.40}$$

We can use this relation and $\partial_\tau\Theta(\tau) = \delta(\tau)$ to differentiate the Green functions:

$$\begin{aligned} i\hbar\partial_t G^\pm(t,t_0) &= \pm i\hbar\partial_t\Big[U(t,t_0)\Theta[\pm(t-t_0)]\Big] \\ &= \pm HU(t,t_0)\Theta[\pm(t-t_0)] \pm i\hbar U(t,t_0)\big[\pm\delta(t-t_0)\big] \\ &= HG^\pm(t,t_0) + i\hbar\delta(t-t_0). \end{aligned} \tag{13.41}$$

In the last step, we used $U(t_0,t_0) = 1$. Thus, we have shown that

$$(i\hbar\partial_t - H)\,G^\pm(t,t_0) = i\hbar\delta(t-t_0)$$

(Green operators for the Schrödinger equation) (13.42)

(noting that this equation is also valid if the underlying Hamiltonian is explicitly time-dependent). Remember that the solution to a differential equation with a delta-function "driving" term *defines* a Green function (or impulse-response function) in general. Thus, $G^\pm(t,t_0)$ is the solution to the Schrödinger equation, driven by a delta-function impulse at $t = t_0$. In particular, $G^+(t,t_0)$ is the "retarded" Green operator, because the "source" is in the past, and the response follows after the impulse, $t > t_0$. Similarly, $G^-(t,t_0)$ is the "advanced" Green operator, because the source is in the future, and the response comes *before* the impulse, $t < t_0$. (Note, however, that there is no kick in the form of an added *potential*; it's an impulse that normally wouldn't show up in the Schrödinger equation.) Both Green operators obey the same equation, but correspond to different boundary conditions as $t \longrightarrow \pm\infty$.

Inverting the Fourier-transform relation (13.39) gives

$$G^\pm(\tau,0) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, e^{-iE\tau/\hbar}\, G^\pm(E).$$

(Green-function inverse Fourier transform) (13.43)

[Reading off the Fourier transform is the easiest way to infer this equation, but a contour integral of the type coming up in Eq. (13.78) will also do the trick; see Problem 13.9.] In particular, the case of $G^+(\tau,0)$ is important, as it gives the time-evolution operator for evolving the system forward from $t = 0$ to τ:

$$U(\tau,0) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, e^{-iE\tau/\hbar}\, G^+(E) \qquad (\tau > 0).$$

(Green-function Fourier relation) (13.44)

This relation is particularly useful in that it shows that matrix elements of the evolution operator,

$$K(\beta,t;\alpha,t_0) := \langle\beta|U(t,t_0)|\alpha\rangle,$$

(propagator) (13.45)

collectively called the **propagator**, can be computed from matrix elements of the retarded Green function. The term ''propagator'' is commonly used to refer specifically to matrix elements in the position representation as

$$K(x,t;x_0,t_0) := \langle x|U(t,t_0)|x_0\rangle, \tag{13.46}$$

(propagator, position representation)

although it is of course useful to think of this concept more generally. The propagator gives the transition amplitude, or the probability amplitude for the system to be in state β at time t, given that it was in state α at the (earlier) time t_0. Note that in the case of forward propagation $t > t_0$, the propagator can also be regarded as the collection of matrix elements of of the retarded Green operator $G^+(t,t_0)$ in view of the definition (13.38). In this way we can also talk about a retarded propagator K^+ and advanced propagator K^-, in exactly the same way as the Green operators (because they're really the same thing).

13.2.2.1 Free-Particle Green Function

As a (relatively) simple example of a Green function, let's compute the retarded (causal) Green function for the free particle with $H = p^2/2m$. Then the Green operator is

$$G^+(E) = \frac{1}{E - p^2/2m + i0^+}, \tag{13.47}$$

and we can proceed to compute the Green function in the position representation by inserting a momentum identity:

$$\begin{aligned} G^+(\mathbf{x},\mathbf{x}_0;E) &= \langle \mathbf{x}|\frac{1}{E - p^2/2m + i0^+}|\mathbf{x}_0\rangle \\ &= \int d^3p\, \langle \mathbf{x}|\frac{1}{E - p^2/2m + i0^+}|\mathbf{p}\rangle\langle \mathbf{p}|\mathbf{x}_0\rangle \\ &= \frac{1}{(2\pi\hbar)^3}\int d^3p\, \frac{e^{i\mathbf{p}\cdot(\mathbf{x}-\mathbf{x}_0)/\hbar}}{E - p^2/2m + i0^+}. \end{aligned} \tag{13.48}$$

Note that in the last equality the p^2 went from an operator to an eigenvalue, and then we used $\langle x|p\rangle = e^{ikx}/\sqrt{2\pi\hbar}$ in each dimension. Now setting

$$\mathbf{r} := \mathbf{x} - \mathbf{x}_0, \tag{13.49}$$

we can write out the integral in spherical coordinates as

$$G^+(\mathbf{x},\mathbf{x}_0;E) = \frac{1}{4\pi^2\hbar^3}\int_0^\infty dp\, p^2 \int_0^\pi d\theta\, \sin\theta\, \frac{e^{ipr\cos\theta/\hbar}}{E - p^2/2m + i0^+}, \tag{13.50}$$

where the angular integral is

$$\int_0^\pi d\theta\, \sin\theta\, e^{ipr\cos\theta/\hbar} = \int_{-1}^1 d\mu\, e^{ipr\mu/\hbar} = 2\,\mathrm{sinc}\Big(\frac{pr}{\hbar}\Big), \tag{13.51}$$

and $\mathrm{sinc}(x) := \sin(x)/x$ [i.e., basically $j_0(x)$]. Then

$$\begin{aligned} G^+(\mathbf{x},\mathbf{x}_0;E) &= \frac{1}{2\pi^2\hbar^3}\int_0^\infty dp\, p^2\, \frac{\mathrm{sinc}(pr/\hbar)}{E - p^2/2m + i0^+} \\ &= \frac{1}{2\pi^2 r^3}\int_0^\infty dz\, \frac{z^2\,\mathrm{sinc}\, z}{E - \frac{\hbar^2}{2mr^2}z^2 + i0^+}, \end{aligned} \tag{13.52}$$

where

$$z := \frac{pr}{\hbar}. \tag{13.53}$$

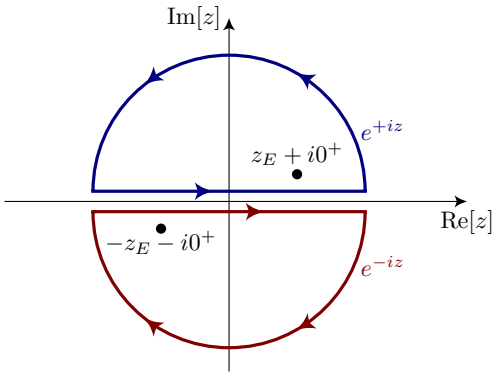
Also defining

$$z_E^2 := \frac{2mr^2E}{\hbar^2}, \tag{13.54}$$

we find

$$\begin{aligned} G^+(\mathbf{x},\mathbf{x}_0;E) &= \frac{m}{\pi^2\hbar^2 r}\int_0^\infty dz\,\frac{z\sin z}{z_E^2 - z^2 + i0^+} \\ &= \frac{m}{4i\pi^2\hbar^2 r}\int_{-\infty}^\infty dz\,\frac{z\big(e^{-iz}-e^{iz}\big)}{[z-(z_E+i0^+)][z+(z_E+i0^+)]}. \end{aligned} \tag{13.55}$$

Note that in the last step, $(z_E + i0^+)^2 = z_E^2 + i0^+$, counting only the "linear" terms in $i0^+$, and discarding the second-order term $(i0^+)^2$. To carry out the integral, we have to handle the $e^{\pm iz}$ components as separate contour integrals: e^{-iz} damps the contour going around the lower half-plane, while e^{+iz} damps the contour going around the upper half-plane. The contours are shown below; each contour encloses one pole.



Now applying the Cauchy integral formula (12.18) in each case, we obtain

$$\begin{aligned} G^+(\mathbf{x},\mathbf{x}_0;E) &= \frac{m}{4i\pi^2\hbar^2 r}(2\pi i)\left[-\frac{e^{iz_E}}{2} - \frac{e^{iz_E}}{2}\right] \\ &= -\frac{m}{2\pi\hbar^2 r}\,e^{iz_E}. \end{aligned} \tag{13.56}$$

Putting in the expression for z_E, we arrive at

$$G^+(\mathbf{x},\mathbf{x}_0;E) = -\frac{m}{2\pi\hbar^2}\,\frac{e^{ip_E r/\hbar}}{r}, \tag{13.57}$$

(free-particle Green function)

where $p_E := \sqrt{2mE}$. (Quick units check: the resolvent should have units of $1/(\text{energy})$, and $G^+(\mathbf{x},\mathbf{x}_0;E)$ should thus have units of $(\text{energy})^{-1}(\text{length})^{-3}$, which is true here.) This Green function has the form of a spherical wave; indeed, it is the Green function for the Helmholtz equation $(\nabla^2 + k^2)\psi = 0$, for which the solution is the radiation from a point source e^{ikr}/r. Here the boundary condition for the retarded Green function is more clear, since it corresponds to outgoing radiation at large r. In the calculation of the advanced Green function $G^-(\mathbf{x},\mathbf{x}_0;E)$, the poles hop over the real axis, and the net effect is that the functional form is an *ingoing* solution e^{-ikr}/r, where the wave is "absorbed" by the source at $r = 0$. Which brings up another point: We discussed the Green functions as impulse-response functions for the Schrödinger equation, but note that in the position representation there is *another* sense of impulse response in that, in the absence of the resolvent, the inner product $\langle\mathbf{x}|\mathbf{x_0}\rangle = \delta^3(\mathbf{r})$ defines a spatial impulse (i.e., the radiation source).

13.2.3 Resolvent as a Laplace Transform

The Laplace transform of a function $y(t)$ is, in our notation here, $\mathscr{L}[y](s)$, and is defined by the integral

$$\mathscr{L}[y](s) := \int_0^\infty dt\,e^{-st}y(t). \tag{13.58}$$

Now consider the Laplace transform of the derivative $\dot{y}$, with an integration by parts.

$$\begin{aligned}\mathscr{L}[\dot{y}](s) &= \int_0^\infty dt\, e^{-st}\dot{y}(t) \\ &= e^{-st}y(t)\Big|_0^\infty + s\int_0^\infty dt\, e^{-st}y(t).\end{aligned} \tag{13.59}$$

Thus we have the formula for the Laplace transform of a time derivative:

$$\mathscr{L}[\dot{y}(t)] = s\mathscr{L}[y(t)] - y(0). \tag{13.60}$$

The Laplace transform of $\partial_t U(t,t_0)$ is then

$$\mathscr{L}[\partial_t U(t,t_0)] = s\mathscr{L}[U(t,t_0)] - U(t_0,t_0) = s\mathscr{L}[U(t,t_0)] - 1, \tag{13.61}$$

and since the evolution operator satisfies the Schrödinger equation [Eq. (13.40)],

$$i\hbar\partial_t U(t,t_0) - i\hbar = H\,U(t,t_0), \tag{13.62}$$

the Laplace transform of this equation reads

$$i\hbar s\mathscr{L}[U(t,t_0)] - i\hbar = H\mathscr{L}[U(t,t_0)], \tag{13.63}$$

or

$$(i\hbar s - H)\mathscr{L}[U(t,t_0)] = i\hbar, \tag{13.64}$$

so that the Laplace transform of the evolution operator becomes

$$\frac{1}{i\hbar}\mathscr{L}[U(t,t_0)] = \frac{1}{i\hbar s - H}. \tag{13.65}$$

Comparing this to the definition $G(z) = (z-H)^{-1}$ [Eq. (12.4)] of the resolvent, we can identify $z = i\hbar s$ as the rescaled coordinate, and $G(z)$ is proportional to the Laplace transform of the evolution operator, but with a rescaled coordinate, rotated along the imaginary axis. The propagator relation (13.44) is essentially the inverse Laplace transform for $\tau > 0$, representing a convenient method to algebraically solve the initial-value problem for the propagator.

13.2.3.1 Connection of the Time-Independent and Time-Dependent Perturbation Expansions

Another useful identity involving the Laplace transform is in the convolution theorem. Recall that, given two functions $f(t)$ and $g(t)$, their convolution $(f*g)(t)$ is defined by the integral

$$(f*g)(t) := \int_0^t f(\tau)\, g(t-\tau)\, d\tau. \tag{13.66}$$

Then it isn't hard to show that the Laplace transform of the convolution is just the product of individual Laplace transforms

$$\mathscr{L}[f*g] = \mathscr{L}[f]\mathscr{L}[g]. \tag{13.67}$$
(Laplace convolution theorem)

This is the same result that applies to Fourier transforms of convolutions (Problem 2.5).

At this point, we can return to the Born expansion

$$G^+ = G_0^+ + G_0^+VG_0^+ + G_0^+VG_0^+VG_0^+ + G_0^+VG_0^+VG_0^+VG_0^+ + \cdots. \tag{13.68}$$

now applied to the retarded Green function. Since the resolvents are Laplace transforms, we can see that the products of G_0^+'s here correspond to convolutions of the evolution operator in time. To show this explicitly, we can return to Eq. (13.36), which says that $G^+(E)$ is the Fourier transform of $U(\tau)\,\Theta(\tau)/i\hbar$, where $U(\tau)$

is shorthand for $U(\tau,0)$; this is the equivalent of the Laplace transform because of the Heaviside function [and the factor of $i\hbar$ also appears in the same way in Eq. (13.65)]. Then inverting the Fourier transform in the Born series, we find

$$\begin{aligned}\frac{\Theta(\tau)\,U(\tau)}{i\hbar} = \frac{\Theta(\tau)\,U_0(\tau)}{i\hbar} &+ \frac{1}{(i\hbar)^2}\int_0^\tau d\tau_1\,\Theta(\tau-\tau_1)\,U_0(\tau-\tau_1)\,V\,\Theta(\tau_1)\,U_0(\tau_1)\\ &+ \frac{1}{(i\hbar)^3}\int_0^\tau d\tau_2\int_0^{\tau_1} d\tau_1\,\Theta(\tau-\tau_2)\,U_0(\tau-\tau_2)\,V\,\Theta(\tau_2-\tau_1)\,U_0(\tau_2-\tau_1)\,V\,\Theta(\tau_1)\,U_0(\tau_1)\\ &+ \cdots .\end{aligned} \tag{13.69}$$

This is equivalent to the Laplace-transform inversion, but it is somewhat easier to do bookkeeping of dummy variables with the explicit Heaviside functions. In the first-order term, for example, $0 \le \tau_1 \le \tau$, while in the secodn-order term, $\tau_1 \le \tau_2 \le \tau$ $0 \le \tau_1 \le \tau_2$. Continuing the pattern, we obtain

$$U(\tau) = U_0(\tau) + \sum_{n=1}^{\infty} \frac{1}{(i\hbar)^n} \int\limits_{0\le\tau_1\le\cdots\le\tau_n\le\tau} d\tau_n\cdots d\tau_1\,U_0(\tau-\tau_n)\,V\,U_0(\tau_n-\tau_{n-1})\,V\cdots V\,U_0(\tau_2-\tau_1)\,V\,U_0(\tau_1). \tag{13.70}$$

This expression matches up with the expressions (13.9) and (13.10) for the perturbation series of $U(t,t_0)$ that we derived directly from the evolution operator; however, those relations are more general in allowing for a time-dependent interaction potential. Remember that $G(z)$ corresponded by construction to a stationary Hamiltonian (where this operator makes the most sense), although in principle it could be generalized if taken to be defined by the Laplace/Fourier transform of the evolution operator as in Eq. (13.36).

13.3 Perturbed State Evolution

13.3.1 Static Perturbation

As a simple example of a perturbation, consider a potential $V(t)$ that is *constant* after it is turned on at $t = 0$:[2]

$$V(t) = V\,\Theta(t). \tag{13.71}$$

To characterize the time response to the perturbation, we will want to work out matrix elements $\langle \mathsf{f}\,|\tilde{U}(t,0)|\,\mathsf{i}\,\rangle$ of the evolution operator between an initial state $|\,\mathsf{i}\,\rangle$ and final state $|\,\mathsf{f}\,\rangle$, both eigenstates of H_0. This is a **transition amplitude** (i.e., the square of this quantity is the probability that a system starting in $|\,\mathsf{i}\,\rangle$ at $t = 0$ is found by an appropriate measurement at time $t > 0$ to be in $|\,\mathsf{f}\,\rangle$). This also has the form of a (retarded) propagator, so we will use the shorthand

$$\tilde{K}_{\mathsf{fi}}(t) := \langle\,\mathsf{f}\,|\tilde{U}(t,0)|\,\mathsf{i}\,\rangle. \tag{13.72}$$

Then keeping terms in the Dyson series (13.26) through third order, we obtain

$$\begin{aligned}\tilde{K}_{\mathsf{fi}}(t) \;\approx\; \langle\,\mathsf{f}\,|\,\mathsf{i}\,\rangle &- \frac{i}{\hbar}\int_0^t dt_1\,V_{\mathsf{fi}}\,e^{iE_{\mathsf{fi}}t_1/\hbar} - \frac{1}{\hbar^2}\sum_k \int_0^t dt_2\int_0^{t_2} dt_1\,V_{\mathsf{f}k}V_{k\mathsf{i}}\,e^{iE_{\mathsf{f}k}t_2/\hbar}\,e^{iE_{k\mathsf{i}}t_1/\hbar}\\ &+ \frac{i}{\hbar^3}\sum_{jk}\int_0^t dt_3\int_0^{t_3} dt_2\int_0^{t_2} dt_1\,V_{\mathsf{f}j}V_{jk}V_{k\mathsf{i}}\,e^{iE_{\mathsf{f}j}t_3/\hbar}\,e^{iE_{jk}t_2/\hbar}\,e^{iE_{k\mathsf{i}}t_1/\hbar}\\ =:\; \langle\,\mathsf{f}\,|\,\mathsf{i}\,\rangle &+ \tilde{K}^{(1)}_{\mathsf{fi}}(t) + \tilde{K}^{(2)}_{\mathsf{fi}}(t) + \tilde{K}^{(3)}_{\mathsf{fi}}(t).\end{aligned} \tag{13.73}$$

[2]Here we are following Claude Cohen-Tannoudji, Jacques Dupont-Roc, and Gilbert Grynberg, *Atom–Photon Interactions: Basic Processes and Applications* (Wiley, 1992), pp. 25-31 (ISBN: 0471625566).

Here we wrote the perturbation operator back in the Schrödinger picture, using for example

$$\tilde{V}_{\mathsf{fi}} = \langle\, \mathsf{f}\,|e^{iH_0 t/\hbar} V e^{-iH_0 t/\hbar}|\, \mathsf{i}\,\rangle = V_{\mathsf{fi}}\, e^{i(E_{\mathsf{f}}-E_{\mathsf{i}})t/\hbar} = V_{\mathsf{fi}}\, e^{iE_{\mathsf{fi}}t/\hbar}, \tag{13.74}$$

and as usual we are using the shorthand

$$E_{\beta\alpha} := E_\beta - E_\alpha \tag{13.75}$$

for energy differences. Now we can study separately the integral expressions for the first- and second-order evolutions.

13.3.1.1 First-Order Evolution

The first-order correction from Eq. (13.73) reads

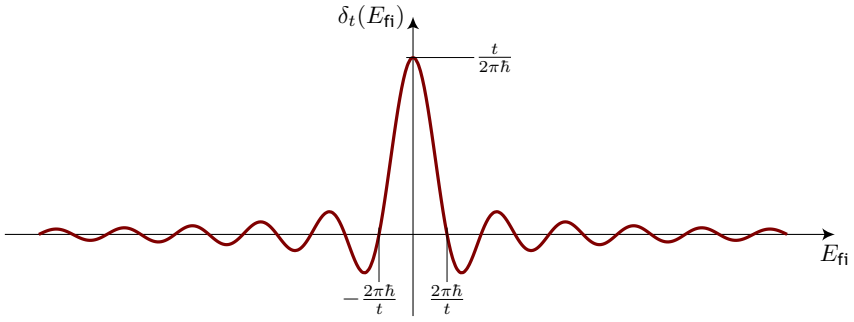
$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) = -\frac{iV_{\mathsf{fi}}}{\hbar}\int_0^t dt_1\, e^{iE_{\mathsf{fi}}t_1/\hbar} = -\frac{V_{\mathsf{fi}}}{E_{\mathsf{fi}}}\left(e^{iE_{\mathsf{fi}}t/\hbar}-1\right) = -2\pi i V_{\mathsf{fi}}\, e^{iE_{\mathsf{fi}}t/2\hbar}\,\delta_t(E_{\mathsf{fi}}),$$

(first-order evolution) (13.76)

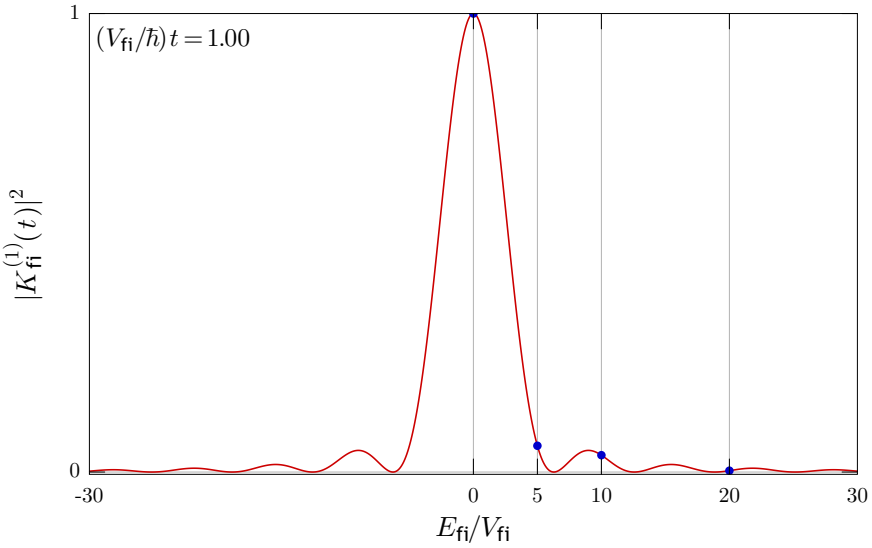
where

$$\delta_t(E_{\mathsf{fi}}) := \frac{1}{2\pi\hbar}\int_{-t/2}^{t/2} dt'\, e^{iE_{\mathsf{fi}}t'/\hbar} = \frac{1}{2\pi i E_{\mathsf{fi}}}\left(e^{iE_{\mathsf{fi}}t/2\hbar} - e^{-iE_{\mathsf{fi}}t/2\hbar}\right) = \frac{\sin(E_{\mathsf{fi}}t/2\hbar)}{\pi E_{\mathsf{fi}}} = \frac{t}{2\pi\hbar}\,\mathrm{sinc}(E_{\mathsf{fi}}t/2\hbar). \tag{13.77}$$

The function $\delta_t(E_{\mathsf{fi}})$ is something like a finite-width approximation to a delta function. As seen from the integral definition, as $t \longrightarrow \infty$, $\delta_t(E_{\mathsf{fi}}) \longrightarrow \delta(E_{\mathsf{fi}})$; also, the integral is unity, and the width is of order h/t. The function is plotted below.



Hence, at this order, in the long-time limit a transition only occurs if $E_{\mathsf{fi}} = 0$, a statement of energy conservation. For a finite interaction time t, some "slop" in the energy is permitted, due to an uncertainty of order h/t in the interaction energy.



The first-order evolution according to the amplitude (13.76) is illustrated in the animation above. Note the evolution at fixed values of E_{fi} undergo sinusoidal oscillations, with an amplitude that decays with increasing $|E_{\mathrm{fi}}|$, a point to which we will return later when discussing Rabi oscillations in Section 13.3.1.3. Because this is only first-order perturbation theory, these oscillations accurately reflect the true dynamics when the amplitude is small compared to unity—clearly the behavior at $E_{\mathrm{fi}} \approx 0$ is only valid at short times.

Remember that the amplitude (13.76) is still in the interaction picture. For the regular amplitude in the Schrödinger picture, you can simply restore a factor of $e^{-iE_{\mathrm{fi}}t/\hbar}$, which amounts to changing the sign of the exponential factor in Eq. (13.76).

13.3.1.2 Second- and Higher-Order Evolution

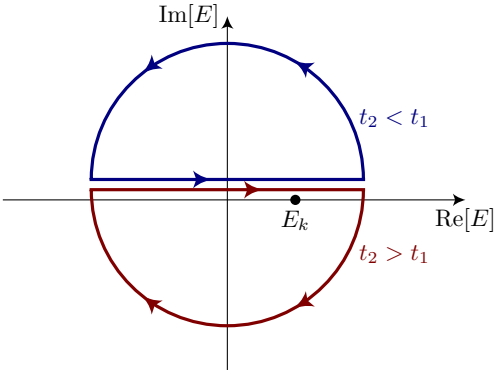
The second-order correction to the transmission amplitude from Eq. (13.73) reads

$$\tilde{K}_{\mathrm{fi}}^{(2)}(t) = -\frac{1}{\hbar^2}\sum_k V_{\mathrm{f}k}V_{k\mathrm{i}}\int_0^t dt_2 \int_0^{t_2} dt_1\, e^{iE_{\mathrm{f}k}t_2/\hbar}\, e^{iE_{k\mathrm{i}}t_1/\hbar}. \tag{13.78}$$

To start working with this, first consider the integral

$$\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, \frac{e^{-iE(t_2-t_1)/\hbar}}{E + i0^+ - E_k} = -e^{-iE_k(t_2-t_1)/\hbar}\,\Theta(t_2 - t_1), \tag{13.79}$$

where as in the Green-function discussion above, 0^+ stands for ϵ, with the limit $\epsilon \to 0^+$ taken at the end of any integration. The above identity follows from applying the Cauchy integral formula (12.18) on one of the contours shown below.



There are two possibilities, depending on the sign of $t_2 - t_1$, because we need the exponential factor to damp away the contribution from the great-semicircular part of the contour. The straight sections of both contours are displaced above the real axis due to the $+i0^+$. Note that only the lower contour encloses the pole at E_k, and in the clockwise direction, so the result is the residue of the pole with a minus sign. Using this integral result in Eq. (13.78), we have

$$\tilde{K}^{(2)}_{\mathsf{fi}}(t) = \frac{1}{2\pi i\hbar^2} \sum_k V_{\mathsf{f}k} V_{k\mathsf{i}} \int_0^t dt_2 \int_0^t dt_1 \int_{-\infty}^{\infty} dE \, \frac{e^{i(E_\mathsf{f}-E)t_2/\hbar}\, e^{i(E-E_\mathsf{i})t_1/\hbar}}{E + i0^+ - E_k}. \tag{13.80}$$

Then using Eq. (13.77) for the t_1 and t_2 integrals (notice that both limits are now the same),

$$\tilde{K}^{(2)}_{\mathsf{fi}}(t) = -2\pi i \sum_k V_{\mathsf{f}k} V_{k\mathsf{i}} \int_{-\infty}^{\infty} dE \, \frac{1}{E + i0^+ - E_k} \, \delta_t(E_\mathsf{f} - E) \, \delta_t(E - E_\mathsf{i}) \, e^{i(E_\mathsf{f}-E)t/2\hbar} \, e^{i(E-E_\mathsf{i})t/2\hbar}. \tag{13.81}$$

The finite-time delta functions are highly localized, and provided that no eigenenergy E_k lies extremely close to $E_\mathsf{i} \approx E_\mathsf{f}$, we can regard the factor $(E+i0^+-E_k)^{-1}$ as varying slowly over the extent of the δ_t's. (Note that we are excluding the cases $k = i$ and $k = f$, because we assume that the matrix-element product vanishes in this case; direct couplings arising from V_{ii} or V_{ff} could simply be absorbed into H_0.) Then we can pull this factor out of the integral with $E \approx E_\mathsf{i} \approx E_\mathsf{f}$, so that

$$\tilde{K}^{(2)}_{\mathsf{fi}}(t) \approx -2\pi i \sum_k \frac{V_{\mathsf{f}k} V_{k\mathsf{i}}}{E_\mathsf{i} - E_k + i0^+} \int_{-\infty}^{\infty} dE \, \delta_t(E_\mathsf{f} - E) \, \delta_t(E - E_\mathsf{i}) \, e^{i(E_\mathsf{f}-E_\mathsf{i})t/2\hbar}. \tag{13.82}$$

The last integral has the form of a convolution, and the result is

$$\begin{aligned} \int_{-\infty}^{\infty} dE \, \delta_t(E_\mathsf{f} - E) \, \delta_t(E - E_\mathsf{i}) &= \frac{1}{(2\pi\hbar)^2} \int_{-\infty}^{\infty} dE \int_{-t/2}^{t/2} dt' \int_{-t/2}^{t/2} dt'' \, e^{i(E_\mathsf{f}-E)t'/\hbar} \, e^{i(E-E_\mathsf{i})t''/\hbar} \\ &= \frac{1}{2\pi\hbar} \int_{-t/2}^{t/2} dt' \int_{-t/2}^{t/2} dt'' \, e^{iE_\mathsf{f}t'/\hbar} \, e^{-iE_\mathsf{i}t''/\hbar} \, \delta(t' - t'') \\ &= \frac{1}{2\pi\hbar} \int_{-t/2}^{t/2} dt' \, e^{i(E_\mathsf{f}-E_\mathsf{i})t'/\hbar} = \delta_t(E_\mathsf{f} - E_\mathsf{i}) \end{aligned} \tag{13.83}$$

after using Eq. (13.77), and so

$$\tilde{K}^{(2)}_{\mathsf{fi}}(t) \approx -2\pi i \sum_k \frac{V_{\mathsf{f}k} V_{k\mathsf{i}}}{E_\mathsf{i} - E_k + i0^+} \, e^{iE_\mathsf{fi}t/2\hbar} \, \delta_t(E_\mathsf{fi}). \tag{13.84}$$

(second-order evolution)

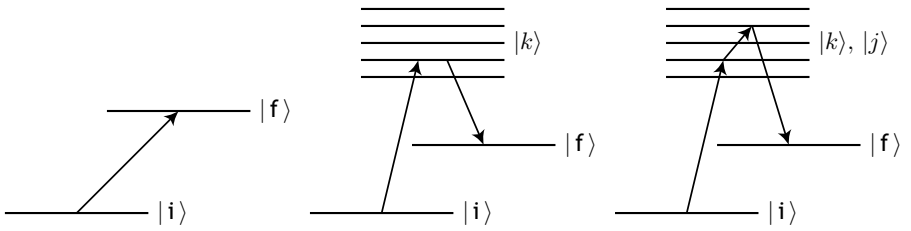
Thus, the same comments that applied to the first-order case apply here also: The transition probability is small unless $E_\mathsf{f} \approx E_\mathsf{i}$, particularly at long interaction times, as expected from energy conservation. Note that the product $V_{\mathsf{f}k}V_{k\mathsf{i}}$ has the interpretation that the transition from $|\,\mathsf{i}\,\rangle \longrightarrow |\,\mathsf{f}\,\rangle$ proceeds via all possible intermediate states, and that there is a resonant enhancement for the transitions between states where E_k is relatively close to E_I (but not *too* close, or this whole procedure breaks down).

Continuing in the same way, the third-order correction is (Problem 13.3)

$$\tilde{K}^{(3)}_{\mathsf{fi}}(t) \approx -2\pi i \sum_{jk} \frac{V_{\mathsf{f}j} V_{jk} V_{k\mathsf{i}}}{(E_\mathsf{i} - E_j + i0^+)(E_\mathsf{i} - E_k + i0^+)} \, e^{iE_\mathsf{fi}t/2\hbar} \, \delta_t(E_\mathsf{fi}).$$

(third-order evolution) (13.85)

The pattern should be reasonably clear by now: each successive order picks up another energy difference in the denominator, another intermediate matrix element like V_{jk}, and another sum over intermediate states. While the first-order perturbation had the interpretation of V causing direct transitions $|\,\mathsf{i}\,\rangle \longrightarrow |\,\mathsf{f}\,\rangle$, the second-order term sums over transitions through all possible intermediate states, $|\,\mathsf{i}\,\rangle \longrightarrow |k\rangle \longrightarrow |\,\mathsf{f}\,\rangle$; the third-order term sums over transitions through two intermediate states, $|\,\mathsf{i}\,\rangle \longrightarrow |k\rangle \longrightarrow |j\rangle \longrightarrow |\,\mathsf{f}\,\rangle$; and so on. These first-, second-, and third-order processes are illustrated schematically in the energy-level diagrams below.



Putting together Eqs. (13.73), (13.76), (13.84), and (13.85), we can summarize the transition amplitude to third order as

$$\tilde{K}_{\mathsf{fi}}(t) \approx \langle\, \mathsf{f} \,|\, \mathsf{i} \,\rangle - 2\pi i \left[V_{\mathsf{fi}} + \sum_k \frac{V_{\mathsf{f}k} V_{k\mathsf{i}}}{E_{\mathsf{i}} - E_k + i0^+} + \sum_{jk} \frac{V_{\mathsf{f}j} V_{jk} V_{k\mathsf{i}}}{(E_{\mathsf{i}} - E_j + i0^+)(E_{\mathsf{i}} - E_k + i0^+)} \right] e^{iE_{\mathsf{fi}}t/2\hbar}\, \delta_t(E_{\mathsf{fi}}).$$

(transition amplitude, second order) (13.86)

The phase factor here reflects that the evolution is taken over the interval $[0, t]$ rather than $[-t/2, t/2]$, as fits the definition of $\delta_t(E)$. Note that the summation here does not explicitly exclude the case where the an intermediate state $|k\rangle$ or $|j\rangle$ in the sum is either $|\,\mathsf{i}\,\rangle$ or $|\,\mathsf{f}\,\rangle$. These terms are divergent unless $V_{\mathsf{ii}} = V_{\mathsf{ff}} = 0$; again, these matrix elements can be absorbed back into H_0 anyway, so at this order there should be no problem. Note also that the $i0^+$ in the second-order denominator doesn't seem to be of much consequence here, and for a discrete spectrum it indeed isn't. This result carries over to the case of a continuous spectrum, however, in which case this little bump away from the real axis is important in telling us which side of a branch cut we're on.

13.3.1.3 Rabi Oscillations

Now let's apply time-dependent perturbation theory to an old problem, that of tunneling between two slightly asymmetric wells. In this case we want the transmission probability between two *different* states, where $\langle\, \mathsf{f} \,|\, \mathsf{i} \,\rangle = 0$. Then from Eq. (13.86), the transition *probability*, keeping only the first-order contribution, is

$$\left|\tilde{K}_{\mathsf{fi}}(t)\right|^2 = (2\pi)^2 |V_{\mathsf{fi}}|^2 \left[\delta_t(E_{\mathsf{fi}})\right]^2 = (2\pi)^2 |V_{\mathsf{fi}}|^2 \frac{\sin^2(E_{\mathsf{fi}}t/2\hbar)}{(\pi E_{\mathsf{fi}})^2} = |2V_{\mathsf{fi}}|^2 \frac{\sin^2(E_{\mathsf{fi}}t/2\hbar)}{(E_{\mathsf{fi}})^2}. \tag{13.87}$$

In the ''exact'' treatment of this problem (i.e., exact to the extent of restricting the Hilbert space to one state in each well), we can adapt the current notation to the previous notation by setting $V_{\mathsf{fi}} \longrightarrow \hbar\Omega/2$ [with Ω the Rabi frequency; cf. Eq. (3.45)] and $E_{\mathsf{fi}} \longrightarrow \hbar\Delta$ (with $\hbar\Delta$ the energy mismatch between the wells). Then the first-order perturbation result becomes

$$\left|\tilde{K}_{\mathsf{fi}}(t)\right|^2 = \frac{\Omega^2}{\Delta^2} \sin^2(\Delta t/2).$$

(Rabi oscillations, first-order perturbation theory) (13.88)

Comparing the perturbation result to the exact tunneling probability from Eq. (3.94),

$$P(t) = \frac{\Omega^2}{\Omega^2 + \Delta^2}\, \sin^2\!\left(\frac{\sqrt{\Omega^2 + \Delta^2}\, t}{2} \right), \tag{13.89}$$

we see that these are equivalent in the limit of small $|\Omega|^2$—that is, where Ω^2 is neglected compared to Δ^2. For $\Delta \neq 0$ and small Ω, the perturbation expression produces the correct (off-resonance) Rabi oscillations. In the limit $\Delta \longrightarrow 0$, the perturbation result (13.88) reduces to

$$\left|\tilde{K}_{\mathsf{fi}}(t)\right|^2 = \frac{\Omega^2 t^2}{4}. \tag{13.90}$$

This expression represents resonant Rabi oscillations, but from the full expression $\sin^2(\Omega t/2)$ expanded to lowest order in Ω at some fixed t, or equivalently in this case, expanded to lowest order in t at fixed Ω.

Perturbation theory only picks up the short-time behavior in the exactly resonant case, which is sensible in that we assumed the perturbation to be weak, but this obviously breaks down in the resonant case where the perturbation induces a full transition given enough time. Of course, resumming the perturbation series at all orders will reproduce the correct time dependence (13.89), even at resonance (Problem 13.7) or even near resonance.

13.3.1.4 Harmonic Perturbation

An important problem in time-dependent perturbation theory is the temporally harmonic perturbation, of the form

$$V(t) = V_0 \cos\omega t = \frac{V_0}{2}\Big(e^{-i\omega t} + e^{i\omega t}\Big), \tag{13.91}$$

with $\omega > 0$ and V_0 some operator, and this is only slightly more complicated to handle than the constant-perturbation case. In fact, the first-order static-perturbation transition amplitude (13.76) is simply modified to read

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) = -\frac{i}{2\hbar}\int_0^t dt_1\,(V_0)_{\mathsf{fi}}\left(e^{i(E_{\mathsf{fi}}-\hbar\omega)t_1/\hbar} + e^{i(E_{\mathsf{fi}}+\hbar\omega)t_1/\hbar}\right). \tag{13.92}$$

We will leave the modification of the second-order correction (13.78) as an exercise (Problem 13.12). Then the algebra leading up to the first-order, static-perturbation result (13.76) carries through, with $e^{\pm i\omega t}$ acting as energy-shift operators, with the result

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) = -\pi i (V_0)_{\mathsf{fi}}\left(e^{i(E_{\mathsf{fi}}-\hbar\omega)t/2\hbar}\,\delta_t(E_{\mathsf{fi}}-\hbar\omega) + e^{i(E_{\mathsf{fi}}+\hbar\omega)t/2\hbar}\,\delta_t(E_{\mathsf{fi}}+\hbar\omega)\right). \tag{13.93}$$

This equation is a little easier to look at if we translate energy differences into (angular) frequencies by

$$\omega_{\alpha\beta} := \frac{E_{\alpha\beta}}{\hbar} = \frac{E_\alpha - E_\beta}{\hbar}, \tag{13.94}$$

so that

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) = -\frac{\pi i}{\hbar}(V_0)_{\mathsf{fi}}\left(e^{i(\omega_{\mathsf{fi}}-\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}-\omega) + e^{i(\omega_{\mathsf{fi}}+\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}+\omega)\right),$$

(first-order evolution, harmonic perturbation) (13.95)

where we used $\delta_t(\hbar\omega) = \delta_t(\omega)/\hbar$, which is also true for the ordinary delta function, and we are now assuming orthogonal initial and final states so that $\langle\,\mathsf{f}\,|\,\mathsf{i}\,\rangle = 0$.

13.3.1.5 Rotating-Wave Approximation

Again, remember that the functions $\delta_t(\omega)$ will only be nonzero if the argument approximately vanishes. Then the two terms act separately. If $\omega_{\mathsf{fi}} > 0$ (the initial state is of lower energy) and $\omega \approx \omega_{\mathsf{fi}}$, then the first term will be much more important than the second term; in this case the transition amplitude is approximately

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) \approx -\frac{\pi i}{\hbar}(V_0)_{\mathsf{fi}}\,e^{i(\omega_{\mathsf{fi}}-\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}-\omega).$$

(absorption due to harmonic perturbation) (13.96)

This is a case of **resonance** of the harmonic perturbation ω with the transition frequency ω_{fi}, and the approximation of ignoring the nonresonant term ("counter-rotating term") is called the **rotating-wave approximation** (RWA). In this case we can associate the $e^{-i\omega t}$ part of the perturbation with absorption of energy. For a laser (monochromatic electric field) excitation of an atom, for example, this process corresponds to absorption of a photon from the field by an atom making an upward transition (say, from the ground state to an excited state).

In the case where $\omega_{\mathsf{fi}} < 0$ (the initial state has higher energy), resonance occurs for $\omega \approx -\omega_{\mathsf{fi}}$, and the second term in Eq. (13.95) dominates. In the rotating-wave approximation, we then have

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) \approx -\frac{\pi i}{\hbar}(V_0)_{\mathsf{fi}}\,e^{i(\omega_{\mathsf{fi}}+\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}+\omega).$$

(stimulated emission due to harmonic perturbation) (13.97)

Thus we see that the $e^{+i\omega t}$ part of the perturbation drives downward energy transitions. In the example of a laser field driving an atom, this case is thus associated with **stimulated emission** of a photon.

There is another important point here: Notice that the RWA solution (13.96) has the same form as the static solution (13.76), apart from a factor of 2 and the shift by ω. The lesson here is that the problem of two levels of energy separation ΔE coupled by a harmonic perturbation ω is equivalent to the problem of two levels of energy separation $\Delta E \pm \hbar\omega$ (whichever is smaller), but coupled by a *static* field. This means that the discussion of resonant and nonresonant tunneling as Rabi oscillations carry over to two atomic levels coupled by a microwave or optical field, or to two levels of a particle in *any* potential coupled by an oscillating perturbation. The Rabi oscillation frequency is then $\Omega = |(V_0)_{\mathsf{fi}}|/\hbar$ (minding the factor of 2 difference from the static case). We have only shown this to be true within first-order perturbation theory, but this statement is generally true. In the atom–laser case, the RWA is often well-justified, since the mismatch of the laser from resonance could be on the order of GHz, MHz, or smaller (depending on the atomic transition and the intended purpose of the atom–laser coupling), in which case the nonresonant term has a corresponding factor of the optical frequency, ∼PHz. Then the nonresonant term is suppressed by 6 or more orders of magnitude compared to the resonant term.

We can also interpret the nonresonant terms that are discarded in the RWA. The language is easier to deal with in the case of an atom–laser interaction, so let's stick with that example. The nonresonant part ($e^{+i\omega t}$) of the perturbation in the absorption ($E_{\mathsf{fi}} > 0$) case corresponds to an upward transition of the atom while a photon is created; this doesn't conserve energy, which is why it is suppressed. Similarly, the nonresonant part ($e^{-i\omega t}$) of the perturbation in the stimulated-emission ($E_{\mathsf{fi}} < 0$) case corresponds to a photon being destroyed while the atom makes a downward energy transition—also not conserving energy. Note, however, that it *is* possible for these nonresonant processes to conserve energy, provided one is immediately followed by the other—something that can happens at next order in perturbation theory. Even there, though, the effect of these terms is weak, but in certain cases their effect can be amplified into something significant (the Lamb shift mentioned earlier is one example).

By the way, a straightforward generalization of the harmonic perturbation (13.91) is

$$V(t) = \frac{1}{2}\Big(V_0 e^{-i\omega t} + V_0^\dagger e^{i\omega t}\Big). \tag{13.98}$$

Since the conjugate operator is associated with $e^{i\omega t}$, tracing through the same derivation with this change in mind leads to a generalization of Eq. (13.95):

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) = -\frac{\pi i}{\hbar}\Big((V_0)_{\mathsf{fi}}\, e^{i(\omega_{\mathsf{fi}}-\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}-\omega) + (V_0^\dagger)_{\mathsf{fi}}\, e^{i(\omega_{\mathsf{fi}}+\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}+\omega)\Big),$$

(first-order evolution, harmonic perturbation) (13.99)

Thus, matching this expression to the atom–laser discussion above, V_0 would be associated with annihilation of photons, while $V_0^\dagger$ would be associated with photon creation. In a treatment with a properly quantized electromagnetic field, V_0 would include the part of the electric-field annihilation operator (remember, e.g., from Problem 5.7, that the harmonic-oscillator annihilation operator is associated with a time dependence $e^{-i\omega t}$).

13.3.2 Application: Bragg Diffraction

A particularly nice example of the action of a static perturbation is the problem of Bragg diffraction, or the dynamics of a particle in one dimension subject to the weak potential

$$V(x) = 2A\cos kx = A\Big(e^{ikx} + e^{-ikx}\Big), \tag{13.100}$$

which will serve as a perturbation to the free-particle Hamiltonian. The key to the solution here is to recall that the $e^{\pm ikx}$ act as momentum-shift operators, as we can quickly verify:

$$\langle x|e^{\pm ikx}|p\rangle = e^{\pm ikx}\frac{1}{\sqrt{2\pi\hbar}}\,e^{ipx/\hbar} = \frac{1}{\sqrt{2\pi\hbar}}\,e^{i(p\pm\hbar k)x/\hbar} = \langle x|p\pm\hbar k\rangle. \tag{13.101}$$

An immediate consequence is that this perturbation only connects momentum states on a ''ladder'' of momenta $p_0 + n\hbar k$ for $n \in \mathbb{Z}$. Thus, while we haven't discussed how perturbation theory works with a continuous spectrum, it doesn't matter here: this problem is effectively one of many separate discrete spectra.

The transition amplitude (13.86) states, due to the presence of $\delta_t(E_{\mathsf{fi}})$, that at long times energy must be conserved, and so a particle with momentum p can only couple to the other state with the *same* (unperturbed) energy, the momentum $-p$. With the constraint of staying on the ladder $p_0 + n\hbar k$, the potential (13.100) can only couple the (degenerate) pairs of states with $p = \pm n\hbar k/2$. Thus, we can set this problem up as a transition between initial state $|\,\mathsf{i}\,\rangle = |+n\hbar k/2\rangle$ and final state $|\,\mathsf{f}\,\rangle = |-n\hbar k/2\rangle$, making use of the matrix element

$$\langle (n \pm 2)\hbar k/2|V|n\hbar k/2\rangle = A. \tag{13.102}$$

In the case $n = 1$, there is only one relevant matrix element,

$$V_{\mathsf{fi}} = \langle -\hbar k/2|V|\hbar k/2\rangle = A. \tag{13.103}$$

The transition goes directly between the initial and final states, because they are separated by $\hbar k$ in momentum, which is accomplished by V directly. This is not the case for the more distant ($n > 1$) cases, where multiple factors of V are needed to shift the initial state in momentum to the final state. The process here, represented by V_{fi}, is called **first-order Bragg diffraction** (remember, here n indexes the momentum gap between the initial and final states as $n\hbar k$, but it does *not* refer to the order of perturbation theory).

In the case of the $n = 2$ transition, this is only allowed at second order in perturbation theory, which involves the matrix-element product

$$\sum_j V_{\mathsf{f}j} V_{j\mathsf{i}} = \langle -\hbar k|V|0\rangle\langle 0|V|\hbar k\rangle = A^2. \tag{13.104}$$

This process is called **second-order Bragg diffraction**, and notice that the transition uses $|p = 0\rangle$ as an intermediate step.

Similarly, the $n = 3$ transition is only allowed at third order in perturbation theory, because

$$\sum_{jj'} V_{\mathsf{f}j} V_{jj'} V_{j\mathsf{i}} = \langle -3\hbar k/2|V|-\hbar k/2\rangle\langle -\hbar k/2|V|\hbar k/2\rangle\langle \hbar k/2|V|3\hbar k/2\rangle = A^3, \tag{13.105}$$

leading to **third-order Bragg diffraction**. At the same order in perturbation theory, we also have a contribution to first-order diffraction ($n = 1$) via the combination

$$\sum_{jj'} V_{\mathsf{f}j} V_{jj'} V_{j\mathsf{i}} = \langle -\hbar k/2|V|+\hbar k/2\rangle\langle +\hbar k/2|V|-\hbar k/2\rangle\langle -\hbar k/2|V|+\hbar k/2\rangle = A^3, \tag{13.106}$$

although this contribution will require some more careful discussion.

The perturbation expressions also require division by energy differences of the involved states. Since the unperturbed states are momentum eigenstates with $p = \pm n\hbar k/2$, it is convenient to write the energies in terms of an energy scale,

$$E_n = \frac{n^2\hbar^2k^2}{8m} =: n^2 E_{\text{B}}, \tag{13.107}$$

which we can call the ''Bragg energy'' $E_{\text{B}} := \hbar^2k^2/8m$.

Now to put all the pieces together and summarize. First-order diffraction occurs between $|\,\mathsf{i}\,\rangle = |\hbar k/2\rangle$ and $|\,\mathsf{f}\,\rangle = |-\hbar k/2\rangle$; we will use the matrix element (13.103) in the first-order term of the amplitude (13.86) to write

$$\tilde{K}_{\mathsf{fi}}(n = 1, t) \approx -\frac{i}{\hbar} At \longrightarrow -i\sin(At/\hbar) \tag{13.108}$$

(first-order Bragg diffraction)

where we have used, from Eq. (13.77), that

$$\lim_{E_{\mathsf{fi}}\to 0} e^{iE_{\mathsf{fi}}t/2\hbar}\,\delta_t(E_{\mathsf{fi}}) = \frac{t}{2\pi\hbar}. \tag{13.109}$$

We also used our knowledge of the problem of two coupled states to infer the beyond-linear-in-t dependence, in the form of resonance Rabi oscillations. Note, however that we dropped the A^3 correction here from Eq. (13.106) because of the pathology of the vanishing energy denominator (the initial and final states are degenerate). The divergent nature of this correction is a signal that we are approaching it in the wrong way. The problem is that, in the way we are doing this calculation, the term had a time dependence of t; however, this term is really associated with the t^3 part of the transition amplitude. The mismatch in the time dependence results in the pathology of this term. A different evaluation of a term of this form shows that it works out correctly (Problem 13.7).

Second-order diffraction occurs between $|\,\mathsf{i}\,\rangle = |\hbar k\rangle$ and $|\,\mathsf{f}\,\rangle = |-\hbar k\rangle$ via $|0\rangle$. The matrix-element product (13.104) leads in the second-order term of the amplitude (13.86) to

$$\tilde{K}_{\mathsf{fi}}(n=2,t) \approx -\frac{i}{\hbar}\frac{A^2}{4E_{\text{B}}}t \longrightarrow -i\sin(A^2t/4\hbar E_{\text{B}}),$$

(second-order Bragg diffraction) (13.110)

where the energy difference came from the initial state at $4E_{\text{B}}$ and the intermediate state at zero energy.

Finally, third-order diffraction occurs between $|\,\mathsf{i}\,\rangle = |3\hbar k/2\rangle$ and $|\,\mathsf{f}\,\rangle = |-3\hbar k/2\rangle$ via $|\pm\hbar k/2\rangle$. The matrix-element product (13.105) leads in the third-order term of the amplitude (13.86) to

$$\tilde{K}_{\mathsf{fi}}(n=3,t) \approx -\frac{i}{\hbar}\frac{A^3}{(8E_{\text{B}})^2}t \longrightarrow -i\sin(A^3t/64\hbar E_{\text{B}}^2).$$

(third-order Bragg diffraction) (13.111)

An important consequence of this treatment is that, while multistep transitions are possible, their transition rate is strongly suppressed. First, the suppression is exponential in the small potential parameter A, and it is also suppressed by progressively larger energy differences involving the intermediate states.

13.3.2.1 Exact Eigenenergies and Band Structure

For comparison, the eigenfunctions and eigenenergies of the sinusoidal potential may be calculated in terms of a special function. Starting with the time-independent Schrödinger equation

$$-\frac{\hbar^2}{2m}\psi''(x) + 2A\cos(kx)\,\psi(x) = E\psi(x), \tag{13.112}$$

we can simplify this to

$$\psi''(x) + \frac{2m}{\hbar^2}\big[E - 2A\cos(kx)\big]\,\psi(x) = 0, \tag{13.113}$$

and then change variables by $2z = kx$ to obtain

$$\psi''(z) + \frac{8m}{\hbar^2k^2}\big[E - 2A\cos(2z)\big]\,\psi(z) = 0. \tag{13.114}$$

This has the form of **Mathieu's equation**,[3] which can be written in canonical form as

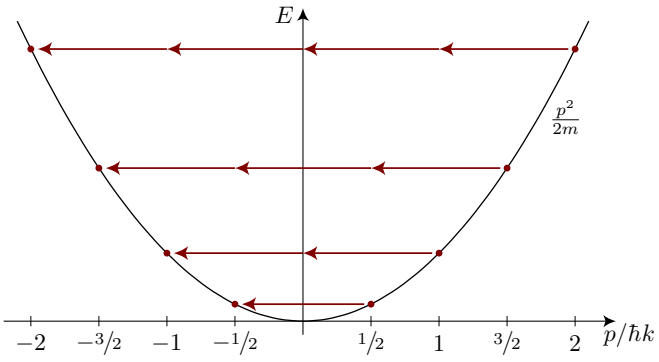
$$y''(z) + (a - 2q\cos 2z)y = 0, \tag{13.115}$$

where we can identify the coefficient values $q = A/E_{\text{B}}$, $a = E/E_{\text{B}}$. The solutions of this equation are **Mathieu functions**, for which there are well studied numerical algorithms.[4]

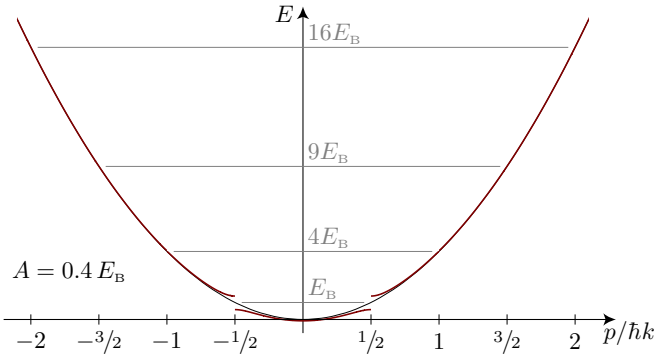
To relate the exact solutions to the perturbation treatment above, recall that the unperturbed energy is $p^2/2m$, but that momentum only changes by $\pm\hbar k$. Thus, the allowed Bragg transitions at first through fourth diffraction order are shown in the dispersion diagram below.

[3] Milton Abramowitz and Irene A. Stegun, *Handbook of Mathematical Functions* (Dover, 1965), Chapter 20, p. 722 (ISBN: 0486612724).

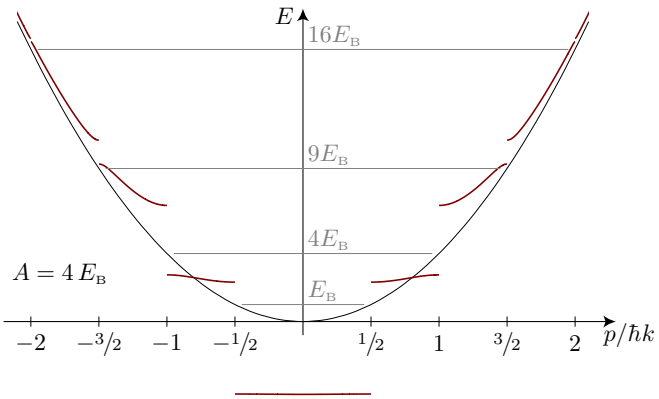
[4] Walter R. Leeb, "Algorithm 537: Characteristic Values of Mathieu's Differential Equation," *ACM Transactions on Mathematical Software* **5**, 112 (1979) (doi: 10.1145/355815.355824); Randall B. Shirts, "Algorithm 721: MTIEU1 and MTIEU2: Two Subroutines to Compute Eigenvalues and Solutions of Mathieu's Differential Equation for Noninteger and Integer Order," *ACM Transactions on Mathematical Software* **19**, 391 (1993) (doi: 10.1145/155743.155847); Randall B. Shirts, "The Computation of Eigenvalues and Solutions of Mathieu's Differential Equation for Noninteger Order," *ACM Transactions on Mathematical Software* **19**, 377 (1993) (doi: 10.1145/155743.155796).



These transitions couple degenerate states, lifting the degeneracy, and leading to avoided-crossing behavior. This is illustrated below for a relatively small perturbation, and the avoided crossing is only easy to see for first-order diffraction. The avoided crossing here leads to a *band gap* in the energy spectrum.



There are of course band gaps corresponding to each of the other diffraction orders, but to make them visible, we need to look at solutions corresponding to a larger perturbation. This is shown below; note that the "perturbation" here is strong enough that the spectrum is quite different from the unperturbed parabola. However, the band gaps at each order are visible, and it's also clear that the band gaps become rapidly narrower with increasing order.



These diagrams are conventionally plotted in a different way that requires some explanation. First, note that because the potential is periodic (with period $\lambda = 2\pi/k$), the solution should in some sense be invariant under translations by this spatial period. Certainly the probability density should be invariant, and thus we can require that eigenfunctions satisfy

$$|\psi(x+\lambda)|^2 = |\psi(x)|^2. \tag{13.116}$$

Then the shifted eigenfunction differs from the original by at most some complex phase:

$$\psi(x+\lambda) = \psi(x)\, e^{i\theta}. \tag{13.117}$$

Here $e^{i\theta}$ is essentially the eigenvalue of the operator that effects a translation by one lattice site. Now multiplying through by $e^{-i\kappa(x+\lambda)}$

$$e^{-i\kappa(x+\lambda)}\, \psi(x+\lambda) = e^{-i\kappa x}\, \psi(x)\, e^{-i\kappa\lambda}\, e^{i\theta}, \tag{13.118}$$

and then choosing κ such that $e^{-i(\kappa\lambda-\theta)} = 1$, we have

$$e^{-i\kappa(x+\lambda)}\psi(x+\lambda) = e^{-i\kappa x}\, \psi(x) =: u_\kappa(x), \tag{13.119}$$

where $u_\kappa(x)$ is by definition periodic with period $\lambda = 2\pi/k$. Thus, we can write the eigenfunction as the product of a periodic function and a plane-wave-type factor:

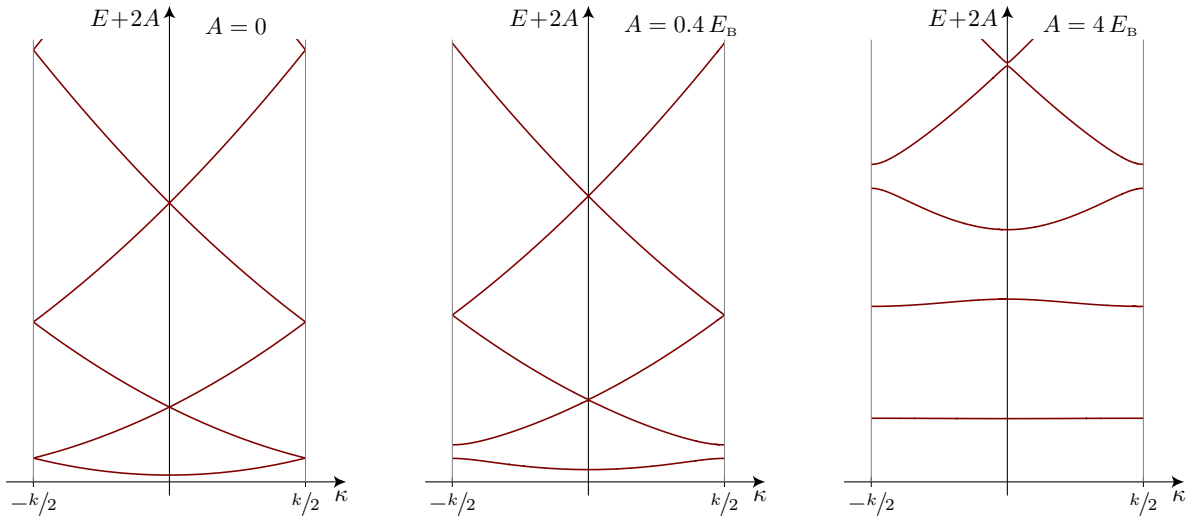
$$\psi_\kappa(x) = e^{i\kappa x} u_\kappa(x). \tag{13.120}$$

(Bloch's theorem)

This decomposition is known as **Bloch's theorem**,[5] and the (conserved) quantum number κ is called the **quasimomentum**, because it is analogous (up to a factor of $\hbar$) to the regular momentum in the form of the phase-modulation factor. In general, the Bloch wave function will not be a momentum eigenstate, but will be a superposition of momenta $\hbar\kappa \pm j\hbar k$ for $j \in \mathbb{Z}$. From the Bloch theorem (13.120), κ is really only defined by its phase $\kappa\lambda = 2\pi\kappa/k$ due to a shift by one spatial period. Thus, values of κ that differ by integer multiples of k are redundant in the sense of this phase shift, although they index different states. It is thus conventional to separate out the integer part by writing $\kappa = \kappa' + nk$, where n is any integer and $\kappa' \in [-k/2, k/2)$. In this case we simply write Bloch's theorem as

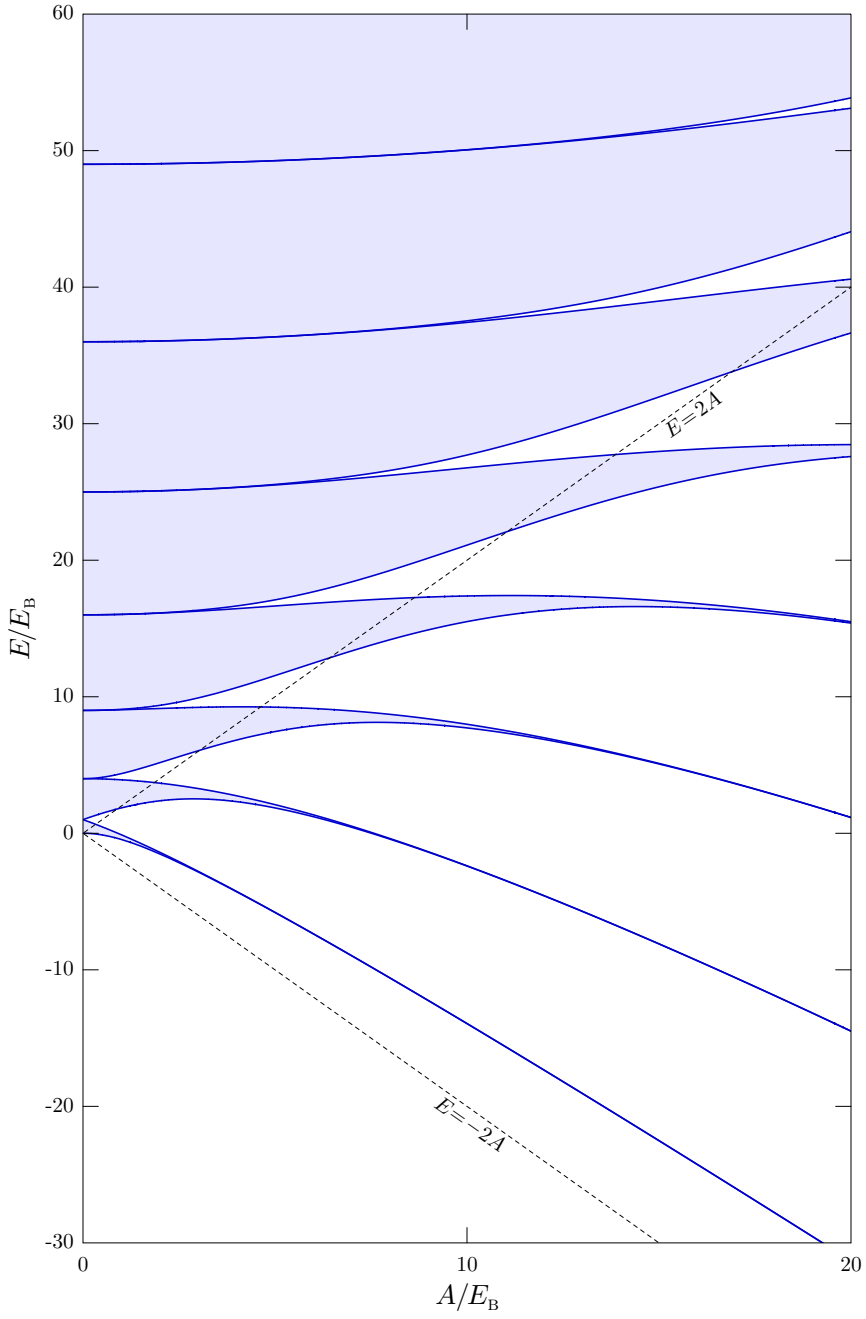
$$\psi_{n,\kappa}(x) = e^{i\kappa x} u_{n,\kappa}(x), \tag{13.121}$$

after dropping the prime on κ. Here n is called the **band index**, and the modulus of n is sufficient to specify the state along with the reduced κ. Now the above band plots are typically plotted in terms of this reduced quasimomentum κ rather than the unperturbed momentum p. The corresponding plots are below, including the unperturbed case for reference on the left, which is just the free-particle parabola folded over onto itself. The states are all shifted so that they are relative to the minimum potential energy of the sinusoidal lattice.



[5] Felix Bloch, "Über die Quantenmechanik der Elektronen in Kristallgittern," *Zeitschrift für Physik* **52**, 555 (1928) (doi: 10.1007/BF0133945).

In these diagrams, the avoided-crossing nature of the band gaps is somewhat more obvious. The (numerically computed exact) eigenenergies are also plotted below as a function of the potential-depth parameter A. At the far left-hand side of the plot, where the perturbative treatment applies, it is possible to see how the band gaps again become rapidly smaller with increasing order (energy). Also, a nice feature is that on the far left, the band gaps are spaced quadratically, in agreement with the parabola/Bragg-scattering argument above. As the potential depth grows, though, the bands become narrow and linearly spaced in energy. The upper and lower limits of the potential lattice are marked in the plot by dashed lines; note that deep in the potential lattice, the states are approximately harmonic-oscillator states, explaining the uniform level spacing and the nearly discrete nature of the eigenenergies (as tunneling between wells is also suppressed by the growing barriers, which is another way to understand the presence of energy bands).



13.3.3 Application: Dynamic Polarizability

Another nice application of time-dependent perturbation theory is in analyzing the polarizability of an atom due to an oscillating electric field (i.e., a monochromatic laser field). This is a generalization of the static polarizability that we considered in Section 12.6.3.2 in the context of time-independent perturbation. The time dependence of the perturbation here makes for a natural fit with time-dependent perturbation theory. However, this same problem can be handled in the time-independent formalism if the problem is set up correctly—this setup is most natural if the field is handled quantum-mechanically, but we will treat the electric field classically here. Also, this problem will serve nicely to illustrate some of the subtleties of the perturbation formalism.

The idea will be to return to the dipole moment $\mathbf{d} = -e\mathbf{r}$ of an atom, and to compute its expectation value in some state $|\,\mathsf{i}\,\rangle$. The mean dipole moment is the expectation value

$$\langle \mathbf{d}(t) \rangle = \langle\, \mathsf{i} \,|\mathbf{d}(t)|\, \mathsf{i} \,\rangle, \tag{13.122}$$

written on the right-hand side in the Heisenberg picture. It is more convenient to work in the interaction picture in order to apply time-dependent perturbation theory, however. Recalling the Heisenberg-picture transformation rule $A_{\text{H}}(t) = U(0,t)A_{\text{S}}U(t,0)$ [Eq. (1.190)], along with the interaction-picture transformation $A_{\text{I}}(t) = U_0(0,t)A_{\text{S}}U_0(t,0)$ [Eq. (13.17)] and the evolution-operator transformation $U_{\text{I}}(t,0) = U_0(0,t)\,U_{\text{S}}(t,0)$ [Eq. (13.21)], we have

$$\begin{aligned} A_{\text{I}}(t) &= U_0(0,t)A_{\text{S}}U_0(t,0) \\ &= U_0(0,t)\big[U(t,0)A_{\text{H}}(t)U(0,t)\big]U_0(t,0) \\ &= U_{\text{I}}(t,0)A_{\text{H}}(t)U_{\text{I}}(0,t). \end{aligned} \tag{13.123}$$

Thus we have the transformation rule

$$A_{\text{H}}(t) = U_{\text{I}}(0,t)A_{\text{I}}(t)U_{\text{I}}(t,0)$$

(Heisenberg–interaction picture transformation) (13.124)

for an operator going from the interaction picture to the Heisenberg picture.

Now working in the interaction representation (and denoting interaction-picture operators again via twiddles), and assuming $\langle\, \mathsf{i} \,|\mathbf{d}|\, \mathsf{i} \,\rangle = 0$ at $t = 0$ (so that $\langle\, \mathsf{i} \,|\tilde{\mathbf{d}}(t)|\, \mathsf{i} \,\rangle = 0$), we have

$$\begin{aligned} \langle \mathbf{d}(t) \rangle &= \langle\, \mathsf{i} \,|\mathbf{d}(t)|\, \mathsf{i} \,\rangle \\ &= \langle\, \mathsf{i} \,|\tilde{U}(0,t)\,\tilde{\mathbf{d}}(t)\,\tilde{U}(t,0)|\, \mathsf{i} \,\rangle \\ &\approx \langle\, \mathsf{i} \,|\tilde{\mathbf{d}}(t)\,\tilde{U}_1(t,0)|\, \mathsf{i} \,\rangle + \langle\, \mathsf{i} \,|\tilde{U}_1(0,t)\,\tilde{\mathbf{d}}(t)|\, \mathsf{i} \,\rangle \\ &= \sum_{k \neq \mathsf{i}} \Big[\langle\, \mathsf{i} \,|\tilde{\mathbf{d}}(t)|k\rangle\langle k|\tilde{U}_1(t,0)|\, \mathsf{i} \,\rangle + \langle\, \mathsf{i} \,|\tilde{U}_1(0,t)|k\rangle\langle k|\tilde{\mathbf{d}}(t)|\, \mathsf{i} \,\rangle \Big] \\ &= \sum_{k \neq \mathsf{i}} \langle\, \mathsf{i} \,|\tilde{\mathbf{d}}(t)|k\rangle \tilde{K}^{(1)}_{k\mathsf{i}}(t) + \text{c.c.}, \end{aligned} \tag{13.125}$$

in terms of the first-order correction $\tilde{U}_1(t,0)$ to the evolution operator, recalling that $\tilde{U}(t,0) \approx 1 + \tilde{U}_1(t,0)$ and $\tilde{K}^{(1)}_{\mathsf{fi}}(t) = \langle\, \mathsf{f} \,|\tilde{U}_1(t,0)|\, \mathsf{i} \,\rangle$. The perturbation operator is the dipole interaction energy

$$V(t) = -\mathbf{d} \cdot \boldsymbol{\mathscr{E}}(t), \tag{13.126}$$

which is justified when the atom can be treated approximately as a point dipole, which means the electric field is approximately constant over the extent of the atom (i.e., the **long-wavelength approximation**, which is in turn justified for optical transitions in atoms, since wavelengths are on the order of μm, while atomic diameters are of order Å). The electric field is

$$\boldsymbol{\mathscr{E}}(t) = \frac{\mathscr{E}_0}{2}\Big(\hat{\varepsilon}\, e^{-i\omega t} + \hat{\varepsilon}^*\, e^{i\omega t}\Big). \tag{13.127}$$

Here, the unit polarization vector must in general be complex, in order to represent, for example, circular polarizations, which are of the form $(\hat{x} \pm i\hat{y})/\sqrt{2}$. Also, we will use the first-order propagator (13.99)

$$\tilde{K}^{(1)}_{\mathsf{fi}}(t) = -\frac{\pi i}{\hbar}\left((V_0)_{\mathsf{fi}}\, e^{i(\omega_{\mathsf{fi}}-\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}-\omega) + (V_0^\dagger)_{\mathsf{fi}}\, e^{i(\omega_{\mathsf{fi}}+\omega)t/2}\,\delta_t(\omega_{\mathsf{fi}}+\omega)\right) \tag{13.128}$$

as appropriate for the form of this interaction potential, with $\mathbf{f}$ replaced by k, and with $V_0 = -\hat{\varepsilon}\cdot\mathbf{d}\,\mathscr{E}_0$. Thus the expected dipole moment becomes

$$\langle \mathbf{d}(t)\rangle = \frac{\pi i}{\hbar}\sum_{k\neq \mathsf{i}}\langle \mathsf{i}\,|\tilde{\mathbf{d}}|k\rangle\left(\hat{\varepsilon}\cdot\mathbf{d}_{k\mathsf{i}}\, e^{i(\omega_{k\mathsf{i}}-\omega)t/2}\,\delta_t(\omega_{k\mathsf{i}}-\omega) + \hat{\varepsilon}^*\cdot\mathbf{d}_{k\mathsf{i}}\, e^{i(\omega_{k\mathsf{i}}+\omega)t/2}\,\delta_t(\omega_{k\mathsf{i}}+\omega)\right)\mathscr{E}_0 + \text{c.c.}, \tag{13.129}$$

again to linear order in perturbation theory.

Now the task at hand will be to put the time dependence in a more useful form. From Eq. (13.77), we can write out

$$e^{iEt/2\hbar}\delta_t(E) = \frac{e^{iEt/2\hbar}}{2\pi\hbar}\int_{-t/2}^{t/2} dt'\, e^{iEt'/\hbar} = \frac{e^{iEt/\hbar}}{2\pi\hbar}\int_{-t}^{0} dt'\, e^{iEt'/\hbar}, \tag{13.130}$$

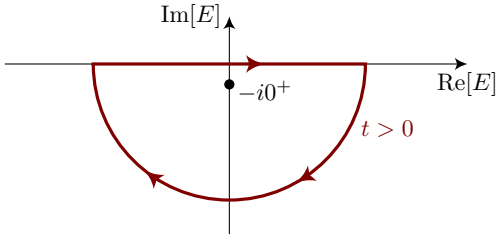
after shifting the range of the integral into the past by replacing $t' \longrightarrow t' + t/2$. Now we will suppose that the field amplitude $\mathscr{E}_0$ was turned on *adiabatically* in the distant past—we would like to focus on the atomic response once it has settled in to the perturbation, ignoring any transients from the field's turn-on. This is consistent with our discussion of the static polarizability [see the discussion leading up to Eq. (12.112)], where we considered the energy due to bringing the electric field adiabatically from zero to obtain the factor of 1/2 in the induced interaction energy. Effectively, this means that in carrying out the integral (13.130), we can ignore the contribution from the limit at $-t$:

$$e^{iEt/2\hbar}\delta_t(E) = \frac{e^{iEt/\hbar}}{2\pi\hbar}\int_{-t}^{0} dt'\, e^{iEt'/\hbar} \approx \frac{e^{iEt/\hbar}}{2\pi i E} \qquad \text{(almost!)}. \tag{13.131}$$

Note that the result here has a simple pole at $E = 0$. Previously we have been careful to specify how to avoid the pole when integrating along the real axis, because this has a huge impact on the behavior of the function (leading to advanced vs. retarded Green functions, for example). Let's try integration with the two usual possibilities of avoiding the pole with a small imaginary swerve, setting up the integral of the right-hand side of Eq. (13.131) in two ways. First, with the pole effectively just below the real axis, we obtain

$$\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\,\frac{e^{-iEt/\hbar}}{E + i0^+} = -\Theta(t), \tag{13.132}$$

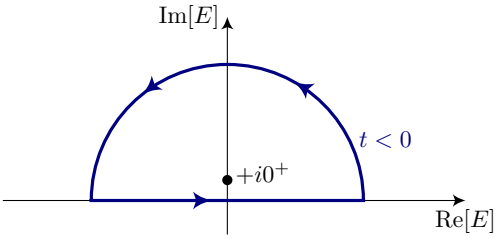
via the contour below for the nonzero case.



The other option is to displace the pole just above the real axis, obtaining the integral

$$\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\,\frac{e^{-iEt/\hbar}}{E - i0^+} = \Theta(-t), \tag{13.133}$$

where the contour for the nonvanishing case is shown below.



Then, in the limit $t \longrightarrow \infty$, Eq. (13.131) has the form of a Fourier transform of $\Theta(-t)$,

$$\int_{-\infty}^{\infty} dt\, \Theta(-t)\, e^{iEt/\hbar} = \frac{\hbar}{i(E - i0^+)}, \tag{13.134}$$

and then Eq. (13.133) can be written

$$\frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dE\, \frac{\hbar}{i(E - i0^+)}\, e^{-iEt/\hbar} = \Theta(-t), \tag{13.135}$$

showing that $\Theta(-t)$ and $\hbar/i(E - i0^+)$ form a Fourier-transform pair [and so you could then also guess that $-\Theta(t)$ forms a Fourier-transform pair with $\hbar/i(E + i0^+)$]. Thus, we should have concluded

$$e^{iEt/2\hbar}\delta_t(E) = \frac{e^{iEt/\hbar}}{2\pi\hbar} \int_{-t}^{0} dt'\, e^{iEt'/\hbar} \approx \frac{e^{iEt/\hbar}}{2\pi i(E - i0^+)} \tag{13.136}$$

in place of the naïve expression (13.131). A quick-and-dirty, formal trick for coming to this same conclusion is that we could have enforced the adiabatic turn-on of the field amplitude $\mathscr{E}$ by adding a small imaginary part to E while carrying out the integration:

$$\frac{1}{\hbar}\, e^{iEt/2\hbar}\delta_t(E/\hbar) = e^{iEt/2\hbar}\delta_t(E) \longrightarrow \frac{e^{i(E-i0^+)t/\hbar}}{2\pi\hbar} \int_{-t}^{0} dt'\, e^{i(E-i0^+)\,t'/\hbar} \approx \frac{e^{i(E-i0^+)t/\hbar}}{2\pi i(E - i0^+)} = \frac{e^{iEt/\hbar}}{2\pi i(E - i0^+)}. \tag{13.137}$$

The sign of the imaginary part makes sure that transients in the distant past are damped away, and the result is the same.

Again, we are working in the limit of large t, to capture the (dynamical) steady-state behavior of the dipole's response to the field. With this expression (13.136) or (13.137) for the time-dependent factors, the expected dipole moment becomes

$$\langle \mathbf{d}(t) \rangle = \frac{\pi i}{\hbar} \sum_{k \neq \mathrm{i}} \langle\, \mathrm{i}\, |\tilde{\mathbf{d}}| k \rangle \left(\hat{\varepsilon} \cdot \mathbf{d}_{k\mathrm{i}}\, \frac{e^{i(\omega_{k\mathrm{i}} - \omega)t}}{2\pi i(\omega_{k\mathrm{i}} - \omega - i0^+)} + \hat{\varepsilon}^* \cdot \mathbf{d}_{k\mathrm{i}}\, \frac{e^{i(\omega_{k\mathrm{i}} + \omega)t}}{2\pi i(\omega_{k\mathrm{i}} + \omega - i0^+)} \right) \mathscr{E}_0 + \text{c.c.} \tag{13.138}$$

Now in the same way as in Eq. (13.74), we can take $\tilde{\mathbf{d}}$ out of the interaction representation via

$$\langle\, \mathrm{i}\, |\tilde{\mathbf{d}}| k \rangle = \langle\, \mathrm{i}\, |\mathbf{d}| k \rangle\, e^{i\omega_{\mathrm{i}k}t} \tag{13.139}$$

to obtain

$$\langle \mathbf{d}(t) \rangle = \frac{1}{2\hbar} \sum_{k \neq \mathrm{i}} \mathbf{d}_{\mathrm{i}k} \left(\hat{\varepsilon} \cdot \mathbf{d}_{k\mathrm{i}}\, \frac{e^{-i\omega t}}{\omega_{k\mathrm{i}} - \omega - i0^+} + \hat{\varepsilon}^* \cdot \mathbf{d}_{k\mathrm{i}}\, \frac{e^{i\omega t}}{\omega_{k\mathrm{i}} + \omega - i0^+} \right) \mathscr{E}_0 + \text{c.c.} \tag{13.140}$$

for the dipole moment.

To compute the energy shift due to the oscillating field, or the **ac Stark shift**, we compute the time-averaged dipole interaction energy, using the electric field (13.127) and the dipole moment (13.140):

$$\begin{aligned} \Delta E &= -\overline{\langle \mathbf{d}(t) \rangle \cdot \boldsymbol{\mathscr{E}}(t)} \\ &= -\frac{1}{4\hbar} \sum_{k \neq \mathrm{i}} \left(\frac{\hat{\varepsilon}^* \cdot \mathbf{d}_{\mathrm{i}k} \mathbf{d}_{k\mathrm{i}} \cdot \hat{\varepsilon}}{\omega_{k\mathrm{i}} - \omega - i0^+} + \frac{\hat{\varepsilon} \cdot \mathbf{d}_{\mathrm{i}k} \mathbf{d}_{k\mathrm{i}} \cdot \hat{\varepsilon}^*}{\omega_{k\mathrm{i}} + \omega - i0^+} + \frac{\hat{\varepsilon}^* \cdot \mathbf{d}_{\mathrm{i}k} \mathbf{d}_{k\mathrm{i}} \cdot \hat{\varepsilon}}{\omega_{k\mathrm{i}} - \omega + i0^+} + \frac{\hat{\varepsilon} \cdot \mathbf{d}_{\mathrm{i}k} \mathbf{d}_{k\mathrm{i}} \cdot \hat{\varepsilon}^*}{\omega_{k\mathrm{i}} + \omega + i0^+} \right) \mathscr{E}_0^{\,2}. \end{aligned} \tag{13.141}$$

The overbar here indicates the time average, which amounts to dropping terms proportional to $e^{\pm 2i\omega t}$. The energy oscillations at the optical frequencies are too fast to detect anyway, so we simply discard them (in the same way we would discard the time dependence of the Poynting vector in computing the intensity of the electromagnetic field). Note that we have also written out explicitly the complex-conjugate terms in the dipole moment (13.140), which appear as the last two terms in Eqs. (13.141).

To neatly hide some of the terms here, we will define the **Cauchy principal value** as

$$\mathscr{P}\left(\frac{1}{x}\right) := \frac{1}{2}\left(\frac{1}{x+i0^+} + \frac{1}{x-i0^+}\right). \tag{13.142}$$

This definition is meant to be sensible in the context of an integral; it means that we handle an integration through a pole on the real axis by averaging the effects of avoiding it just above and just below the real axis. (This definition still holds if the $1/x$ is multiplied by an analytic function.) Applying the principal value to the present case, the last two terms in Eq. (13.141) are the same as the first two, but with $-i0^+$ replaced by $+i0^+$. Thus we may write

$$\Delta E = -\frac{1}{2\hbar}\mathscr{P}\sum_{k\neq \mathsf{i}}\left(\frac{\hat{\varepsilon}^*\cdot\mathbf{d}_{\mathsf{i}k}\mathbf{d}_{k\mathsf{i}}\cdot\hat{\varepsilon}}{\omega_{k\mathsf{i}}-\omega} + \frac{\hat{\varepsilon}\cdot\mathbf{d}_{\mathsf{i}k}\mathbf{d}_{k\mathsf{i}}\cdot\hat{\varepsilon}^*}{\omega_{k\mathsf{i}}+\omega}\right)\mathscr{E}_0{}^2. \tag{13.143}$$

The two terms here have the form of a dipole tensor $\mathbf{D} := \mathbf{d}_{\mathsf{i}k}\otimes\mathbf{d}_{k\mathsf{i}}$ coupling to field polarization tensor $\boldsymbol{\epsilon} := \hat{\varepsilon}\otimes\hat{\varepsilon}^*$; the first term has the form $\mathrm{Tr}[\mathbf{D}\cdot\boldsymbol{\epsilon}]$ while the second has the form $\mathrm{Tr}[\mathbf{D}\cdot\boldsymbol{\epsilon}^*]$. In general, these couplings are not equivalent, but to proceed we will specialize to the case where they are the same: that is, to the case where the polarization tensor is not merely Hermitian, but also real-symmetric. Essentially, this means we are assuming a linear polarization, and not circular or elliptical polarization of the optical field. In this case the ac Stark shift becomes

$$\Delta E = -\frac{1}{\hbar}\mathscr{P}\sum_{k\neq \mathsf{i}}\frac{\omega_{k\mathsf{i}}(\hat{\varepsilon}\cdot\mathbf{d}_{\mathsf{i}k}\mathbf{d}_{k\mathsf{i}}\cdot\hat{\varepsilon})}{\omega_{k\mathsf{i}}^2-\omega^2}\,\mathscr{E}_0{}^2. \tag{13.144}$$

Now we can define an atomic **ac polarizability tensor** $\vec{\alpha}(\omega)$ to give the mean dipole response to a perturbation of the form $e^{-i\omega t}$, with $\vec{\alpha}(-\omega)$ giving the response to the conjugate perturbation $e^{i\omega t}$:

$$\begin{aligned}\langle\mathbf{d}(t)\rangle &= \vec{\alpha}(\omega)\cdot\hat{\varepsilon}\,\frac{\mathscr{E}_0}{2}e^{-i\omega t} + \vec{\alpha}(-\omega)\cdot\hat{\varepsilon}^*\,\frac{\mathscr{E}_0}{2}e^{i\omega t}\\ &= \vec{\alpha}(\omega)\cdot\hat{\varepsilon}\,\frac{\mathscr{E}_0}{2}e^{-i\omega t} + \vec{\alpha}^{\,*}(\omega)\cdot\hat{\varepsilon}^*\,\frac{\mathscr{E}_0}{2}e^{i\omega t}.\end{aligned} \tag{13.145}$$

(ac polarizability definition)

In the second expression we are noting that $\vec{\alpha}(-\omega) = \vec{\alpha}^{\,*}(\omega)$ because the induced dipole is real. Also we are using dyadic notation for the polarizability tensor, which is a fancy way of distinguishing it from a vector while saying that it's a 3×3 matrix (that is, it ''takes a vector on either side,'' which is to say that a contraction with two vectors looks like $\hat{\varepsilon}^*\cdot\vec{\alpha}\cdot\epsilon = \hat{\varepsilon}^*_\mu\alpha_{\mu\nu}\epsilon_\nu$ in tensor–index notation). Now the time-averaged dipole-interaction energy is (where again the overline indicates the time average, which amounts to dropping the $e^{\mp 2i\omega t}$ terms)

$$\Delta E = -\overline{\langle\mathbf{d}(t)\rangle\cdot\boldsymbol{\mathscr{E}}(t)} = -\frac{1}{4}\,\hat{\varepsilon}^*\cdot\vec{\alpha}(\omega)\cdot\hat{\varepsilon}\,\mathscr{E}_0{}^2 - \frac{1}{4}\,\hat{\varepsilon}\cdot\vec{\alpha}^{\,*}(\omega)\cdot\hat{\varepsilon}^*\,\mathscr{E}_0{}^2,$$

(energy in terms of polarizability) (13.146)

where we are being careful to write the shift in terms of the amplitudes ($\mathscr{E}_0/2$) of the positive- and negative-frequency components of the perturbation, so that the results will agree with the dc-Stark analysis. Again, specializing to the case of a real, symmetric polarizability tensor, this reduces to

$$\Delta E = -\frac{1}{2}\,\hat{\varepsilon}\cdot\mathrm{Re}[\vec{\alpha}(\omega)]\cdot\hat{\varepsilon}\,\mathscr{E}_0{}^2, \tag{13.147}$$

(energy in terms of polarizability)

which agrees with the dc limit (12.112), $\Delta E = -\frac{1}{2}\alpha_0 \mathscr{E}^2$, provided we identify α_0 with $\mathrm{Re}[\vec{\alpha}(\omega = 0)]$. The main difference here is that we can allow for anisotropic response to dc fields, which we didn't need in the hydrogen-atom ground state. Then comparison with the energy shift (13.144) gives the (real part of the) polarizability tensor

$$\mathrm{Re}[\vec{\alpha}(\omega)] = \mathscr{P}\sum_{k\neq \mathfrak{i}} \frac{2\omega_{k\mathfrak{i}}(\mathbf{d}_{\mathfrak{i}k} \otimes \mathbf{d}_{k\mathfrak{i}})}{\hbar(\omega_{k\mathfrak{i}}^2 - \omega^2)}, \qquad \text{(polarizability tensor, linear polarization)} \quad (13.148)$$

which appears here as a rank-2 Cartesian tensor. Note that this expression reduces to the correct (scalar) dc result from time-independent perturbation theory, from which Eq. (12.120) had $\alpha_0 = \sum_{k\neq \mathfrak{i}} \frac{2|d_{0k}|^2}{E_{0k}}$. The expression (13.148) is an example of a more general relation for the linear response of a system to a time-dependent perturbation, and is often called a **Kramers–Heisenberg formula**.

13.3.3.1 An Induced Factor of 2

Note that the agreement here between the ac result (13.148) and the corresponding dc result is somewhat remarkable. First, note that we computed the dc result in *second*-order, time-independent perturbation theory, but the results here came from *first*-order, time-dependent perturbation theory. Both ended up being second-order in dipole matrix elements, however, and both have the interpretation of level shifts due to two-step transitions (i.e., two-photon transitions) through all possible intermediate states.

However, another remarkable point is that in the dc Stark case, we had to argue in a factor of $1/2$ due to the induced dipole moment [see the discussion leading up to Eq. (12.112)], but in the corresponding treatment here, in Eqs. (13.143) and (13.146) we explicitly did not include such a factor. Nevertheless, the expressions worked out. Remember that we built in the assumption of an adiabatic turn-on of the perturbation, which resembles the same argument, though this doesn't obviously yield a factor of 2. It also appears that we could attribute the difference in the factor of 2 to the discarded $e^{\mp 2i\omega t}$ terms that in the time average, which would not be discarded in the dc limit. However, we did so consistently in Eqs. (13.143) and (13.146), so any factor of 2 there would cancel in the expression for the polarizability.

The key to this factor of 2 is somewhat more subtle. In the treatment here, Eqs. (13.143) and (13.146) amount to an expectation value of the perturbation operator, and thus the energy shift *due to* the perturbation. That is, here we are explicitly considering the *response to* the perturbation. In the argument in the time-independent case, we were essentially considering a classical dipole interacting with a field, and then we had to work out the proper interaction energy by accounting for the induced nature of the dipole.

A quick calculation will make this distinction more clear. Since we are working to linear order in (time-dependent) perturbation theory, we are linearizing the response of the atom to the perturbation. Thus, we can think of it approximately as a harmonic oscillator, and for these purposes (where we are interested only in the expectation value of the dipole moment, and thus the electron position), a classical calculation suffices. Thus consider a static dipole perturbation to the harmonic-oscillator Hamiltonian:

$$H = H_0 + V = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 + eEx. \quad (13.149)$$

Here, p and x are the canonical coordinates of the electron, and we are assuming a perturbation of the form $-\mathbf{d}\cdot\mathbf{E}$. The (linear-response) potential is a quadratic function of x, and we simply complete the square to find

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 (x - x_0)^2 + \Delta E, \quad (13.150)$$

where the new center of the harmonic potential is

$$x_0 = -\frac{eE}{m\omega_0^2}, \quad (13.151)$$

and the new energy offset is

$$\Delta E = -\frac{1}{2}m\omega_0^2 \left(\frac{eE}{m\omega_0^2}\right)^2 = -\frac{1}{2}\left|eEx_0\right|. \quad (13.152)$$

Noting that the *induced* dipole moment is just $d_{\text{induced}} = -ex_0$, the energy offset is simply given by $-(1/2)d_{\text{induced}}E$. *This* is the origin of the factor of 1/2—it is built into the fact that we are computing a mean response to a perturbation, rather than dealing directly with the perturbation itself..

13.3.3.2 Interpretation of the Poles

Now let's take a closer look at the meaning of the principal value and the avoided poles on the real axis. As an alternative to identifying the real part of the polarizatility tensor from the energy shift, we can return to the definition (13.145), comparing it to the polarization expression (13.140) to find

$$\vec{\vec{\alpha}}(\omega) = \sum_{k\neq \mathrm{i}} \frac{(\mathbf{d}_{\mathrm{i}k} \otimes \mathbf{d}_{k\mathrm{i}})}{\hbar} \left(\frac{1}{\omega_{k\mathrm{i}} - \omega - i0^+} + \frac{1}{\omega_{k\mathrm{i}} + \omega + i0^+} \right). \tag{13.153}$$

As a quick note, if ω is close to some atomic resonance, the second (counter-rotating) term here could be ignored (as well as all of the other nonresonant terms, to be consistent) in the rotating-wave approximation. Now using the identity (Problem 13.11)

$$\frac{1}{x \pm i0^+} = \mathscr{P}\frac{1}{x} \mp i\pi\delta(x), \tag{13.154}$$

we can rewrite the principal-value form of this expression as

$$\vec{\vec{\alpha}}(\omega) = \mathscr{P}\sum_{k\neq \mathrm{i}} \frac{(\mathbf{d}_{\mathrm{i}k} \otimes \mathbf{d}_{k\mathrm{i}})}{\hbar} \left(\frac{1}{\omega_{k\mathrm{i}} - \omega} + \frac{1}{\omega_{k\mathrm{i}} + \omega} \right) + i\sum_{k\neq \mathrm{i}} \frac{\pi(\mathbf{d}_{\mathrm{i}k} \otimes \mathbf{d}_{k\mathrm{i}})}{\hbar} \Big(\delta(\omega - \omega_{k\mathrm{i}}) - \delta(\omega + \omega_{k\mathrm{i}}) \Big).$$

(complex polarizability tensor) (13.155)

Note that the first sum here is manifestly real and equivalent to Eq. (13.148). To understand the imaginary parts, recall how a classical, driven, damped harmonic oscillator works—remember, this is linear order in perturbation theory, so we are making a harmonic approximation, and remember that quantum harmonic oscillators are pretty much classical. We will also consider the atom to be in the ground state for simplicity, so that $\omega_{k\mathrm{i}} > 0$. If an oscillator is driven far below resonance, the oscillator follows the drive with small amplitude; there is no phase shift in the small-frequency limit. Far above resonance, the oscillator lags the drive by 180°, and on resonance, the oscillator lags by only 90°. This is what we see here if we look at the co-rotating ($\omega_{k\mathrm{i}} - \omega$) terms. Far below resonance (small ω), the polarizability is positive, while far above resonance, the polarizability is negative. Right on resonance, the delta function takes over, and there is a 90° phase shift [i.e., a complex phase of $e^{i\pi/2}$, which combines with $e^{-i\omega t}$ to give a phase lag $e^{-i(\omega t - \pi/2)}$]. In the case of the counter-rotating terms ($\omega_{k\mathrm{i}} + \omega$), these correspond to something like a negative driving frequency that is always below the resonance frequency, in which case the contribution from this term is always positive, as in the low-frequency case. In any case, the resonances here are divergent because we started from a Hamiltonian, and we haven't incorporated any damping—a nontrivial task in quantum mechanics.

13.3.3.3 Heuristic Incorporation of Damping

In this sense, the avoidance of the poles on the real axis contains some fingerprints of damping, although damping is not explicitly included anywhere. To see this more clearly, it is useful to see what happens if we heuristically incorporate damping. To do this, consider the time dependence of the amplitude of an energy eigenstate $|n\rangle$, and how we might phenomenologically incorporate damping:

$$\langle n|\psi(t)\rangle = \langle n|\psi(0)\rangle\, e^{-iE_n t/\hbar} = \langle n|\psi(0)\rangle\, e^{-i\omega_n t} \longrightarrow \langle n|\psi(0)\rangle\, e^{-i\omega_n t - \Gamma t/2}. \tag{13.156}$$

In this way, $|\langle n|\psi(t)\rangle|^2 = |\langle n|\psi(t)\rangle|^2\, e^{-\Gamma_n t}$, so that Γ_n is the decay rate of the population of $|n\rangle$ (every state decays in general at its own rate). We can't *really* do this, at least not without something more, because probability is no longer conserved. But casting aside this (important) detail, we can conclude that incorporating damping should be something like a replacement $\omega_n \longrightarrow \omega_n - i\Gamma_n/2$ for excited-state

frequencies. Then suppose that we go back to the expression (13.153) drop the specification for principal-value part, and make this replacement for the excited state, regarding all states $|k\rangle$ to be excited states, with the result:

$$\begin{aligned}\vec{\alpha}(\omega) &= \sum_{k\neq \mathsf{i}} \frac{(\mathbf{d}_{\mathsf{i}k}\otimes\mathbf{d}_{k\mathsf{i}})}{\hbar}\left(\frac{1}{\omega_{k\mathsf{i}}-\omega-i\Gamma/2}+\frac{1}{\omega_{k\mathsf{i}}+\omega+i\Gamma/2}\right)\\ &= \sum_{k\neq \mathsf{i}} \frac{(\mathbf{d}_{\mathsf{i}k}\otimes\mathbf{d}_{k\mathsf{i}})}{\hbar}\left(\frac{2\omega_{k\mathsf{i}}}{(\omega_{k\mathsf{i}}^2+\Gamma^2/4)-\omega^2-i\Gamma\omega}\right)\\ &\approx \sum_{k\neq \mathsf{i}} \frac{2\omega_{k\mathsf{i}}(\mathbf{d}_{\mathsf{i}k}\otimes\mathbf{d}_{k\mathsf{i}})}{\hbar(\omega_{k\mathsf{i}}^2-\omega^2-i\Gamma\omega)}.\end{aligned} \tag{13.157}$$

In the second term, note that the imaginary pole shift has the opposite sign, in agreement with Eq. (13.153). In the last step we then assumed weak damping such that $\Gamma^2 \ll \omega_{k\mathsf{i}}^2$. It's in the last form that we can verify independently that Γ is incorporated correctly, because to lowest order in perturbation theory the atom should be responding like a harmonic oscillator (i.e., classically). A classical, monochromatically driven oscillator has the form

$$\ddot{x}+\gamma\dot{x}+\omega_0^2 x = \frac{F_0 e^{-i\omega t}}{m}, \tag{13.158}$$

and taking the solution to have the form $x(t) = x_0\, e^{-i\omega t}$, the solution is

$$x_0(\omega) = \frac{F_0}{m(\omega_0^2-\omega^2-i\gamma\omega)}, \tag{13.159}$$

which matches the form of the damping in the last polarizability expression above, and adds a bit more plausibility to this procedure. Now in the first form in Eqs. (13.157), we have terms of the form

$$\begin{aligned}\frac{1}{\omega_{k\mathsf{i}}\pm\omega\pm i\Gamma/2} &= \frac{\omega_{k\mathsf{i}}\pm\omega\mp i\Gamma/2}{(\omega_{k\mathsf{i}}\pm\omega)^2+\Gamma^2/4}\\ &= \frac{\omega_{k\mathsf{i}}\pm\omega}{(\omega_{k\mathsf{i}}\pm\omega)^2+\Gamma^2/4} \mp i\pi L(\mp\omega_{k\mathsf{i}},\Gamma;\omega),\end{aligned} \tag{13.160}$$

where we have identified the Lorentzian distribution

$$L(\omega_{k\mathsf{i}},\Gamma;\omega) := \frac{\Gamma/2}{\pi[(\omega_{k\mathsf{i}}-\omega)^2+\Gamma^2/4]}, \tag{13.161}$$

normalized to unit area:

$$\int_{-\infty}^{\infty} d\omega\, L(\omega_{k\mathsf{i}},\Gamma;\omega) = 1. \tag{13.162}$$

Thus, Eq. (13.157) becomes

$$\begin{aligned}\vec{\alpha}(\omega) = \sum_{k\neq \mathsf{i}} \frac{(\mathbf{d}_{\mathsf{i}k}\otimes\mathbf{d}_{k\mathsf{i}})}{\hbar}&\left(\frac{\omega_{k\mathsf{i}}-\omega}{(\omega_{k\mathsf{i}}-\omega)^2+\Gamma^2/4}+\frac{\omega_{k\mathsf{i}}+\omega}{(\omega_{k\mathsf{i}}+\omega)^2+\Gamma^2/4}\right)\\ &+ i\sum_{k\neq \mathsf{i}} \frac{\pi(\mathbf{d}_{\mathsf{i}k}\otimes\mathbf{d}_{k\mathsf{i}})}{\hbar}\Big(L(\omega_{k\mathsf{i}},\Gamma;\omega)-L(-\omega_{k\mathsf{i}},\Gamma;\omega)\Big),\end{aligned} \tag{13.163}$$

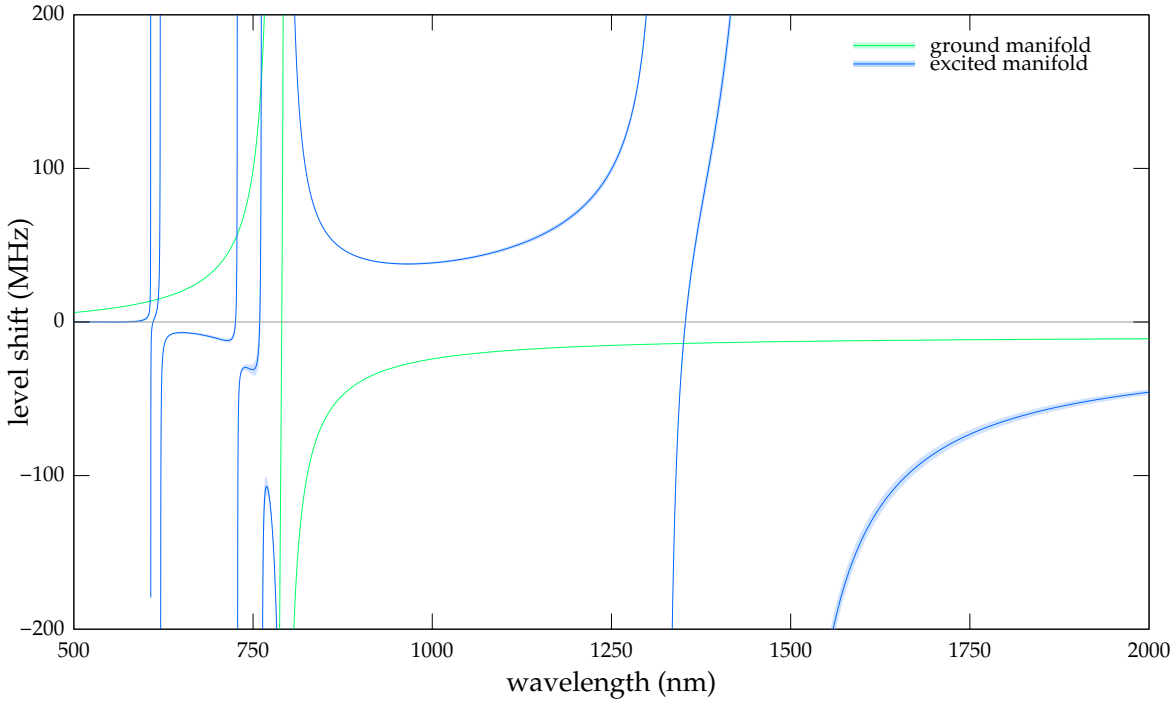
after separating real and imaginary parts. This expression looks like the polarizability in (13.155), in the limit where $\Gamma \longrightarrow 0^+$, where the Lorentzian distributions become delta functions. Here, the principal value is no longer needed for the for the real part of the polarizability, since the pole has been changed to two poles, moved symmetrically away from the real axis.

Now there remains one more detail to address: Remember that in leading up to the polarizability expression (13.148), we assumed a real-symmetric polarization tensor. But how do things work out without

this assumption? The answer requires more analysis in terms of irreducible tensor operators than we have studied so far, so we will just briefly note the results. Because the polarizability tensor (13.148) is real and symmetric, remember that in terms of irreducible tensors it can be decomposed into scalar (rank-0) and rank-2 irreducible components (see the decomposition example in Section 7.4.2.3). The scalar part arises anyway for an isotropic atom, and this means that the Stark shift is orientation-independent: degenerate levels of different m_J or m_F have the same shift. A rank-2 tensor polarizability, on the other hand, will have (weak-field) Stark shifts proportional to m_J^2 or m_F^2, depending on the relevant level structure. If we allow for circular polarization, then the polarization tensor is no longer symmetric, and the polarizability acquires a rank-1 component. The reason that things don't work out simply is that the rank-1 component differs slightly from the form (13.148). It also turns out to give rise to (weak-field) Stark shifts proportional to m_J or m_F, analogous to the Zeeman shift due to a weak magnetic field.

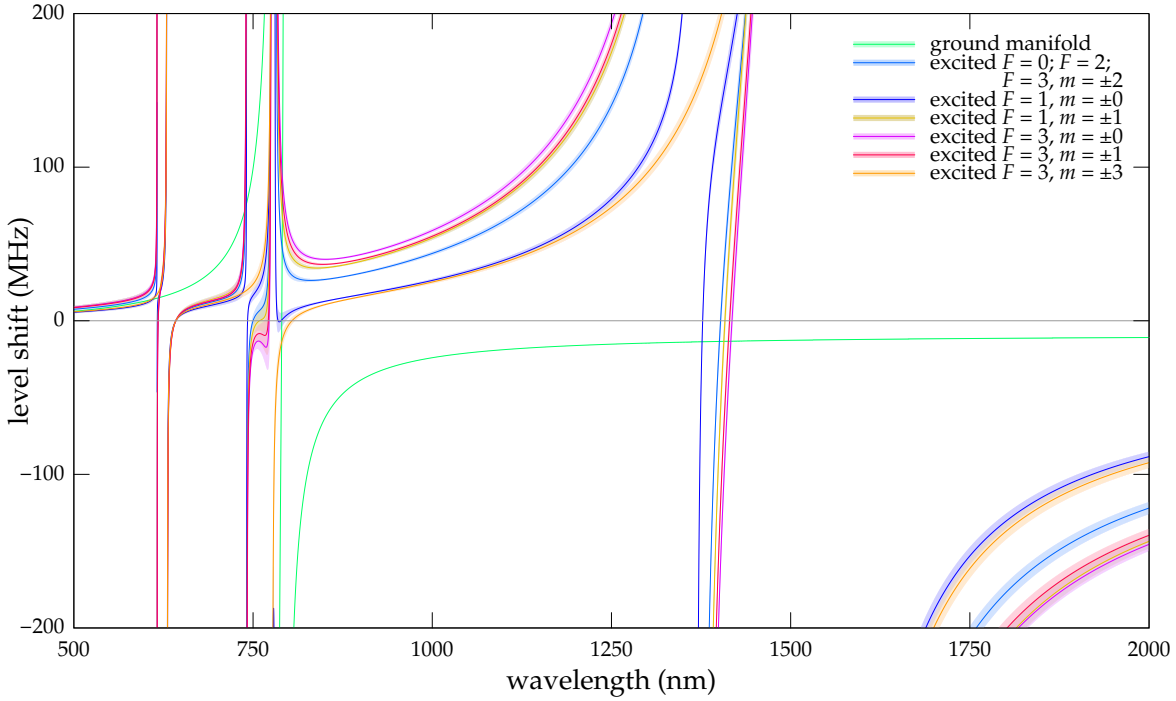
13.3.3.4 Applications

The ac Stark shift (13.147) gives the energy shift of an atomic level in response to a monochromatic electric field, for example a laser field. An example of this calculation is shown below, where the ground and excited states belong to the D_1 transition of ^{87}Rb ($5S_{1/2} \longrightarrow 5P_{1/2}$, 794 nm). The Stark shifts correspond to the center of a 1-W beam with a Gaussian profile of radius $w_0 = 10$ μm, with linear polarization.



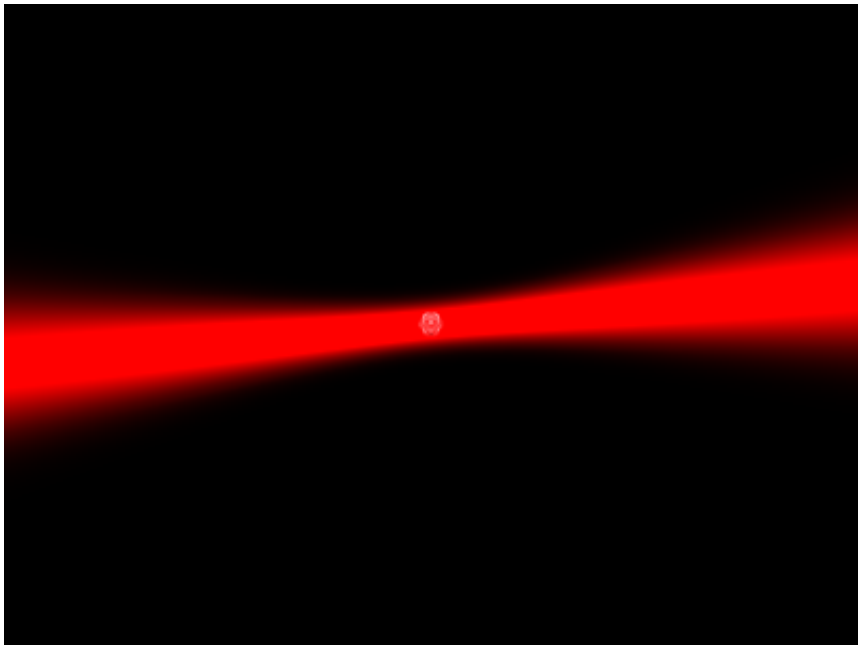
Because the sign of ω_{ki} changes for a state of higher energy than the intermediate state, and because the ground and excited states are coupled to different sets of levels, the shifts can be quite different. Of particular interest here are the crossings of the two levels, which occur at **magic wavelengths** (at 1350 nm, for example, in this plot). Here the transition frequency (energy difference of the two levels) is independent of the laser intensity. This is handy, for example, in atomic clocks based on optical transitions, because a laser can be used to interact with or hold on to an atom without disturbing the transition frequency (which would cause timekeeping errors in an atomic clock).

A similar calculation of Stark shifts of the ground and excited states in the D_2 transition of ^{87}Rb ($5S_{1/2} \longrightarrow 5P_{3/2}$, 780 nm) is shown below for the same driving laser field.



This case is more complicated because of the hyperfine structure of the excited state; the tensor nature of the polarizability is manifest as different shifts for different hyperfine sublevels m_F, but the energy shift only depends on $|m_F|$. The tensor polarizability vanishes for the D_1 excited state because $L = 0$, so there is no electron orientation.

We also discussed before the idea of an **optical tweezer**, where a laser beam may be focused to form a potential well, which can confine an atom, as shown below. The condition is that for an atom in the ground state, the laser frequency should be below any atomic resonance frequencies involving transitions from the ground state, in which case the ac Stark shift will be negative (thus producing a potential well at the focus).



We discussed the idea of optical tweezers before in Section 12.6.3.2, in the approximation of a laser beam by

a dc field, but of course the treatment here is more appropriate if the laser field is not so low in frequency compared to the resonances. Also the formalism here handles shifts of excited states (which are important in analyzing shifts of transition frequencies). This ties in to the above discussion on magic wavelengths. For an atom in an optical tweezer, away from the magic wavelength the atom sees different potential wells in the ground and excited state (or perhaps a potential bump instead of a well). An atom coupled to a laser field also makes effectively random transitions between the states due to spontaneous emission (which we haven't yet discussed). In the case of mismatched potentials this leads to a fluctuating potential well, and thus to heating. At the magic wavelength, the potential wells are matched, and this heating effect is suppressed.

As an example of an optical tweezer in action, the movie below shows $\sim 10^3$ laser-cooled ^{87}Rb atoms confined to an optical tweezer of wavelength around 1090 nm (so not at a magic wavelength). The atoms are loaded to the left of the focus, and once released, oscillate back and forth in the optical potential.

13.4 Exercises

Problem 13.1

Verify that

$$U(t,t_0) = U_0(t,t_0) - \frac{i}{\hbar}\int_{t_0}^{t} dt_1\, U_0(t,t_1)\, V(t_1)\, U(t_1,t_0) \tag{13.164}$$

is a solution to the differential equation

$$\partial_t U(t,t_0) = -\frac{i}{\hbar}\big[H_0 + V(t)\big]U(t,t_0), \tag{13.165}$$

with the proper initial condition, provided that $U_0(t,t_0)$ satisfies

$$\partial_t U_0(t,t_0) = -\frac{i}{\hbar} H_0\, U_0(t,t_0) \tag{13.166}$$

with $U_0(t_0,t_0) = 1$.

Problem 13.2

Differentiate the interaction-picture state (13.16) and operator (13.17),

$$\begin{aligned} |\psi\rangle_{\text{I}} &= U_0(0,t)|\psi\rangle_{\text{S}} = e^{iH_0 t/\hbar}|\psi\rangle_{\text{S}} \\ A_{\text{I}}(t) &= U_0(0,t) A_{\text{S}} U_0(t,0) = e^{iH_0 t/\hbar} A_{\text{S}} e^{-iH_0 t/\hbar}, \end{aligned} \tag{13.167}$$

to derive the equations of motion (13.18) and (13.19),

$$\begin{aligned} \partial_t |\psi\rangle_{\text{I}} &= -\frac{i}{\hbar} V_{\text{I}}(t)|\psi\rangle_{\text{I}} \\ \partial_t A_{\text{I}} &= -\frac{i}{\hbar}\left[A_{\text{I}}, H_0\right]. \end{aligned} \tag{13.168}$$

Problem 13.3

Show that, for a time-independent perturbation operator V, the third-order correction to the transition amplitude is

$$\tilde{K}^{(3)}_{\text{fi}}(t) \approx -2\pi i \sum_{jk} \frac{V_{\text{f}j} V_{jk} V_{k\text{i}}}{(E_{\text{i}} - E_j + i0^+)(E_{\text{i}} - E_k + i0^+)}\, e^{iE_{\text{fi}}t/2\hbar}\, \delta_t(E_{\text{fi}}). \tag{13.169}$$

Problem 13.4

Suppose that an arbitrary state vector (in the interaction picture) is projected into eigenstates $|n\rangle$ of H_0 as

$$|\tilde{\psi}(t)\rangle = \sum_n c_n(t)|n\rangle. \tag{13.170}$$

Time-dependent perturbation theory is often presented in terms of these expansion coefficients. For example, to first order in the perturbation, the coefficients satisfy the coupled differential equations

$$\dot{c}_n(t) \approx -\frac{i}{\hbar}\sum_m V_{nm}(t)\, e^{i\omega_{nm}t}\, c_m(t). \tag{13.171}$$

Show that these equations of motion are implied by the first-order truncation of the Dyson series (13.26)

$$\tilde{U}(t,0) \approx 1 - \frac{i}{\hbar}\int_0^t dt_1\, \tilde{V}(t_1) \tag{13.172}$$

for the interaction-picture evolution operator.

Problem 13.5

Consider the harmonic oscillator

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{13.173}$$

with perturbation potential

$$V(t) = -bx\,\Theta(t), \tag{13.174}$$

turned on suddenly at $t = 0$ and left on statically thereafter. Assume that the state for $t < 0$ is the ground state $|0\rangle$ of H_0.

(a) Describe the exact solution to this problem.

(b) Compute $\tilde{K}_{00}(t)$ (i.e., the amplitude to remain in $|0\rangle$) for $t > 0$. How does your expression reflect your answer from (a)? You can start from the general first-order expression

$$\tilde{K}_{\mathsf{fi}}(t) \approx \langle\, \mathsf{f} \,|\, \mathsf{i} \,\rangle - 2\pi i V_{\mathsf{fi}}\, e^{iE_{\mathsf{fi}}t/2\hbar}\, \delta_t(E_{\mathsf{fi}}) \tag{13.175}$$

for a constant perturbation.

(c) Compute $\tilde{K}_{10}(t)$ (i.e., the amplitude to make a transition to $|1\rangle$) for $t > 0$. How does your expression reflect your answer from (a)?

Problem 13.6

Consider a quantum free particle, $H_0 = p^2/2m$, and suppose that it is kicked by the impulse potential

$$V(t) = -\lambda x \delta(t - 0^+) \tag{13.176}$$

(with an infinitesimal time shift to guarantee the impulse happens just after $t = 0$).

(a) In what sense is it valid to use first-order, time-dependent perturbation theory to analyze the perturbed evolution for small λ? (The issue of course being the divergently large potential at one instant in time.)

(b) Use the first-order truncation of the Dyson series,

$$U(t,0) \approx U_0(t,0) - \frac{i}{\hbar}\int_0^t dt'\, U_0(t,t')\, V(t')\, U_0(t',0), \tag{13.177}$$

to derive an approximate expression for the evolution operator.

(c) Interpret the first-order response in terms of the evolution of the expectations $\langle x\rangle$ and $\langle p\rangle$.

(d) Discuss the unperturbed resolvent operator $G_0(z) := 1/(z - H_0)$, in particular where in the complex plane is it analytic?

Problem 13.7

Recall that, according to first-order, time-dependent perturbation theory, the transition probability between two degenerate levels is $P(t) = \Omega^2 t^2/4$. This is only the short-time behavior, where the full time dependence should have Rabi oscillations of the form $P(t) = \sin^2(\Omega t/2)$.

Using the perturbation-theory results from Section 13.3.1.3 show how resumming the entire perturbation series reproduces the correct time dependence. To get you started:

First, start with the perturbation series in the form (13.73)

$$\begin{aligned}\tilde{K}_{\mathsf{fi}}(t) = \langle\, \mathsf{f} \,|\, \mathsf{i} \,\rangle &- \frac{i}{\hbar}\int_0^t dt_1\, V_{\mathsf{fi}}\, e^{iE_{\mathsf{fi}}t_1/\hbar} - \frac{1}{\hbar^2}\sum_k \int_0^t dt_2 \int_0^{t_2} dt_1\, V_{\mathsf{f}k} V_{k\mathsf{i}}\, e^{iE_{\mathsf{f}k}t_2/\hbar}\, e^{iE_{k\mathsf{i}}t_1/\hbar} \\ &+ \frac{i}{\hbar^3}\sum_{jk}\int_0^t dt_3 \int_0^{t_3} dt_2 \int_0^{t_2} dt_1\, V_{\mathsf{f}j} V_{jk} V_{k\mathsf{i}}\, e^{iE_{\mathsf{f}j}t_3/\hbar}\, e^{iE_{jk}t_2/\hbar}\, e^{iE_{k\mathsf{i}}t_1/\hbar} + \cdots .\end{aligned} \tag{13.178}$$

Assume $\langle\, \mathsf{f} \,|\, \mathsf{i} \,\rangle = 0$, ignore transitions to any other level than $|\, \mathsf{i} \,\rangle$ or $|\, \mathsf{f} \,\rangle$, and assume $V_{\mathsf{ii}} = V_{\mathsf{ff}} = 0$. Eliminate the time-ordering of the integrals and then evaluate them all separately; work out the first three terms, indicate how the series continues, and show that the sum gives you the correct result.

Problem 13.8

Work out the retarded Green function $G^+(E)$ for the free particle

(a) in one (spatial) dimension. Be careful to ensure that your result is a function of $|x - x_0|$.

Note that the setup of the expression in terms of a momentum integral will be the same as in three dimensions, the difference is in the evaluation of the integral.

(b) in two (spatial) dimensions. There is a trick to doing the integral here. Working in polar coordinates, you should get a Bessel function after carrying out the angular integral. But it's not straightforward to see how to proceed with setting up a contour integral along the whole real axis. If you use the integral representation

$$J_0(x) = \frac{2}{\pi}\int_1^\infty du \frac{\sin ux}{\sqrt{u^2-1}}, \qquad (x > 0), \tag{13.179}$$

you should be able to proceed with the momentum integral. To carry out the final integral, use the integral representation of the Hankel function

$$H_0(x) = -\frac{2i}{\pi}\int_1^\infty du \frac{e^{iux}}{\sqrt{u^2-1}}, \qquad (x > 0). \tag{13.180}$$

Problem 13.9

We wrote down the relations

$$G^\pm(E) = \frac{1}{i\hbar}\int_{-\infty}^\infty d\tau\, e^{i[E+(\mathrm{sgn}\tau)i0^+]\tau/\hbar}\, G^\pm(\tau, 0). \tag{13.181}$$

and

$$G^\pm(\tau, 0) = -\frac{1}{2\pi i}\int_{-\infty}^\infty dE\, e^{-iE\tau/\hbar}\, G^\pm(E), \tag{13.182}$$

[see Eqs. (13.39) and (13.43), respectively] as Fourier-transform relations for the Green operator. We derived Eq. (13.181) as an equivalent form of

$$G^\pm(E) = \frac{1}{E - H \pm i0^+} \tag{13.183}$$

for a time-independent Hamiltonian, while we observed that (13.182) was an inversion of the Fourier transform.

(a) Show that Eqs. (13.181) and (13.182) are consistent with the normal Fourier-transform relations

$$\tilde{f}(\omega) = \int_{-\infty}^\infty dt\, f(t)\, e^{i\omega t}, \qquad f(t) = \frac{1}{2\pi}\int_{-\infty}^\infty d\omega\, \tilde{f}(\omega)\, e^{-i\omega t}, \tag{13.184}$$

here in the "ω–t" convention, by changing variables and defining the transform pair $f(t)$ and $\tilde{f}(\omega)$ in terms of the Green operators.

(b) Now evaluate the integral in Eq. (13.182) directly, assuming Eq. (13.183) holds for $G^{\pm}(E)$, to establish Eq. (13.182) independent of Eq. (13.181).

Problem 13.10

We defined the **Cauchy principal value** as

$$\mathscr{P}\left(\frac{1}{x}\right) := \frac{1}{2}\left(\frac{1}{x+i0^+} + \frac{1}{x-i0^+}\right). \tag{13.185}$$

Again, this definition is meant in the context of an integral, so that a troublesome integration through a pole on the real axis is regularized by averaging the effects of avoiding it just above and just below the real axis. An equivalent definition and notation for the principal value is illustrated by the integral relations below.

$$\mathscr{P}\int_{-\infty}^{\infty}\frac{dx}{x} \equiv \fint_{-\infty}^{\infty}\frac{dx}{x} := \lim_{\epsilon\to 0}\left[\int_{\epsilon}^{\infty}\frac{dx}{x} + \int_{-\infty}^{-\epsilon}\frac{dx}{x}\right]. \tag{13.186}$$

Set up the integral contours in the first definition to show that the definitions are equivalent, keeping in mind that they must still hold in the case that the $1/x$ is multiplied by some analytic function $f(x)$.

Problem 13.11

Justify the formula

$$\lim_{\epsilon\to 0^+}\frac{1}{x\pm i\epsilon} = \mathscr{P}\frac{1}{x} \mp i\pi\delta(x) \tag{13.187}$$

by setting up an appropriate contour integral. Here, the "$\mathscr{P}$" denotes the Cauchy principal value, i.e.,

$$\int_{-\infty}^{\infty} dx\, \mathscr{P} f(x) \equiv \mathscr{P}\int_{-\infty}^{\infty} dx\, f(x) \equiv \fint_{-\infty}^{\infty} dx\, f(x). \tag{13.188}$$

Note: the delta function is defined in terms of its action on a test function $f(x)$ under an integral, i.e. $\int dx\, f(x)\,\delta(x) = f(0)$. Show that the formula (13.187) holds in the same sense. Are there restrictions on the test functions $f(x)$ for which this formula is valid?

Problem 13.12

The second-order correction to the propagator for a *constant* perturbation V is from Eq. (13.78):

$$\tilde{K}^{(2)}_{\mathsf{fi}}(t) = -\frac{1}{\hbar^2}\sum_k V_{\mathsf{f}k}V_{k\mathsf{i}}\int_0^t dt_2\int_0^{t_2} dt_1\, e^{iE_{\mathsf{f}k}t_2/\hbar}\, e^{iE_{k\mathsf{i}}t_1/\hbar}. \tag{13.189}$$

(a) Write out the generalization of this expression to the case of a harmonic perturbation of the form

$$V(t) = \frac{1}{2}\Big(V_0 e^{-i\omega t} + V_0^{\dagger} e^{i\omega t}\Big). \tag{13.190}$$

(b) Write down the corresponding generalization of the constant-perturbation expression (13.84)

$$\tilde{K}^{(2)}_{\mathsf{fi}}(t) \approx -2\pi i\sum_k \frac{V_{\mathsf{f}k}V_{k\mathsf{i}}}{E_{\mathsf{i}} - E_k + i0^+}\, e^{iE_{\mathsf{fi}}t/2\hbar}\,\delta_t(E_{\mathsf{fi}}). \tag{13.191}$$

to the case of the harmonic perturbation (13.190). (You need not explicitly perform the integration if you can indicate how to generalize the simpler expression by making replacements.)

(c) Suppose that $E_{\mathsf{f}} \approx E_{\mathsf{i}}$, and that there is an intermediate resonance with a state of higher energy than either E_{f} or E_{i}. Which is the dominant term in your answer from (b)? (That is, what does the rotating-wave approximation look like for this case?)

Chapter 14

Linear-Response Theory

In the previous chapter, we delved into the theory for the time-dependent response of a system to a perturbation. The first-order version of perturbation theory, which is the basis for **linear-response theory**, is something of an art on its own and deserves some deeper exploration. In fact, we have already developed a good chunk of the framework for this formalism when we worked out the ac polarizability for an atom in Section 13.3.3; that calculation is prerequisite for the material here.

14.1 Kubo Formula

To connect linear-response theory to the version of time-dependent perturbation theory that we have already developed, consider an interaction potential of the form

$$V(t) = -\mathbf{x} \cdot \mathbf{F}(t), \tag{14.1}$$

where $\mathbf{F}(t)$ is a (real, classical) time-dependent force function, and $\mathbf{x}$ is the (Hermitian) coupling operator by which $\mathbf{F}(t)$ influences the system.

Starting with the Dyson series (13.26) through the first-order term, we will use the expression

$$\tilde{U}(t,0) \approx 1 - \frac{i}{\hbar}\int_0^t dt_1\, \tilde{V}(t_1) \tag{14.2}$$

for the evolution operator. This will thus be the linear [in $V(t)$] response to a linear (in $\mathbf{x}$) perturbation. Then writing out the evolving expectation value in the interaction picture, we have

$$\langle x_\alpha(t)\rangle = \langle\tilde{\psi}(t)|\tilde{x}_\alpha(t)|\tilde{\psi}(t)\rangle = \langle\psi(0)|\tilde{U}(0,t)\,\tilde{x}_\alpha(t)\,\tilde{U}(t,0)|\psi(0)\rangle, \tag{14.3}$$

where we have used the interaction-picture evolution operator to transform the state back to its initial value, as in Eq. (13.22). Then inserting the evolution operator (14.2) and keeping only first-order terms,

$$\langle x_\alpha(t)\rangle = \langle\tilde{x}_\alpha(t)\rangle + \frac{i}{\hbar}\int_0^t dt' \big\langle[\tilde{x}_\alpha(t),\tilde{x}_\beta(t')]\big\rangle\, F_\beta(t'). \tag{14.4}$$

Note that the expectation values on the right-hand side here are with respect to $|\psi(0)\rangle$, and the first term $\langle\tilde{x}_\alpha(t)\rangle$ represents the natural (average) evolution of the coordinate x_α via the base Hamiltonian H_0. If $|\psi\rangle$ is an eigenstate of H_0, then $\langle\tilde{x}_\alpha(t)\rangle$ is static in time, but if $|\psi\rangle$ is a superposition of eigenstates, then the expectation value will still carry some of the natural time dependence of the unperturbed system.

The commutator expectation value $\langle[\tilde{x}_\alpha(t),\tilde{x}_\beta(t')]\rangle$ represents the system response at time t due to the perturbing force at time t'; this only depends on the time difference $t-t'$ because the base system evolves according to a (time-independent) base Hamiltonian H_0, and thus the response should be homogeneous in time. Now if we define a response function

$$g_{\alpha\beta}(\tau) := \frac{i}{\hbar}\big\langle[\tilde{x}_\alpha(\tau),\tilde{x}_\beta(0)]\big\rangle\,\Theta(\tau), \tag{14.5}$$

(linear-response Green function)

we can use this in Eq. (14.4) to obtain

$$\delta\langle x_\alpha(t)\rangle = \int_0^\infty dt'\, g_{\alpha\beta}(t-t')\, F_\beta(t'), \tag{14.6}$$

where $\delta\langle x_\alpha(t)\rangle := \langle x_\alpha(t)\rangle - \langle \tilde{x}_\alpha(t)\rangle$ represents the modified evolution of $\langle x_\alpha\rangle$ due to the perturbation. We can then extend the arbitrary starting time $t = 0$ into the distant past,

$$\delta\langle x_\alpha(t)\rangle = \int_{-\infty}^\infty dt'\, g_{\alpha\beta}(t-t')\, F_\beta(t'), \tag{14.7}$$

then let $t' \longrightarrow -t'$ and then $t' \longrightarrow t' - t$ to obtain

$$\delta\langle x_\alpha(t)\rangle = \int_{-\infty}^\infty dt'\, g_{\alpha\beta}(t')\, F_\beta(t-t'), \tag{14.8}$$

The response function $g_{\alpha\beta}(\tau)$ is a Green function, though not in the sense of $(z-H)^{-1}$. If the forcing function is an impulse (set up to be definitely within the window of integration),

$$\mathbf{F}(t) = \hat{x}_\gamma\, \delta(t + 0^+), \tag{14.9}$$

then the response is, by definition, the Green function:

$$\delta\langle x_\alpha(t)\rangle = \int_0^\infty dt'\, g_{\alpha\gamma}(t')\, \delta(t + 0^+ - t') = g_{\alpha\gamma}(t). \tag{14.10}$$

Equation (14.8) then expresses that since $F_\beta(t)$ can be regarded as a superposition of delayed delta functions, the general solution is an equivalently weighted superposition of delayed Green functions. The Green-function (14.5) is defined as a correlation function of coupling operators; this definition is called the **Kubo formula**.[1] The Heaviside function in the definition of the Green function is redundant given the integration limits of the response expression (14.10). However, it emphasizes that the Green function is **causal** [i.e., the system at time t only responds to the force $\mathbf{F}(t')$ if $t' < t$].

14.1.1 Generalized Susceptibility

Since the perturbation response (14.8) has the form of a convolution, we can define Fourier transforms of the involved quantities,

$$\begin{aligned}
\chi_{\alpha\beta}(\omega) &= \int_0^\infty d\tau\, g_{\alpha\beta}(\tau)\, e^{i\omega\tau} = \int_{-\infty}^\infty d\tau\, g_{\alpha\beta}(\tau)\, e^{i\omega\tau} \\
\delta\langle x_\alpha(\omega)\rangle &= \int_{-\infty}^\infty dt\, \delta\langle x_\alpha(t)\rangle\, e^{i\omega t} \\
F_\alpha(\omega) &= \int_{-\infty}^\infty dt\, F_\alpha(t)\, e^{i\omega t},
\end{aligned} \tag{14.11}$$

so that the convolution theorem says that in the frequency domain, the perturbation response (14.8) becomes

$$\delta\langle x_\alpha(\omega)\rangle = \chi_{\alpha\beta}(\omega)\, F_\beta(\omega). \tag{14.12}$$

For the convolution theorem see Problem 2.5, but note that to convert Eq. (2.207) to the ω–t convention, all three quantities $\phi_{\rm C}(p)$, $\tilde{K}(p)$, and $\phi(p)$ should be scaled by $1/\sqrt{2\pi\hbar}$. Putting Eq. (14.5) into the first of Eqs. (14.11) leads to the important expression

$$\chi_{\alpha\beta}(\omega) = \frac{i}{\hbar}\int_0^\infty d\tau\, \big\langle [\tilde{x}_\alpha(\tau), \tilde{x}_\beta(0)]\big\rangle\, e^{i\omega\tau}. \tag{14.13}$$

(generalized susceptibility)

[1] Ryogo Kubo and Kazuhisa Tomita, "A General Theory of Magnetic Resonance Absorption," *Journal of the Physical Society of Japan* **8**, 888 (1954); R. B. Stinchcombe, "Kubo and Zubarev Formulations of Response Theory," in *Correlation Functions and Quasiparticle Interactions in Condensed Matter*, J. Woods Halley, Ed. (Plenum, 1978), p. 3; A. D. McLachlan, "Retarded dispersion forces between molecules," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences* **271**, 387 (1963).

This function $\chi_{\alpha\beta}(\omega)$ is called a **generalized susceptibility**, giving the frequency-dependent linear response of the system to an external perturbation.

In fact, in the analysis of the ac polarizability in Section 13.3.3, we have already worked out a generalized susceptibility. The dipole-interaction potential $V(t) = -\mathbf{d}\cdot\boldsymbol{\mathscr{E}}(t)$ in (13.126) is in the form of the linear-response interaction potential (14.1), where the dipole operator plays the role of the generalized coordinate operator $\mathbf{x}$, and the electric field plays the role of the generalized force $\mathbf{F}(t)$. Thus, for example, we can translate the Kramers–Heisenberg formula (13.148) to the present notation as[2]

$$\mathrm{Re}[\chi_{\alpha\beta}(\omega)] = \mathscr{P}\sum_{k\neq \mathrm{i}} \frac{2\omega_{k\mathrm{i}}(\mathbf{x}_{\mathrm{i}k})_\alpha(\mathbf{x}_{k\mathrm{i}})_\beta}{\hbar(\omega_{k\mathrm{i}}^2-\omega^2)},$$

(generalized Kramers–Heisenberg formula) (14.14)

and we can correspondingly read off the imaginary part of Eq. (13.155) to obtain

$$\mathrm{Im}[\chi_{\alpha\beta}(\omega)] = \sum_{k\neq \mathrm{i}} \frac{\pi(\mathbf{x}_{\mathrm{i}k})_\alpha(\mathbf{x}_{k\mathrm{i}})_\beta}{\hbar}\Big(\delta(\omega-\omega_{k\mathrm{i}}) - \delta(\omega+\omega_{k\mathrm{i}})\Big)$$

(generalized Kramers–Heisenberg formula) (14.15)

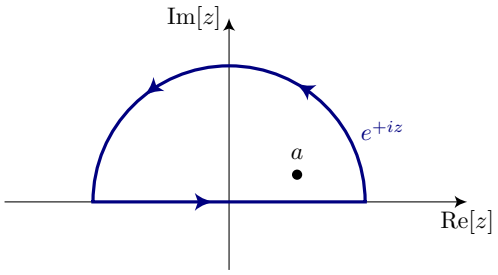
for the imaginary part of the generalized susceptibility.

14.2 Causal Response Functions

Part of the power of the generalized susceptibility is that, via its properties as an analytic function, we can make some fairly strong, general statements about it. In particular, we will use the fact that the susceptibility corresponds to a *causal* response function, as in Eqs. (14.5) and (14.8). To proceed, we will start with the Cauchy integral formula once again, applied to the generalized susceptibility tensor, with a a point in the upper half plane, and completing the integral around the upper half plane:

$$\vec{\chi}(a) = \frac{1}{2\pi i}\oint dz\,\frac{\vec{\chi}(z)}{z-a}. \tag{14.16}$$

The integration contour is illustrated below.



From the Fourier-transform definition of the susceptibility from Eqs. (14.11),

$$\chi_{\alpha\beta}(\omega) = \int_0^\infty d\tau\, g_{\alpha\beta}(\tau)\, e^{i\omega\tau}, \tag{14.17}$$

it is apparent [under the assumption of bounded $\vec{g}(\tau)$] that $\vec{\chi}(\omega)$ is bounded in the upper half plane, since here the integral is strictly convergent. Thus we don't have to worry about any other poles in the contour integral. In fact, the integral definition (14.17) implies that the generalized susceptibility is analytic in the

[2]To make the argument more explicit: Eq. (14.12) is analogous to Eqs. (13.145). However, the form there is more complicated because we assumed time dependence of the form $e^{-i\omega t}$ here but $\cos\omega t$ there, so both positive- and negative-frequency components are present there. Otherwise this analogy justifies the translations $d_\mu \longrightarrow x_\alpha$, $\alpha_{\mu\nu} \longrightarrow \chi_{\alpha\beta}$, and $\varepsilon_\nu\mathscr{E}_0/2 \longrightarrow F_\beta$.

upper half plane. The integral diverges in the lower half plane, so the susceptibility there must be defined via analytic continuation, and there may be poles there.

Now let's subtract the dc component $\vec{\chi}_0 = \vec{\chi}(0)$, replace z by the frequency ω, and take the limit where the pole moves to the real axis, $a \longrightarrow \omega + i0^+$:

$$\vec{\chi}(\omega) - \vec{\chi}_0 = \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \, \frac{\vec{\chi}(\omega') - \vec{\chi}_0}{\omega' - \omega - i0^+}. \tag{14.18}$$

In taking the radius of the semicircle to infinity, we have dropped its contribution and kept only the part of the contour along the real axis. Again using the identity

$$\frac{1}{x \pm i0^+} = \mathscr{P} \frac{1}{x} \mp i\pi\delta(x), \tag{14.19}$$

Eq. (14.18) becomes

$$\begin{aligned} \vec{\chi}(\omega) - \vec{\chi}_0 &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \, \frac{\vec{\chi}(\omega') - \vec{\chi}_0}{\omega' - \omega} + \frac{1}{2} \int_{-\infty}^{\infty} d\omega' \big[\vec{\chi}(\omega') - \vec{\chi}_0\big] \delta(\omega' - \omega) \\ &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \, \frac{\vec{\chi}(\omega') - \vec{\chi}_0}{\omega' - \omega} + \frac{\vec{\chi}(\omega) - \vec{\chi}_0}{2}, \end{aligned} \tag{14.20}$$

so that

$$\vec{\chi}(\omega) - \vec{\chi}_0 = \frac{1}{\pi i} \int_{-\infty}^{\infty} d\omega' \, \frac{\vec{\chi}(\omega') - \vec{\chi}_0}{\omega' - \omega}. \tag{14.21}$$

Now splitting up the real and imaginary parts of this relation, we find the relations

$$\begin{aligned} \mathrm{Re}[\vec{\chi}(\omega) - \vec{\chi}_0] &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{Im}[\vec{\chi}(\omega') - \vec{\chi}_0]}{\omega' - \omega} \, d\omega' \\ \mathrm{Im}[\vec{\chi}(\omega) - \vec{\chi}_0] &= -\frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{Re}[\vec{\chi}(\omega') - \vec{\chi}_0]}{\omega' - \omega} \, d\omega'. \end{aligned} \tag{14.22}$$

(Kramers–Kronig relations)

These are the celebrated **Kramers–Kronig relations**, which relate the real and imaginary parts of $\vec{\chi}(\omega) - \vec{\chi}_0$. These relations can be written more compactly in terms of the **Hilbert transform**, defined as

$$\mathscr{H}[f(x)] := \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{f(x')}{x' - x} \, dx', \tag{14.23}$$

so that

$$\vec{\chi}(\omega) - \vec{\chi}_0 = -i\mathscr{H}\big[\vec{\chi}(\omega) - \vec{\chi}_0\big], \tag{14.24}$$

or separated into real and imaginary parts,

$$\begin{aligned} \mathrm{Re}\,[\vec{\chi}(\omega) - \vec{\chi}_0] &= \mathscr{H}\Big[\mathrm{Im}\,[\vec{\chi}(\omega) - \vec{\chi}_0]\Big] \\ \mathrm{Im}\,[\vec{\chi}(\omega) - \vec{\chi}_0] &= -\mathscr{H}\Big[\mathrm{Re}\,[\vec{\chi}(\omega) - \vec{\chi}_0]\Big]. \end{aligned} \tag{14.25}$$

Note that we *said* that we were deriving the Kramers–Kronig relations based on the assumption that $\vec{\chi}(\omega) - \vec{\chi}_0$ represents a causal response of the system to an input stimulus, to linear order. *Any* causal response function must satisfy the same relations.

But where exactly did this causality come into play? In fact, we glossed right over it, in discarding the contribution from the semicircular part of the integration contour. So far, we've knocked out a number of contour integrals with similar contours, where we've been able to discard the semicircular part because it was suppressed by an exponential factor. But here we're missing that—this is a nice example of a case where you really have to handle this ''undesirable'' part carefully. To investigate this more closely, suppose

that we return to the definition of the susceptibility in terms of the correlation function in Eqs. (14.17). If we integrate this relation by parts, we obtain the series

$$\begin{aligned}\vec{\chi}(\omega) &= \int_0^\infty d\tau\, \vec{g}(\tau)\, e^{i\omega\tau} \\ &= \frac{i\vec{g}(0^+)}{\omega} - \frac{\vec{g}'(0^+)}{\omega^2} - \frac{i\vec{g}''(0^+)}{\omega^3} + \cdots .\end{aligned} \tag{14.26}$$

The arguments are 0^+ because the integral extends over $t \geq 0$, and we are assuming that the correlation tensor decays with τ such that we can ignore the upper boundary terms. Now if we assume that $\vec{g}(t)$ is continuous, then

$$\vec{g}(0^+) = \vec{g}(0^-) = 0, \tag{14.27}$$

so that the first term in the asymptotic expansion vanishes. The continuity requirement is physically reasonable because $\vec{g}(t)$ represents a temporal response of the base system to the perturbation, which involves the displacement of some mass. This cannot happen instantaneously in response to a sudden perturbation. Note that this also explains why we need to consider $\vec{\chi}(\omega) - \vec{\chi}_0$ rather than $\vec{\chi}(\omega)$—any dc component in the susceptibility leads to a delta function in the Green function at $t = 0^+$, so that the continuity argument breaks down. Thus, we have the asymptotic behavior

$$\begin{aligned}\mathrm{Re}[\vec{\chi}(\omega) - \vec{\chi}_0] &= O(\omega^{-2}) \\ \mathrm{Im}[\vec{\chi}(\omega) - \vec{\chi}_0] &= O(\omega^{-3}).\end{aligned} \tag{14.28}$$

It is evident as the semicircle is taken out to infinity, its contribution to the contour integral vanishes.

From the Kramers–Kronig relations, some features of the susceptibility are immediately apparent. First, notice that the Hilbert transform acts ''something like'' a derivative. To see this, note that the Hilbert transform of a constant vanishes:

$$\mathscr{H}[c] = \frac{c}{\pi} \int_{-\infty}^{\infty} \frac{dx'}{x' - x} = 0. \tag{14.29}$$

This is because the convolution kernel $1/(x' - x)$ is antisymmetric about x, and even though the integrand is singular the contributions to the integral on either side of x cancel. This is precisely how the Cauchy principle value avoids problems with the singular integrand. However, as soon as the function has a slope, the antisymmetry of the kernel ''picks it out,'' because it upsets the cancellation in the above integral. In terms of the Kramers–Kronig relations, this implies that any variation in the real part of $\vec{\chi}$ implies a nonzero imaginary part, and vice versa. Since the real part of the polarizability tensor reflected an energy shift (or ''dispersion,'' in optical terminology), and the imaginary part reflected absorptive behavior, we can rephrase this statement as: *The existence of dispersion implies the existence of absorption* (though possibly at some *other* frequency). This is quite a general result, and it was due to the causal nature of the temporal response function $\vec{g}(t) = \vec{g}(t)\,\Theta(t)$, which implied that $\vec{\chi}(\omega)$ is analytic in the upper half-plane (and decaying sufficiently in the imaginary direction), which allowed us to do the whole contour-integral calculation. Of course, these conclusions apply to *any* causal, dispersive response function.

The other obvious implication of the Kramers–Kronig relations is that for the integrals in Eqs. (14.22) to converge, the integrands must vanish at large frequencies, so that $\vec{\chi}(\omega) \longrightarrow \vec{\chi}_0$ as $\omega \longrightarrow \infty$. Physically, this means that the base system becomes immune to perturbations at very large frequencies. This is reasonable for any system that has any kind of associated mass. But we see here that this property is also implied by causality.

Note that in the above derivation, we ignored any possible pole at $\omega = 0$. There are important cases where there is a dc divergence in the response function, such as for the refractive index of a conductive material. In cases like these the Kramers–Kronig relations as derived here must be adapted to handle this extra pole.

It's worth reiterating that no damping has been included, but the Kramers–Kronig relations point to the necessity of damping when a quantum system interacts with an external force. This works essentially because the assumption of causality is sufficient to break time-reversal symmetry and thus admit the existence

of damping. We already saw this in the calculation of the atomic polarization, in the assumption of the adiabatic turn-on of the interaction in the distant past [see the discussion leading up to Eq. (13.137)]. We will develop the damping aspect of the susceptibility further in the next section.

14.3 Fluctuation–Dissipation Theorem

Note that if we identify $\lambda = it/\hbar$, then $e^{-\lambda H_0}$ has the form of an evolution operator $e^{-iH_0 t/\hbar}$. Furthermore, if

$$\rho_0 = \frac{e^{-\beta H_0}}{Z}, \tag{14.30}$$

where $\beta = 1/k_{\text{B}}T$, and

$$Z = \text{Tr}\big[e^{-\beta H_0}\big] = \sum_j e^{-\beta E_j} \tag{14.31}$$

is the (canonical) partition function (i.e., this gives the Boltzmann distribution for incoherent occupation of the energy eigenstates), then ρ_0 is the equilibrium density operator for a system at temperature T; this density operator also has the form (ignoring the Z) of a propagator with a similar identification of β as an imaginary time (in fact, the "endpoint" of imaginary time). This "imaginary time" identification is a useful way to carry out statistical mechanics. As an illustration, first consider the following identity for an arbitrary operator A:

$$\begin{aligned}
\partial_\lambda\Big(e^{\lambda H_0}[A, e^{-\lambda H_0}]\Big) &= \partial_\lambda\Big(e^{\lambda H_0} A e^{-\lambda H_0} - A\Big) \\
&= H_0 e^{\lambda H_0} A e^{-\lambda H_0} - e^{\lambda H_0} A e^{-\lambda H_0} H_0 \\
&= H_0 \tilde{A}(-i\hbar\lambda) - \tilde{A}(-i\hbar\lambda) H_0 \\
&= [H_0, \tilde{A}(-i\hbar\lambda)] \\
&= -i\hbar \dot{\tilde{A}}(-i\hbar\lambda).
\end{aligned} \tag{14.32}$$

Here we used the equation of motion (13.18)

$$\partial_t \tilde{A} = -\frac{i}{\hbar}\big[\tilde{A}, H_0\big], \tag{14.33}$$

for the operator in the interaction picture, with $t \longrightarrow -i\hbar\lambda$. The dot here is as usual a derivative with respect to the argument (here, $-i\hbar\lambda$). Now integrating over λ from 0 to $\beta = 1/k_{\text{B}}T$,

$$e^{\beta H_0}[A, e^{-\beta H_0}] = -i\hbar \int_0^\beta d\lambda\, \dot{\tilde{A}}(-i\hbar\lambda), \tag{14.34}$$

and then we can multiply through by $\rho_0 = e^{-\beta H_0}/Z$ to obtain

$$[A, \rho_0] = -i\hbar\rho_0 \int_0^\beta d\lambda\, \dot{\tilde{A}}(-i\hbar\lambda). \tag{14.35}$$

Now let's return to the generalized susceptibility from Eq. (14.13); the expectation value can be averaged over an ensemble, and thus it is still valid to write it out in terms of a density operator (namely, the unperturbed density operator in a thermal state):

$$\chi_{\mu\nu}(\omega) = \frac{i}{\hbar}\int_0^\infty d\tau\, \text{Tr}\Big\{[\tilde{x}_\mu(\tau), \tilde{x}_\nu(0)]\,\rho_0\Big\}\, e^{i\omega\tau} = \frac{i}{\hbar}\text{Tr}\int_0^\infty d\tau\, \tilde{x}_\mu(\tau)\,[x_\nu, \rho_0]\, e^{i\omega\tau}. \tag{14.36}$$

Recall that at $t = 0$, there is no difference between the operator in the Schrödinger and interaction pictures, so that $\tilde{x}_\nu(0) = x_\nu$. Now with expression (14.35) for the last commutator, we have

$$\chi_{\mu\nu}(\omega) = \mathrm{Tr} \int_0^\infty d\tau\, \tilde{x}_\mu(\tau)\, \rho_0 \int_0^\beta d\lambda\, \dot{\tilde{x}}_\nu(-i\hbar\lambda)\, e^{i\omega\tau}. \tag{14.37}$$

In a stationary unperturbed state, the unperturbed evolution operator commutes with the density operator, so that for example

$$\begin{aligned}
\big\langle \tilde{x}(t_1)\, \tilde{y}(t_2) \big\rangle &= \mathrm{Tr}\big[\tilde{x}(t_1)\, \tilde{y}(t_2)\, \rho_0\big] \\
&= \mathrm{Tr}\big[\tilde{x}(t_1)\, e^{iH_0 t_2/\hbar}\, y\, e^{-iH_0 t_2/\hbar}\, \rho_0\big] \\
&= \mathrm{Tr}\big[e^{-iH_0 t_2/\hbar}\, \tilde{x}(t_1)\, e^{iH_0 t_2/\hbar}\, y\, \rho_0\big] \\
&= \mathrm{Tr}\big[\tilde{x}(t_1 - t_2)\, \tilde{y}(0)\, \rho_0\big] \\
&= \big\langle \tilde{x}(t_1 - t_2)\, \tilde{y}(0) \big\rangle.
\end{aligned} \tag{14.38}$$

This is a more formal way of stating that for a system in a stationary state, two-time correlation functions only depend on the difference of the times [as in the discussion leading up to Eq. (14.5)]. Thus we can proceed by shifting the imaginary-time component:

$$\begin{aligned}
\chi_{\mu\nu}(\omega) &= \mathrm{Tr} \int_0^\infty d\tau \int_0^\beta d\lambda\, \rho_0\, \dot{\tilde{x}}_\nu(-\tau - i\hbar\lambda)\, \tilde{x}_\mu(0)\, e^{i\omega\tau} \\
&= i\omega \mathrm{Tr} \int_0^\infty d\tau \int_0^\beta d\lambda\, \rho_0\, \tilde{x}_\nu(-\tau - i\hbar\lambda)\, \tilde{x}_\mu(0)\, e^{i\omega\tau} \\
&= i\omega \mathrm{Tr} \int_0^\beta d\lambda \int_{i\hbar\lambda}^{\infty + i\hbar\lambda} d\tau\, \rho_0\, \tilde{x}_\nu(-\tau)\, \tilde{x}_\mu(0)\, e^{i\omega(\tau - i\hbar\lambda)} \\
&= i\omega \mathrm{Tr} \int_0^\beta d\lambda\, e^{\hbar\omega\lambda} \int_{i\hbar\lambda}^{\infty + i\hbar\lambda} d\tau\, \rho_0\, \tilde{x}_\nu(-\tau)\, \tilde{x}_\mu(0)\, e^{i\omega\tau}.
\end{aligned} \tag{14.39}$$

The step of replacing the time derivative by $-i\omega$ is an integration by parts with respect to τ (remember the minus sign in the argument of $\tilde{x}_\nu$), and we are unceremoniously dropping the boundary term at $\tau = 0$ due to continuity of the correlation function as in Eq. (14.27), while the boundary term at ∞ vanishes due to assumed decay of the correlation function. Now writing the trace as an expectation value and subtracting the Hermitian conjugate of the susceptibility tensor,

$$\begin{aligned}
\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega) &= i\omega \int_0^\beta d\lambda\, e^{\hbar\omega\lambda} \int_{i\hbar\lambda}^{\infty + i\hbar\lambda} d\tau \,\big\langle \tilde{x}_\nu(-\tau)\, \tilde{x}_\mu(0) \big\rangle\, e^{i\omega\tau} \\
&\qquad + i\omega \int_0^\beta d\lambda\, e^{\hbar\omega\lambda} \int_{-i\hbar\lambda}^{\infty - i\hbar\lambda} d\tau \,\big\langle \tilde{x}_\nu(\tau)\, \tilde{x}_\mu(0) \big\rangle\, e^{-i\omega\tau} \\
&= i\omega \int_0^\beta d\lambda\, e^{\hbar\omega\lambda} \int_{-\infty + i\hbar\lambda}^{\infty + i\hbar\lambda} d\tau \,\big\langle \tilde{x}_\nu(-\tau)\, \tilde{x}_\mu(0) \big\rangle\, e^{i\omega\tau},
\end{aligned} \tag{14.40}$$

noting that the conjugate of a correlation function reverses the order of the operators. Now assuming that the correlation function is analytic in the upper half plane, we can shift the integration back to the real line, and then carry out the imaginary-time integral:

$$\begin{aligned}
\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega) &= i\omega \int_0^\beta d\lambda\, e^{\hbar\omega\lambda} \int_{-\infty}^{\infty} d\tau \,\big\langle \tilde{x}_\nu(0)\, \tilde{x}_\mu(\tau) \big\rangle\, e^{i\omega\tau} \\
&= \frac{i}{\hbar}\Big(e^{\beta\hbar\omega} - 1\Big) \int_{-\infty}^{\infty} d\tau \,\big\langle \tilde{x}_\nu(0)\, \tilde{x}_\mu(\tau) \big\rangle\, e^{i\omega\tau}.
\end{aligned} \tag{14.41}$$

Collecting the frequency-dependent parts on the left-hand side, we have

$$\frac{\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega)}{e^{\beta\hbar\omega} - 1} = \frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau \left\langle \tilde{x}_\nu(0)\, \tilde{x}_\mu(\tau)\right\rangle e^{i\omega\tau}. \tag{14.42}$$

This is already a usable result, but we will expend a bit more effort to put it in a nicer form. Look at Eq. (14.13), which we can rewrite as

$$\chi_{\mu\nu}(\omega) = -\frac{i}{\hbar}\int_{0}^{\infty} d\tau \left\langle [\tilde{x}_\nu(0), \tilde{x}_\mu(\tau)]\right\rangle e^{i\omega\tau}. \tag{14.43}$$

We can combine this equation with its Hermitian conjugate to obtain

$$\begin{aligned}\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega) &= -\frac{i}{\hbar}\int_{0}^{\infty} d\tau \left\langle [\tilde{x}_\nu(0), \tilde{x}_\mu(\tau)]\right\rangle e^{i\omega\tau} - \frac{i}{\hbar}\int_{0}^{\infty} d\tau \left\langle [\tilde{x}_\nu(\tau), \tilde{x}_\mu(0)]\right\rangle e^{-i\omega\tau} \\ &= -\frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau \left\langle [\tilde{x}_\nu(0), \tilde{x}_\mu(\tau)]\right\rangle e^{i\omega\tau}.\end{aligned} \tag{14.44}$$

This is basically an identification of complex conjugation with time reversal. We can then multiply Eq. (14.42) by 2 and then add Eq. (14.44). The temperature dependence enters via

$$2\left(\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2}\right) = \frac{e^{\beta\hbar\omega} + 1}{e^{\beta\hbar\omega} - 1} = \coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{14.45}$$

Note that the first term $[e^{\beta\hbar\omega} - 1]^{-1}$ represents the mean thermal occupation number for a harmonic oscillator, while the second term $1/2$ represents the zero-point energy (see Problem 10.10; the same temperature dependence appears in the position variance for a thermal state of the harmonic oscillator). Again, though we haven't made any specific assumptions about the unperturbed Hamiltonian H_0, to linear order in perturbation theory the unperturbed system responds like a harmonic oscillator. The net result of this combination of Eqs. (14.42) and (14.44) is

$$\left(\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega)\right)\coth\left(\frac{\beta\hbar\omega}{2}\right) = \frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau \left\langle [\tilde{x}_\nu(0), \tilde{x}_\mu(\tau)]_+\right\rangle e^{i\omega\tau}. \tag{14.46}$$

Now we can invert the Fourier transform (remembering the factor of $1/2\pi$ in the inverse transform) to obtain

$$\left\langle [\tilde{x}_\mu(\tau), \tilde{x}_\nu(0)]_+\right\rangle = \frac{\hbar}{2\pi i}\int_{-\infty}^{\infty} d\omega \left(\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega)\right)\coth\left(\frac{\beta\hbar\omega}{2}\right) e^{-i\omega\tau}.$$

(fluctuation–dissipation theorem) (14.47)

This is one form of the **fluctuation–dissipation theorem**,[3] which relates the antisymmetric (imaginary) part of the susceptibility tensor—remember that this is related to absorption in the cast of atomic polarizability, and to dissipation more generally—to fluctuations, here in the coupling operator $\mathbf{x}$, as specified by a symmetrized, two-time correlation function. If we make the same assumption of a symmetric susceptibility that we made in the polarizability case [see the discussion leading up to Eq. (13.144)], then $\chi_{\mu\nu} = \chi_{\nu\mu}$ and Eq. (14.47) simplifies to

$$\frac{1}{2}\left\langle [\tilde{x}_\mu(\tau), \tilde{x}_\nu(0)]_+\right\rangle = \frac{1}{2}\left\langle [\tilde{x}_\mu(0), \tilde{x}_\nu(\tau)]_+\right\rangle = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty} d\omega\, \mathrm{Im}[\chi_{\mu\nu}(\omega)]\coth\left(\frac{\beta\hbar\omega}{2}\right) e^{-i\omega\tau}.$$

(fluctuation–dissipation theorem) (14.48)

Remember that this symmetry assumption amounts to an assertion that the driving force $\mathbf{F}(t)$ has no helicity (i.e., no circular polarization in the optical case). The symmetry of the correlation function in τ in this case

[3] Herbert B. Callen and Theodore A. Welton, "Irreversibility and Generalized Noise," *Physical Review* **83**, 34 (1951) (doi: 10.1103/PhysRev.83.34); L. D. Landau and E. M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, 1980), §124 (ISBN: 0750633727); J. M. Ziman, *Elements of Advanced Quantum Theory*, (Cambridge, 1969), Section 4.4, p. 101 (ISBN: 0521074584).

follows from the form of the inverse Fourier integral, because both $\coth(\beta\hbar\omega/2)$ and $\mathrm{Im}[\chi_{\mu\nu}(\omega)]$ are odd functions of ω; the antisymmetry of the latter follows from Eq. (14.40), which implies $\chi_{\mu\nu}(-\omega) = \chi^*_{\mu\nu}(\omega)$ $\mathrm{Im}[\chi_{\mu\nu}(-\omega)] = -\mathrm{Im}[\chi_{\mu\nu}(\omega)]$. Since this is a Fourier transform of a real, even function, the resulting correlation function must be real and even.

The fluctuations in the generalized displacement are a bit more obvious if we set $\tau = 0$, in which case

$$\left\langle x_\mu x_\nu \right\rangle = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty} d\omega\, \mathrm{Im}[\chi_{\mu\nu}(\omega)]\coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{14.49}$$

(fluctuation–dissipation theorem)

where we have dropped the anticommutator under the assumption of a symmetric susceptibility. This is an expression for the covariance matrix of x_μ, given as an integral over the thermal fluctuations $\coth(\beta\hbar\omega/2)$, filtered through the imaginary part of the response function $\chi_{\mu\nu}(\omega)$ (which is thus ''responsible'' for the fluctuations) and then summed over all frequencies. Of course, at this point you could wonder, back in Eq. (14.43), couldn't we just have set $\tau = 0$ to get an expression for $\left\langle x_\mu x_\nu \right\rangle$, without going through the trouble to symmetrize the correlation function? The answer is yes, though the result isn't the same, and in fact although x_μ and x_ν may commute, it is better to think about this expectation value as the limit of a correlation function as $\tau \longrightarrow 0$, where the operators at different times do *not* commute. In fact Eq. (14.42) is missing the contribution due to the zero-point energy, as discussed after Eq. (14.45), and the zero-point contribution is sensibly due to the correlation function involving the commutator, as in Eq. (14.44), where the operators at different times obviously do not commute. The lesson here is that operator orderings matter, and to get something that can be interpreted in some classical way (like the fluctuations in some quantity), it's appropriate to work with symmetrized operator products. An example is the symmetrized covariance that we worked with in the harmonic oscillator, which couples most naturally to the evolution of the position and momentum variances, as in Eqs. (5.181). The symmetrized correlation function also is the intuitively proper choice for considering the limit $\tau \longrightarrow 0$, since the limit must be the same, independent of the direction of approach.

14.3.1 Dissipative Susceptibility

We have mentioned that the imaginary part of the generalized susceptibility is related to dissipation, and now we will run through a more quantitative argument that this is indeed the case. First consider the evolution of the expectation value of a Schrödinger-picture operator $Q(t)$ with some explicit time dependence (like $x\sin\omega t$). The time derivative of the expectation value gives

$$\begin{aligned}\frac{d}{dt}\langle Q(t)\rangle &= \frac{d}{dt}\langle\psi(t)|Q(t)|\psi(t)\rangle \\ &= \langle\dot\psi|Q|\psi\rangle + \langle\psi|\frac{\partial Q}{\partial t}|\psi\rangle + \langle\psi|Q|\dot\psi\rangle \\ &= -\frac{i}{\hbar}\langle[Q,H]\rangle + \frac{\partial\langle Q\rangle}{\partial t},\end{aligned} \tag{14.50}$$

after using the Schrödinger equation $|\dot\psi\rangle = -iH|\psi\rangle/\hbar$. The partial derivative in the last expression only operates on the explicit tine dependence of Q. Now replacing $Q(t)$ by $H(t) = H_0 + V(t)$, we find that the rate of energy change is

$$\frac{dE}{dt} = \frac{d\langle H\rangle}{dt} = \frac{\partial\langle V\rangle}{\partial t}. \tag{14.51}$$

In linear response, we assumed a generic interaction of the form [Eq. (14.1)]

$$V(t) = -\mathbf{x}\cdot\mathbf{F}(t), \tag{14.52}$$

so that

$$\frac{dE}{dt} = -\langle x\rangle\cdot\frac{\partial\mathbf{F}(t)}{\partial t}. \tag{14.53}$$

For the moment let's assume a real, monochromatic external force of the form

$$\mathbf{F}(t) = \mathbf{F}(\omega)\, e^{-i\omega t} + \text{c.c.}, \tag{14.54}$$

where we can later sum over all frequencies. The response to the perturbation is [Eq. (14.12)]

$$\langle \mathbf{x}(t) \rangle = \vec{\chi}(\omega) \cdot \mathbf{F}(\omega)\, e^{-i\omega t} + \text{c.c.}, \tag{14.55}$$

where we are taking the expectation value to vanish under unperturbed evolution (i.e., the expectation value is with respect to an eigenstate of H_0). Putting these last two expressions into Eq. (14.53), we have

$$\frac{dE}{dt} = -\Big(\vec{\chi}(\omega) \cdot \mathbf{F}(\omega)\, e^{-i\omega t} + \text{c.c.}\Big) \cdot \Big(- i\omega \mathbf{F}(\omega)\, e^{-i\omega t} + \text{c.c.}\Big). \tag{14.56}$$

We interested only in the relatively slow change of energy, so as customary we will introduce an average over time scales of order ω^{-1}, with the result

$$\begin{aligned} \overline{\frac{dE}{dt}} &= -i\omega \mathbf{F}^*(\omega) \cdot \vec{\chi}(\omega) \cdot \mathbf{F}(\omega) + \text{c.c.} \\ &= -i\omega \mathbf{F}^*(\omega) \cdot \Big(\vec{\chi}(\omega) - \vec{\chi}^\dagger(\omega)\Big) \cdot \mathbf{F}(\omega). \end{aligned} \tag{14.57}$$

In the case of a symmetric susceptibility $\vec{\chi}^\dagger(\omega) = \vec{\chi}^*(\omega)$, this becomes

$$\overline{\frac{dE}{dt}} = 2\omega \mathbf{F}^*(\omega) \cdot \text{Im}[\vec{\chi}(\omega)] \cdot \mathbf{F}(\omega). \tag{14.58}$$

The energy here *increases* due to the influence of the force $\mathbf{F}(t)$. For a system in thermal equilibrium, this must be equal to the average rate R at which energy is *dissipated* into heat:

$$R = \overline{\frac{dE}{dt}}. \tag{14.59}$$

Thus the rate of energy dissipation is

$$R = 2\int_0^\infty d\omega\, \omega\, \mathbf{F}^*(\omega) \cdot \text{Im}[\vec{\chi}(\omega)] \cdot \mathbf{F}(\omega) = \int_{-\infty}^\infty d\omega\, \omega\, \mathbf{F}^*(\omega) \cdot \text{Im}[\vec{\chi}(\omega)] \cdot \mathbf{F}(\omega), \tag{14.60}$$

(total dissipation rate)

with positive value indicating a flow of energy from the system into heat. That is, for friction-type dissipation, we must have $\text{Im}[\vec{\chi}(\omega)] \geq 0$. Comparing this expression to the fluctuation–dissipation relation (14.49), we see that the fluctuations in $\mathbf{x}$ are related to the rate of energy dissipation, where the power spectral density of the thermal "force" is proportional to $\coth(\beta\hbar\omega/2)$, as expected for thermal fluctuations.

14.3.2 Application: Johnson Noise

The fluctuation–dissipation theorem above can apply in any situation where there is an interaction of the form $-\mathbf{x} \cdot \mathbf{F}(t)$. Returning to the example of the atomic polarizability, we can translate the theorem over to obtain

$$\big\langle d_\mu d_\nu \big\rangle = \frac{\hbar}{2\pi} \int_{-\infty}^\infty d\omega\, \text{Im}[\alpha_{\mu\nu}(\omega)] \coth\left(\frac{\beta\hbar\omega}{2}\right), \tag{14.61}$$

which says that the absorptive component of the polarizability leads to fluctuations of the atomic dipole moment. Of course, if there is *any* nontrivial polarizability, causality says that there must be *some* absorptive component, and thus there will always be dipole fluctuations (even at zero temperature, as we will see). These fluctuations are responsible for van der Waals and Casimir–Polder potentials, which are forces between two neutral atoms or an atom and a macroscopic object (even at zero temperature).

Another classic application of the fluctuation–dissipation theorem is to the conductivity of a material. The microscopic version of Ohm's law reads

$$j_\mu(\mathbf{r},\omega) = \sigma_{\mu\nu}(\mathbf{r},\omega)\,\mathscr{E}_\nu(\mathbf{r},\omega) \tag{14.62}$$

in terms of the conductivity tensor $\sigma_{\mu\nu}(\mathbf{r},\omega)$. That is, this relation serves to define the conductivity tensor, since we expect an applied electric field $\mathscr{E}_\nu(\mathbf{r})$ to induce a current density $j_\mu(\mathbf{r})$, and we expect the relationship to be linear for a sufficiently weak applied field.

The conductivity example requires a bit more manipulation than the atomic polarizability, however, because the interaction potential is of the form Eq. (7.212):

$$V(t) = -\int d^3r\,\mathbf{j}(\mathbf{r})\cdot\mathscr{A}(\mathbf{r},t). \tag{14.63}$$

That is, the current density couples to the vector potential, which is related to the electric field in the Coulomb gauge via $\mathscr{E}(t) = -\partial_t\mathscr{A}(t)$. Thus, the response relation is more like

$$j_\mu(\mathbf{r},\omega) = i\omega\sigma_{\mu\nu}(\mathbf{r},\omega)\,\mathscr{A}_\nu(\mathbf{r},\omega). \tag{14.64}$$

However, the coupling potential also has a volume integral, for which we must also account. Suppose we consider the current summed over a small volume $\mathscr{V}$, over which the current density is uniform. Then our response relation is

$$\mathscr{V} j_\mu(\mathbf{r},\omega) = i\omega\mathscr{V}\sigma_{\mu\nu}(\mathbf{r},\omega)\,\mathscr{A}_\nu(\mathbf{r},\omega), \tag{14.65}$$

if we associate the volume element with the current density, so that the generalized displacement is $\mathscr{V} j_\mu$. Thus, in the fluctuation–dissipation theorem (14.49), we can replace x_μ by $\mathscr{V} j_\mu$ provided we identify $\chi_{\mu\nu}(\omega) \longrightarrow i\omega\mathscr{V}\sigma_{\mu\nu}(\omega)$. The result is

$$\left\langle j_\mu(\mathbf{r})\,j_\nu(\mathbf{r})\right\rangle = \frac{\hbar}{2\pi\mathscr{V}}\int_{-\infty}^{\infty} d\omega\,\omega\,\mathrm{Re}[\sigma_{\mu\nu}(\mathbf{r},\omega)]\coth\left(\frac{\beta\hbar\omega}{2}\right),$$

(fluctuation–dissipation relation for conductivity) (14.66)

which is our basic result for the conductivity tensor. Note that it is the *real* part of the conductivity tensor that is responsible for dissipation (the imaginary parts are capacitive or inductive, or more generally "reactive").

To put this result in more familiar terms, suppose that the current density is homogeneous and now also isotropic over the volume $\mathscr{V}$, which corresponds to area a and length ℓ. Then we can switch to the macroscopic current I and conductance G via the relations

$$I = ja, \qquad G = \sigma\frac{a}{\ell}, \tag{14.67}$$

in which case Eq. (14.66) becomes

$$\left\langle I^2\right\rangle = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty} d\omega\,\omega\,\mathrm{Re}[G(\omega)]\coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{14.68}$$

To simplify the discussion, suppose that the conductance is roughly constant over the bandwidth of interest, so that we can make the approximation $G(\omega) \approx R^{-1}$, where R is the dc resistance. Often the dissipative and reactive components are discussed in terms of the impedance $Z(\omega)$, where $R(\omega) = \mathrm{Re}[Z(\omega)]$, but we have arrived here equivalently in terms of conductance. Then the integral simplifies to

$$\left\langle I^2\right\rangle \approx \frac{\hbar}{\pi R}\int_0^{\infty} d\omega\,\omega\,\coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{14.69}$$

Using Ohm's law $V = IR$, we can translate this relation into voltage fluctuations via

$$\left\langle V^2\right\rangle \approx \frac{\hbar R}{\pi}\int_0^{\infty} d\omega\,\omega\,\coth\left(\frac{\beta\hbar\omega}{2}\right). \tag{14.70}$$

The remaining integral is divergent, and even when the divergence is taken care of (we'll discuss this in just a bit), the integral can be computed, but isn't especially illuminating. Thus, we will look at the low- and high-temperature limits. In the high-temperature (classical) limit $\beta = 1/k_{\mathrm{B}}T$ is small so we can use $\coth x \approx 1/x$ for small x to write

$$\langle V^2 \rangle \approx \frac{2R}{\pi\beta} \int_0^\infty d\omega = \frac{2Rk_{\mathrm{B}}T}{\pi} \int_0^\infty d\omega \tag{14.71}$$

Again, the remaining integral is divergent, but generally the only part of the noise that is relevant lies within some detection bandwidth. Thus, cutting off the integral on the upper end at a bandwidth limit $\Delta\omega = 2\pi\Delta\nu$, the noise is

$$\langle V^2 \rangle \approx 4Rk_{\mathrm{B}}T\,\Delta\nu. \tag{14.72}$$

(Johnson noise)

Note that $\hbar$ has disappeared, confirming that this is a classical result. The noise here diverges as $\Delta\nu \longrightarrow \infty$, which is characteristic of white noise. The bandwidth $\Delta\nu$ here is called the ''brick-wall bandwidth,'' and corresponds to a crude model of a low-pass filter (a more realistic response cutoff function may be substituted in this integral, but the result we have written is standard). Because this result is given relative to an integration bandwidth, it is often quoted as $\langle V^2 \rangle / \Delta\nu$, or as the square root of this (for an rms voltage noise), which carries the curious units of $\mathrm{V}/\sqrt{\mathrm{Hz}}$. For a sense of scale, at $T = 293\,\mathrm{K}$, a 10-kΩ resistor measured over a 10-kHz bandwidth has an intrinsic, thermal rms voltage noise of $1.2\,\mu\mathrm{V}$. At the same temperature, a 1-MΩ resistor measured over a 1-MHz bandwidth has an rms voltage noise of 0.12 mV, which is starting to become significant on the scale of laboratory voltages.

In the zero-temperature limit, there is *still* a kind of quantum Johnson noise. In this limit (large β), we can use $\coth x \approx 1$ for large x, and Eq. (14.70) becomes

$$\langle V^2 \rangle \approx \frac{\hbar R}{\pi} \int_0^\infty d\omega\,\omega. \tag{14.73}$$

Again cutting off the integral at the brick-wall bandwidth $2\pi\Delta\nu$,

$$\langle V^2 \rangle \approx 2\pi\hbar R(\Delta\nu)^2.$$

(zero-temperature quantum Johnson noise) (14.74)

Again, note the presence of $\hbar$, confirming that this is a quantum effect, and note again that R is assumed to be constant over the integration bandwidth.[4]

[4]For a measurement of the coth dependence of Johnson noise at low temperature, see R. Movshovich, B. Yurke, P. G. Kaminsky, A. D. Smith, A. H. Silver, R. W. Simon, and M. V. Schneider, ''Observation of zero-point noise squeezing via a Josephson-parametric amplifier,'' *Physical Review Letters* **65**, 1419 (1990) (doi: 10.1103/PhysRevLett.65.1419).

14.4 Exercises

Problem 14.1

Prove the integral formula

$$\int_0^\infty dx\, \frac{ab}{(a^2+x^2)(b^2+x^2)} = \frac{\pi}{2(a^2-b^2)}(a\,\mathrm{sgn}\,b - b\,\mathrm{sgn}\,a) \qquad (a,b\in\mathbb{R},\ a,b\neq 0) \tag{14.75}$$

by considering the contour around the great upper half-plane (and justifying the use of this contour).

Problem 14.2

Consider a generalized susceptibility including a dc pole of the form

$$\vec{\zeta}(\omega) := \vec{\chi}(\omega) + \frac{i\vec{\sigma}(\omega)}{\omega}, \tag{14.76}$$

where $\vec{\chi}(\omega)$ is still analytic in the upper half-plane ($\mathrm{Im}[\omega]\geq 0$) and obeys the usual Kramers–Kronig relations (14.22)

$$\begin{aligned}\mathrm{Re}[\vec{\chi}(\omega)-\vec{\chi}_0] &= \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Im}[\vec{\chi}(\omega')-\vec{\chi}_0]}{\omega'-\omega}\,d\omega'\\ \mathrm{Im}[\vec{\chi}(\omega)-\vec{\chi}_0] &= -\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Re}[\vec{\chi}(\omega')-\vec{\chi}_0]}{\omega'-\omega}\,d\omega'.\end{aligned} \tag{14.77}$$

Such a pole can arise, for example, if $\vec{\zeta}(\omega)$ is the dielectric permittivity of a conducting material, and $\vec{\sigma}(\omega)$ is the conductivity tensor. Show that $\vec{\zeta}(\omega)$ satisfies the modified Kramers–Kronig relations

$$\begin{aligned}\mathrm{Re}[\vec{\zeta}(\omega)-\vec{\chi}_0] &= \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Im}[\vec{\zeta}(\omega')-\vec{\chi}_0]}{\omega'-\omega}\,d\omega'\\ \mathrm{Im}[\vec{\zeta}(\omega)-\vec{\chi}_0] &= -\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Re}[\vec{\zeta}(\omega')-\vec{\chi}_0]}{\omega'-\omega}\,d\omega' + \frac{\vec{\sigma}_0}{\omega},\end{aligned} \tag{14.78}$$

where $\vec{\sigma}_0 = \vec{\sigma}(0)$ is the dc conductivity tensor, which is real and symmetric. You may also assume $\vec{\sigma}(\omega)\longrightarrow 0$ as $\omega\longrightarrow\infty$.

Hint: the algebra is simple if you keep the relations as much as possible in terms of the Hilbert-transform operator $\mathscr{H}$.

Problem 14.3

Show that the Kramers–Kronig relations for the generalized susceptibility

$$\begin{aligned}\mathrm{Re}[\vec{\chi}(\omega)-\vec{\chi}_0] &= \frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Im}[\vec{\chi}(\omega')-\vec{\chi}_0]}{\omega'-\omega}\,d\omega'\\ \mathrm{Im}[\vec{\chi}(\omega)-\vec{\chi}_0] &= -\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{\mathrm{Re}[\vec{\chi}(\omega')-\vec{\chi}_0]}{\omega'-\omega}\,d\omega'\end{aligned} \tag{14.79}$$

can be written in the equivalent form

$$\begin{aligned}\mathrm{Re}[\vec{\chi}(\omega)] &= \vec{\chi}_0 + \frac{2}{\pi}\int_0^{\infty}\frac{\omega'\mathrm{Im}[\vec{\chi}(\omega')]}{\omega'^2-\omega^2}\,d\omega'\\ \mathrm{Im}[\vec{\chi}(\omega)] &= -\frac{2\omega}{\pi}\int_0^{\infty}\frac{\mathrm{Re}[\vec{\chi}(\omega')]-\vec{\chi}_0}{\omega'^2-\omega^2}\,d\omega'.\end{aligned} \tag{14.80}$$

Hint: prove and then use the property $\vec{\chi}(-\omega^*) = \vec{\chi}^*(\omega)$ [where $\vec{\chi}^*$ is not the same thing as $\vec{\chi}^\dagger$].

Problem 14.4

In Problem 10.10 you derived the expression

$$\rho(x,x') = \frac{1}{\sqrt{\pi x_{\rm s}^2 \coth(\beta\hbar\omega/2)}} \exp\Big[-\coth(\beta\hbar\omega)\big(x^2+x'^2\big)/2x_{\rm s}^2 + \operatorname{csch}(\beta\hbar\omega)\big(xx'/x_{\rm s}^2\big)\Big] \tag{14.81}$$

for the density matrix $\rho(x,x') = \langle x|\rho|x'\rangle$ in the position representation, corresponding to a harmonic oscillator in thermal equilibrium at temperature T, where $\beta = 1/k_{\rm B}T$. Show how to modify this expression to derive the propagator

$$K(x,t;x_0,t_0) = \sqrt{\frac{m\omega}{2\pi i\hbar\sin\omega(t-t_0)}} \exp\left(\frac{im\omega}{2\hbar\sin\omega(t-t_0)}\Big[\big(x_0^2+x^2\big)\cos\omega(t-t_0) - 2x_0x\Big]\right) \tag{14.82}$$

for the harmonic oscillator.

Problem 14.5

Consider the (classical) forced, damped harmonic oscillator

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = f(t), \tag{14.83}$$

subject to the forcing function $f(t)$.

(a) Find the Green function $g(t,t')$ for the initially undisturbed system, defined as the solution $x(t)$ where the forcing function $f(t) = \delta(t-t')$ is an impulse at time t', and with $x(t) = 0$ for $t < t'$. That is, $g(t,t')$ satisfies

$$\ddot{g} + \gamma\dot{g} + \omega_0^2 g = \delta(t-t'), \tag{14.84}$$

subject to the boundary condition $\lim_{t\to-\infty} g(t,t') = 0$. Assume underdamped oscillation; also, you don't need to derive the solution to Eq. (14.83) [you will need the homogeneous solution for appropriate initial conditions; look this up from a reputable source].

(b) Write down the general solution to Eq. (14.83) [by integrating Eq. (14.84) over t'] for an arbitrary forcing function $f(t)$ as an integral involving the Green function. Noting that $g(t,t') = g(t-t')$, show that the integral is in fact a convolution of $f(t)$ with $g(t)$.

(c) Derive the frequency-space Green function $\tilde{g}(\omega)$, defined as the amplitude $\tilde{x}(\omega)$, where

$$x(t) = \tilde{x}(\omega)\, e^{-i\omega t}, \tag{14.85}$$

and $x(t)$ is the solution to Eq. (14.83) due to a unit-amplitude, monochromatic forcing at frequency ω,

$$f(t) = e^{-i\omega t}. \tag{14.86}$$

(d) For an arbitrary forcing function $f(t)$ with Fourier transform $\tilde{f}(\omega)$, use the convolution theorem to show that the solution $x(t)$ may be written

$$x(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \tilde{g}(\omega)\tilde{f}(\omega)e^{-i\omega t}. \tag{14.87}$$

Thus, $\tilde{g}(\omega)$ is the **transfer function** for the damped harmonic oscillator, because it gives the "transfer efficiency" for the forcing amplitude at frequency ω through the system. Of course $\tilde{g}(\omega)$ is also the generalized susceptibility for the damped harmonic oscillator, and thus, for example, obeys the Kramers–Kronig relations.

Chapter 15

Transitions to the Continuum

In considering transitions between a pair of states in the tunneling problem of Section 3.3, we discovered that sinusoidal oscillations between a pair of states results. As more discrete states are added, more Rabi oscillations may occur at different rates, leading to beating behavior. But when a *continuum* of states enters the picture the behavior is quite different—exponential decay results.

15.1 Fermi's Golden Rule

Going back to time-dependent perturbation theory, the first-order expression for the transition amplitude $\tilde{K}_{\mathsf{fi}}(t) = \langle\, \mathsf{f} \,|\tilde{U}(t,0)|\, \mathsf{i} \,\rangle$, where $|\, \mathsf{f} \,\rangle$ is different from $|\, \mathsf{i} \,\rangle$, due to a constant perturbation V is [Eq. (13.76)]

$$\tilde{K}_{\mathsf{fi}}(t) \approx -2\pi i V_{\mathsf{fi}}\, e^{iE_{\mathsf{fi}}t/2\hbar}\, \delta_t(E_{\mathsf{fi}}), \tag{15.1}$$

where

$$\delta_t(E_{\mathsf{fi}}) = \frac{t}{2\pi\hbar}\,\mathrm{sinc}(E_{\mathsf{fi}}t/2\hbar) \tag{15.2}$$

is a finite-time approximation to the delta function. Before, we interpreted this in terms of a transition probability changing quadratically in time, or as an off-resonant Rabi oscillation. Here we will interpret this expression somewhat differently. The transition probability to $|\, \mathsf{f} \,\rangle$ is just the squared modulus of the amplitude:

$$P_{\mathsf{f}}(t) = |\tilde{K}_{\mathsf{fi}}(t)|^2 = 4\pi^2 |V_{\mathsf{fi}}|^2\, \delta_t^{\,2}(E_{\mathsf{fi}}). \tag{15.3}$$

Let's take a closer look at the time dependence

$$\delta_t^{\,2}(E_{\mathsf{fi}}) = \frac{t^2}{4\pi^2\hbar^2}\,\mathrm{sinc}^2(E_{\mathsf{fi}}t/2\hbar). \tag{15.4}$$

The sinc^2 function, like the sinc function, is localized, and has an area given by

$$\int_{-\infty}^{\infty} dE\ \mathrm{sinc}^2\left(\frac{Et}{2\hbar}\right) = \frac{2\pi\hbar}{t}. \tag{15.5}$$

That is, we can also think of sinc^2 as another approximation to the delta function, and in the long-time limit, we have

$$\delta_t^{\,2}(E) \longrightarrow \frac{t}{2\pi\hbar}\delta(E), \tag{15.6}$$

which leads to the long-time transition probability

$$P_{\mathsf{f}}(t) \approx \frac{2\pi t}{\hbar}|V_{\mathsf{fi}}|^2\, \delta(E_{\mathsf{fi}}). \tag{15.7}$$

Thus, in the long-time limit, the excitation probability increases linearly with time. Clearly, this is only valid for "weak" perturbations (and correspondingly short times) such that the excitation probability is small; on the other hand, we had to make the long-time assumption such justify the approximation of $\delta_t^2(E_{\mathsf{fi}})$ by $\delta(E_{\mathsf{fi}})$. This conflict between time scales is resolved by a sufficiently weak perturbation, such that the transition probability is small even over a usefully long time scale. In any case, the transition rate from $|\,\mathsf{i}\,\rangle$ to $|\,\mathsf{f}\,\rangle$ is simply the time derivative of the transition probability,

$$\Gamma_{\mathsf{i}\to\mathsf{f}} := \partial_t P_{\mathsf{f}}(t), \tag{15.8}$$

and we can thus write the transition rate as

$$\Gamma_{\mathsf{i}\to\mathsf{f}} \approx \frac{2\pi}{\hbar}|V_{\mathsf{fi}}|^2\,\delta(E_{\mathsf{fi}}). \tag{15.9}$$
(Fermi's golden rule)

The transition rate in this regime of intermediate times is time-independent, and this expression for the transition rate is **Fermi's golden rule**. The delta function here is again a statement of energy conservation: transitions only occur when the energies for a final state that matches that of the initial state.

15.1.1 Density of States in the Continuum

The delta function in the golden rule (15.9) really only makes sense under an integral over energies, since it represents the transition probability summed over a range of energies. This is a crucial point: it is the existence of a *continuum* of energy levels that causes the time-independent transition rate; otherwise, the transition rate to a discrete state oscillates in time, due to coherent Rabi flopping. Thus, suppose we consider the transition from $|\,\mathsf{i}\,\rangle$ to a continuous set $\mathcal{F}$ of states. Then we must sum over the transition rate to all final states $|\,\mathsf{f}\,\rangle \in \mathcal{F}$. We need only carry out this sum over a narrow range $(E_{\mathsf{i}}-\varepsilon/2, E_{\mathsf{i}}+\varepsilon/2)$ of final states, where ε defines a narrow range of energies over which the perturbation V is approximately constant. Letting $n(E)$ denote the number of states with energy less than E, the sum over transition rates is

$$\begin{aligned}\Gamma_{\mathsf{i}\to\mathcal{F}} &= \frac{2\pi}{\hbar}\int_{n(E_{\mathsf{i}}-\varepsilon/2)}^{n(E_{\mathsf{i}}+\varepsilon/2)} dn(E')\,|V_{\mathsf{fi}}|^2\delta(E_{\mathsf{i}}-E') \\ &= \frac{2\pi}{\hbar}\int_{E_{\mathsf{i}}-\varepsilon/2}^{E_{\mathsf{i}}+\varepsilon/2} dE'\,\rho(E')\,|V_{\mathsf{fi}}|^2\delta(E_{\mathsf{i}}-E').\end{aligned} \tag{15.10}$$

Here,

$$\rho(E) := \frac{dn}{dE} \tag{15.11}$$

is the **density of states**, or number of states in $\mathcal{F}$ per unit energy interval. Completing the integral and taking $E_{\mathsf{f}} = E_{\mathsf{i}}$, we arrive at an alternate form of Fermi's golden rule:

$$\Gamma_{\mathsf{i}\to\mathcal{F}} = \frac{2\pi}{\hbar}|V_{\mathsf{fi}}|^2\rho(E_{\mathsf{f}}). \tag{15.12}$$
(Fermi's golden rule)

In deriving this form of the golden rule, we implicitly assumed that the density of states is approximately constant over the range of integration, which sets another upper bound on ε. For the delta-function approximation to hold, we needed that the frequency width of the function in the expression (15.6) must be small compared to $\varepsilon/\hbar$, and thus that $t \gg \hbar/\varepsilon$, quantifying the long-time constraint we mentioned above. The short-time constraint is that $\Gamma_{\mathsf{i}\to\mathcal{F}}\,t \ll 1$, but typically this expression is valid to much longer times by accounting explicitly for depletion of $|\,\mathsf{i}\,\rangle$: the decay rate holds so long as the decayed population in the states $\mathcal{F}$ do not influence the decay rate (through coherence effects or reverse decay). In this sense the transition rate (15.12) represents a rate constant for **exponential decay**, because the undecayed fraction decays at a constant rate. We don't necessarily expect the exponential decay law to hold at very short or very long times, and in fact it doesn't in general.

15.2 Spontaneous Decay

A natural application of the formalism here is to the decay of excited atomic states. In a *classical* model of an atom, an excitation corresponds to an oscillating charge (as an electron orbit or oscillating dipole), and in classical electromagnetism an accelerating charge radiates. This is called **radiation reaction**. The analogous quantum effect involves the downward transition between atomic energy states due to interaction with the (vacuum) electromagnetic field, accompanied by the creation of a photon.

15.2.1 Normal-Mode Quantization of the Electromagnetic Field

There are multiple approaches one could take for modeling spontaneous emission. For example, Einstein's famous calculation[1] leverages the Planck radiation law in thermal equilibrium in order to compute the spontaneous emission rate. Here we will consider the interaction with the quantized electromagnetic field, which of course requires us to quantize the electromagnetic field. This is something of a subtle subject, so here we will pursue a relatively simple version,[2] deferring the more formal version until Section 19.3.

Starting with the classical Maxwell equations in vacuum

$$\begin{aligned} \nabla \cdot \boldsymbol{\mathscr{E}} &= 0 \\ \nabla \cdot \boldsymbol{\mathscr{B}} &= 0 \\ \nabla \times \boldsymbol{\mathscr{E}} &= -\partial_t \boldsymbol{\mathscr{B}} \\ \nabla \times \boldsymbol{\mathscr{B}} &= \frac{1}{c^2}\partial_t \boldsymbol{\mathscr{E}}, \end{aligned} \tag{15.13}$$

we can compute the curl of the third equation, eliminate $\nabla \times \mathbf{B}$ using the fourth equation, and use the vector identity $\nabla \times \nabla \times \mathbf{A} = \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A}$ to obtain the wave equation

$$\nabla^2 \boldsymbol{\mathscr{E}} - \frac{1}{c^2}\partial_t^2 \boldsymbol{\mathscr{E}} = 0 \tag{15.14}$$

satisfied by the electric field. For a monochromatic field of frequency ω, we assume a solution of the form

$$\boldsymbol{\mathscr{E}}(\mathbf{r}, t) = \hat{\varepsilon}\mathscr{E}_0 \, f(\mathbf{r}) \, e^{-i\omega t} + \text{c.c.}, \tag{15.15}$$

where $\hat{\varepsilon}$ is the unit polarization vector and $f(\mathbf{r})$ represents the spatial dependence of the field. In this case the wave equation (15.14) reduces to

$$(\nabla^2 + k^2) \, f(\mathbf{r}) = 0, \tag{15.16}$$

where $k = \omega/c$. This is the Helmholtz equation, the same as the time-independent Schrödinger equation for the free particle. The solutions here are thus conveniently represented as plane waves, $f(\mathbf{r}) \propto e^{i\mathbf{k}\cdot\mathbf{r}}$, except that plane waves are not normalizable. In this case it's nice to have normalizable modes so we can associate some finite energy with the occupation of a mode. The trick for doing this is to restrict the mode to a cube of volume $\mathscr{V}$ with periodic boundary conditions, in which case the normalized mode functions are (Problem 1.42)

$$f_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\mathscr{V}}} \, e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{15.17}$$

[1] A. Einstein, "Strahlungs-Emission und -Absorption nach der Quantentheorie" ("Emission and Absorption of Radiation in Quantum Theory") *Deutsche Physikalische Gesellschaft. Verhandlungen* **18**, 318 (1916); A. Einstein, "Zur Quantentheorie der Strahlung" ("On the Quantum Theory of Radiation") *Physikalische Gesellschaft Zürich. Mitteilungen* **16**, 47 (1916). Both papers reprinted and translated into English in A. J. Kox, Martin J. Klein, and Robert Schulmann, Eds., *The Collected Papers of Albert Einstein, Volume 6: The Berlin Years: Writings, 1914-1917* (Princeton, 1997) (ISBN: 0691017344), Doc. 34, p. 363 (`https://einsteinpapers.press.princeton.edu/vol6-trans/224`) and Doc. 38, p. 381 (`https://einsteinpapers.press.princeton.edu/vol6-trans/232`), respectively.

[2] The first quantization of the electromagnetic field by decomposing into normal modes was by P. A. M. Dirac, "The Quantum Theory of the Emission and Absorption of Radiation," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **114**, 243 (1927) (doi: 10.1098/rspa.1927.0039). The treatment here is a variation on the common modern version. For classic treatments along these lines, see Rodney Loudon, *The Quantum Theory of Light*, 3rd ed. (Oxford, 2000) (ISBN: 0198501765); and Peter W. Milonni, *The Quantum Vacuum* (Academic Press, 1993) (ISBN: 0124980805) (doi: 10.1016/C2009-0-21295-5). The first quantum treatment of the electromagnetic field was slightly earlier: M. Born, W. Heisenberg, and P. Jordan, "Zur Quantenmechanik II," *Zeitschrift für Physik* **35**, 557 (1926) (doi: 10.1007/BF01379806).

where as a result of the boundary conditions the wave vector $\mathbf{k}$ satisfies

$$\mathbf{k}(\mathbf{n}) = \frac{2\pi n_x}{L}\hat{x} + \frac{2\pi n_y}{L}\hat{y} + \frac{2\pi n_z}{L}\hat{z}, \tag{15.18}$$

with $L = \sqrt[3]{\mathscr{V}}$ and $n_x, n_y, n_z \in \mathbb{Z}$ (i.e., positive, negative, and zero integer values are all allowed, though not all of them should be zero). The idea will be to take $\mathscr{V} \longrightarrow \infty$ at the end of the calculation to return to the correct free-space modes, in the hope that by that time the quantization volume $\mathscr{V}$ will have dropped out of the calculation. Note that because of the first Maxwell equation, the polarization vector must satisfy $\hat{\varepsilon} \cdot \mathbf{k} = 0$, and so there are two independent polarizations for each $\mathbf{k}$.

Now the total energy of an electromagnetic field is

$$H = \frac{1}{2}\int_{\mathscr{V}} d^3r \left(\epsilon_0 \mathscr{E}^2 + \mu_0 \mathscr{H}^2\right) = \frac{1}{2}\int_{\mathscr{V}} d^3r \left(\epsilon_0 \mathscr{E}^2 + \frac{1}{\mu_0}\mathscr{B}^2\right), \tag{15.19}$$

where $\mu_0 \mathscr{H} = \mathscr{B}$, and the integration is restricted to the quantization volume. We will identify this as the Hamiltonian, since the energy for a time-dependent system is *supposed* to be the Hamiltonian. But this is fundamentally why this quantization will be a shortcut: to properly quantize a classical Hamiltonian, we should identify the canonical coordinates (i.e., canonical fields) and then promote them to operators. However, here we will only find a simple proxy for the canonical-variable pair (in fact the generalized coordinate corresponds to the electromagnetic potential, not to any of the electromagnetic fields). Now the electric-field solutions from Eqs. (15.15) and (15.17) can be written together as

$$\boldsymbol{\mathscr{E}}_{\mathbf{k}}(\mathbf{r}, t) = \hat{\varepsilon}\frac{\mathscr{E}_0}{\sqrt{\mathscr{V}}}\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} + \text{c.c.} \tag{15.20}$$

At this point it will be convenient to write the time dependence as a separate factor, but the structure of the modes makes this unnatural. However, we can consider even and odd combinations of counterpropagating plane waves with the same polarization (that is, assuming $\mathscr{E}_0$ and $\hat{\varepsilon}$ are real):

$$\boldsymbol{\mathscr{E}}_{\mathbf{k}\pm}(\mathbf{r}, t) = \frac{1}{\sqrt{2}}\left[\hat{\varepsilon}\frac{\mathscr{E}_0}{\sqrt{\mathscr{V}}}\left(e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)} \pm e^{i(-\mathbf{k}\cdot\mathbf{r} - \omega t)}\right) + \text{c.c.}\right]. \tag{15.21}$$

This is a switch to standing-wave modes, where the electric and magnetic fields oscillate out of phase (like x and p for the harmonic oscillator), unlike the traveling-wave modes (15.20) where the two fields oscillate in phase. Simplifying the + case, we can write

$$\boldsymbol{\mathscr{E}}_{\mathbf{k}+}(\mathbf{r}, t) = \hat{\varepsilon}\sqrt{\frac{8}{\mathscr{V}}}\,\mathscr{E}_0 \cos(\mathbf{k}\cdot\mathbf{r})\cos(\omega t) =: \hat{\varepsilon}\sqrt{\frac{8}{\mathscr{V}}}\,\mathscr{E}_0 \cos(\mathbf{k}\cdot\mathbf{r})\, \dot{q}(t), \tag{15.22}$$

where $\dot{q}(t) = \cos(\omega t)$ stands for the time-dependent factor. (We won't bother to analyze the $-$ case explicitly, which will turn out to be equivalent.) Now the third Maxwell equation $\nabla \times \boldsymbol{\mathscr{E}} = -\dot{\boldsymbol{\mathscr{B}}}$ allows us to write the corresponding magnetic field as

$$\boldsymbol{\mathscr{B}}_{\mathbf{k}+}(\mathbf{r}, t) = -(\hat{k} \times \hat{\varepsilon})\sqrt{\frac{8}{\mathscr{V}}}\,\frac{\omega \mathscr{E}_0}{c}\sin(\mathbf{k}\cdot\mathbf{r})\, q(t). \tag{15.23}$$

The Hamiltonian (15.19) then becomes

$$H = \frac{4\mathscr{E}_0^{\,2}}{\mathscr{V}}\int_{\mathscr{V}} d^3r \left(\epsilon_0 \dot{q}^2 \cos^2(\mathbf{k}\cdot\mathbf{r}) + \frac{\omega^2 q^2}{\mu_0 c^2}\sin^2(\mathbf{k}\cdot\mathbf{r})\right), \tag{15.24}$$

and then carrying out the integral (noting that the $\cos^2$ and $\sin^2$ factors are periodic over the volume $\mathscr{V}$) and using $\mu_0\epsilon_0 = 1/c^2$, we find

$$H = 2\epsilon_0 \mathscr{E}_0^{\,2}\left(\dot{q}^2 + \omega^2 q^2\right). \tag{15.25}$$

We can put this in more standard form

$$H = \frac{1}{2}m\left(\dot{q}^2 + \omega^2 q^2\right) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2, \tag{15.26}$$

if we identify $m = 4\epsilon_0 \mathscr{E}_0^{\,2}$ and $p = m\dot{q}$. Thus, a single mode of the electromagnetic field of frequency ω acts as a harmonic oscillator of the same frequency; each field mode can be quantized separately as an independent harmonic oscillator.

Now in canonical quantization we can promote p and q to operators, and in particular from Eqs. (5.27) and (5.28) we can identify them in terms of creation and annihilation operators as

$$q = \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^\dagger), \qquad p = \frac{1}{i}\sqrt{\frac{m\hbar\omega}{2}}\,(a - a^\dagger). \tag{15.27}$$

Actually, to match the common convention for the quantized field, we will redefine the phase of the ladder operators by shifting $a \longrightarrow -ia$:

$$q = -i\sqrt{\frac{\hbar}{2m\omega}}\,(a - a^\dagger), \qquad p = -\sqrt{\frac{m\hbar\omega}{2}}\,(a + a^\dagger). \tag{15.28}$$

In this case Eq. (15.22) becomes

$$\boldsymbol{\mathscr{E}}_{\mathbf{k}+}(\mathbf{r}, t) = -\hat{\varepsilon}\sqrt{\frac{8}{\mathscr{V}}}\,\mathscr{E}_0 \cos(\mathbf{k}\cdot\mathbf{r})\sqrt{\frac{\hbar\omega}{2m}}\,(a + a^\dagger) = -\hat{\varepsilon}\cos(\mathbf{k}\cdot\mathbf{r})\sqrt{\frac{\hbar\omega}{\epsilon_0\mathscr{V}}}\,(a + a^\dagger) \tag{15.29}$$

To quantize the mode, in going from Eq. (15.22) to (15.29), we replaced

$$\cos(\omega t) \longrightarrow -\sqrt{\frac{\hbar\omega}{8\epsilon_0}}\,\frac{1}{\mathscr{E}_0}\,(a + a^\dagger). \tag{15.30}$$

Recalling that we identify the time dependence $a(t) = a(0)\,e^{-i\omega t}$ in the Heisenberg picture, then canonical quantization alternately corresponds to the replacement

$$e^{-i\omega t} \longrightarrow -\sqrt{\frac{\hbar\omega}{2\epsilon_0}}\,\frac{1}{\mathscr{E}_0}\,a(t). \tag{15.31}$$

Making this replacement in Eq. (15.20), we then obtain

$$\boldsymbol{\mathscr{E}}_{\mathbf{k}}(\mathbf{r}, t) = -\hat{\varepsilon}\sqrt{\frac{\hbar\omega}{2\epsilon_0\mathscr{V}}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,a(t) + \text{H.c.} \tag{15.32}$$

(quantized electric-field mode)

for a single plane-wave mode of the quantum electric field (here, in the Heisenberg picture). Note that although we assumed $\hat{\varepsilon}$ to be real when constructing the standing wave modes (15.21), this expression is still valid for complex polarizations. Next, again using the Maxwell equation $\nabla \times \boldsymbol{\mathscr{E}} = i\mathbf{k} \times \boldsymbol{\mathscr{E}} = i\omega\boldsymbol{\mathscr{B}} = -\partial_t \boldsymbol{\mathscr{E}}$ for the $e^{-i\omega t}$ component, we can conclude that the magnetic-field counterpart of this mode is

$$\boldsymbol{\mathscr{B}}_{\mathbf{k}}(\mathbf{r}, t) = -(\hat{k} \times \hat{\varepsilon})\sqrt{\frac{\hbar\omega}{2\epsilon_0 c^2\mathscr{V}}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,a(t) + \text{H.c.}$$

(quantized magnetic-field mode) (15.33)

after quantization. In general, as in the classical case, the quantum fields must then be written as a superposition of all possible plane-wave modes. A key point, however, is that only the *time dependence* has been quantized—the spatial profile of the modes comes directly over from classical electromagnetism. This is a symptom of the electromagnetic field corresponding to the generalization of a harmonic oscillator to fields—the quantum version shares quite a lot of features with its classical counterpart.

A couple more comments are in order before moving on. Since one mode of the electromagnetic field is a harmonic oscillator, each mode has an associated occupation number (i.e., energy eigenstate), and the number is referred to by the ''number of photons,'' with an energy $\hbar\omega$ associated with each photon (and an $\hbar\omega/2$ associated with the ground or ''vacuum'' state). Of course, there can be superposition states of different photon numbers, but note that each mode has a separate photon number. Also, one of the main things we are after for the purposes of spontaneous emission is that both the electric- and magnetic-field operators have a nontrivial $\sqrt{\omega}$ dependence on the field frequency. There is, of course, also dependence on the mode volume, which we expect to cancel or become irrelevant at the end of the calculation as $\mathscr{V} \longrightarrow \infty$. As in the free-particle problem, it is possible to take a $\mathscr{V}$-independent normalization in anticipation of this limit, but it is a common convention to keep the volume dependence in the field operators. The reason is that often electromagnetic modes are confined to finite volumes (via optical cavities, resonators, and so on), in which case the combination $\hbar\omega/\mathscr{V}$ that appears in the field operators has the interpretation of a photon energy density.

15.2.2 Transition Amplitude

The decay of an atomic state means that the state is going down in energy from some excited state $|\mathrm{e}\rangle$ to a lower-energy state, say the ground state $|\mathrm{g}\rangle$. In the process, the field will change as well. We will assume that every mode is initially in the vacuum state $|0\rangle$ (''zero photons''), but that one mode, with polarization $\hat{\varepsilon}$ and wave vector $\mathbf{k}$, will make a transition $|0\rangle \longrightarrow |1\rangle$ (creating one photon in that mode). Thus, we can identify the initial and final states for the composite atom–field system as

$$|\,\mathsf{i}\,\rangle = |\mathrm{e}, 0\rangle, \qquad |\,\mathsf{f}\,\rangle = |\mathrm{g}, 1\rangle. \tag{15.34}$$

We are only labeling one field mode here, but this is a continuum-transition problem because there is a continuum of field modes in the same energy range. Then considering the electric-dipole interaction Hamiltonian

$$V = -\mathbf{d} \cdot \boldsymbol{\mathscr{E}}, \tag{15.35}$$

which is justified for optical transitions in atoms [see the discussion following Eq. (13.126)], the relevant transition amplitude is

$$V_{\mathsf{fi}} = -\langle \mathrm{g}|\mathbf{d}|\mathrm{e}\rangle \cdot \langle 1|\boldsymbol{\mathscr{E}}|0\rangle. \tag{15.36}$$

Then putting in the field operator (15.32), only the $a^\dagger$ term contributes, and so

$$V_{\mathsf{fi}}(t) = \hat{\varepsilon}^* \cdot \mathbf{d}_{\mathrm{ge}} \sqrt{\frac{\hbar\omega}{2\epsilon_0 \mathscr{V}}}\, e^{-i\mathbf{k}\cdot\mathbf{r}} e^{-i(\omega_{\mathrm{eg}}-\omega)t}. \tag{15.37}$$

Although it will not end up in the final expression, remember that the operator $e^{-i\mathbf{k}\cdot\mathbf{r}}$ is a momentum-shift operator, here representing the momentum recoil of $-\hbar\mathbf{k}$ associated with emitting the photon in the $\mathbf{k}$ direction. (This momentum shift would have shown up had we also tracked the center-of-mass atomic momentum as part of the initial and final states, in which case $|\mathrm{e}, \mathbf{p}, 0\rangle$ would decay to $|\mathrm{g}, \mathbf{p} - \hbar\mathbf{k}, 1\rangle$ via this dipole interaction.) Also, note that the time-dependence of the transition amplitude does not contribute to the final result, but for an energy-conserving emission ($\omega = \omega_{\mathrm{eg}}$), the interaction itself is time-independent. This is because the initial and final states (15.34) are approximately degenerate in the interaction with a quantized field. In a dipole interaction with a *classical* field the atomic levels are not degenerate, but this is compensated by the explicit time-dependence of the electric field.

15.2.3 Density of States

Ignoring for the moment that we have modes with polarization, the free-space mode functions have the form

$$f_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\mathscr{V}}}\, e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{15.38}$$

when quantized in the fictitious quantization volume $\mathscr{V}$. We can then compute the density of one-emitted-photon states as follows. As in Eq. (15.18), since we quantized the field in a volume with $\mathscr{V} = L^3$, the wave vectors are constrained to be

$$k_{x,y,z} = \frac{2\pi n_{x,y,z}}{L} = \frac{2\pi n_{x,y,z}}{\sqrt[3]{\mathscr{V}}}, \tag{15.39}$$

where the n_{x^j} are any integers, as a result of the periodic boundary conditions on the quantization box. Thus, in $\mathbf{k}$-space, the states form a cubic lattice with spacing $2\pi/\sqrt[3]{\mathscr{V}}$. We can then proceed by associating a cubic volume of $(2\pi)^3/\mathscr{V}$ with each state in $\mathbf{k}$-space, where this mini-volume "surrounds" its particular state. Now the set of all states with energy less than E is given by the set of all states in $\mathbf{k}$-space that fall within a radius $k_E = E/\hbar c$ of $\mathbf{k} = 0$. The volume of the sphere of this radius is $4\pi k_E^3/3$, and thus the number of states is given by dividing this volume by $(2\pi)^3/\mathscr{V}$. To account for polarizations, we can just multiply the result by 2 to count the two independent polarizations:

$$n(E) = 2\frac{4\pi k_E^3}{3}\frac{\mathscr{V}}{(2\pi)^3} = \frac{E^3\mathscr{V}}{3\pi^2\hbar^3c^3}. \tag{15.40}$$

Then the density of states is

$$\rho(E) = \frac{dn}{dE} = \frac{E^2\mathscr{V}}{\pi^2\hbar^3c^3}. \tag{15.41}$$

The relevant initial and final energy in this problem is $E_{\text{eg}} = \hbar\omega_{\text{eg}}$, being the energy of the initially excited atom, so that

$$\rho(E_{\text{f}}) = \frac{\omega_{\text{eg}}^2\mathscr{V}}{\pi^2\hbar c^3} \tag{15.42}$$

is the relevant density of states in the continuum.

15.2.4 Transition Rate

Now we have the pieces we need for the golden rule (15.12),

$$\Gamma_{\text{i}\to\mathcal{F}} = \frac{2\pi}{\hbar}|V_{\text{fi}}|^2\rho(E_{\text{f}}) = \frac{2\pi}{\hbar}|\hat{\varepsilon}\cdot\mathbf{d}_{\text{eg}}|^2\frac{\hbar\omega}{2\epsilon_0\mathscr{V}}\frac{\omega_{\text{eg}}^2\mathscr{V}}{\pi^2\hbar c^3} = |\hat{\varepsilon}\cdot\mathbf{d}_{\text{eg}}|^2\frac{\omega\omega_{\text{eg}}^2}{\pi\epsilon_0\hbar c^3}, \tag{15.43}$$

after using Eqs. (15.37) and (15.42). Remember that the Fermi golden rule came from perturbation theory for a time-independent perturbation, and thus conservation of energy implies $\omega \approx \omega_{\text{eg}}$. Also, for a spherically symmetric atom, $|\hat{\varepsilon}\cdot\mathbf{d}_{\text{eg}}|^2$ is the same as $|\hat{z}\cdot\mathbf{d}_{\text{eg}}|^2$, which is the same as $|\mathbf{d}_{\text{eg}}|^2/3$. (Note that this replacement is valid even for molecules and atomic states that lack spherical symmetry—the vacuum field is isotropic, so the final result can't be changed by an orientational average, which is what this replacement amounts to.) Thus, we finally have

$$\Gamma = \frac{\omega_{\text{eg}}^3|\mathbf{d}_{\text{eg}}|^2}{3\pi\epsilon_0\hbar c^3} = \frac{\omega_{\text{eg}}^3e^2|\mathbf{r}_{\text{eg}}|^2}{3\pi\epsilon_0\hbar c^3}. \tag{15.44}$$

(spontaneous decay rate, free space)

This is the rate of decay for the atomic state $|\text{e}\rangle$ to $|\text{g}\rangle$. If there are other decay paths available to $|\text{e}\rangle$, then the *total* decay rate is simply the sum of the decay rates to all possible lower-energy states. The other notable feature of this equation is the ω_{eg}^3 dependence, which reflects a rapid increase in the instability of a dipole transition as its energy increases. Remember that one factor of ω_{eg} came from the electric-field quantization [i.e., the factor $\sqrt{\omega}$ in Eq. (15.32)], while the other two factors came from the mode density in three dimensions. Also, the decay rate depends on $|\mathbf{d}_{\text{eg}}|^2$, although there is only one atom–field interaction (one photon emitted), and this is only first-order perturbation theory; the reason is that the rate represents a transition *probability*, not an *amplitude*.

15.2.4.1 Hydrogen 2P Decay

As a numerical example, let's compute the decay rate for the 2P states of hydrogen (note that the electron spin doesn't couple into the calculation we've done, so we won't distinguish between the $J = 1/2$ and $J = 3/2$ states). Let's specifically consider the decay from 2P($m_L = 0$) to 1S. We already computed the energy difference in Eq. (12.82), ignoring for the moment any reduced mass effects,

$$\hbar\omega_{\rm eg} = \frac{3\alpha^2 m_{\rm e}c^2}{8}, \tag{15.45}$$

and the nonvanishing component of the matrix element $\mathbf{r}_{\rm ge}$ is [Eq. (12.118)]

$$z_{\rm ge} = \frac{2^8 a_0}{3^5\sqrt{2}}. \tag{15.46}$$

Thus, we will need the square of the matrix element, which is

$$|\mathbf{r}_{\rm eg}|^2 = |z_{\rm ge}|^2 = \frac{2^{15}a_0^2}{3^{10}} = \frac{2^{15}\hbar^2}{3^{10}m_{\rm e}^2c^2\alpha^2}, \tag{15.47}$$

after using $a_0 = \hbar/m_{\rm e}c\alpha$. Also, using $\alpha = e^2/4\pi\epsilon_0\hbar c$, Eq. (15.44) becomes

$$\Gamma = \frac{4\omega_{\rm eg}^3\alpha|\mathbf{r}_{\rm eg}|^2}{3c^2}, \tag{15.48}$$

or putting in Eqs. (15.45) and (15.47), we obtain the result

$$\Gamma = \left(\frac{2}{3}\right)^8 \frac{m_{\rm e}c^2\alpha^5}{\hbar}. \tag{15.49}$$

(hydrogen 2P decay rate)

If we put in numbers, using the reduced mass μ in place of the electron mass $m_{\rm e}$, we find

$$\Gamma = 6.2649\times10^9\,{\rm s}^{-1}, \qquad \frac{\Gamma}{2\pi} = 99.709\,{\rm MHz}, \qquad \tau = \frac{1}{\Gamma} = 1.5962\,{\rm ns}. \tag{15.50}$$

(hydrogen 2P decay rate)

This numerical result is in remarkably good agreement with the accepted values[3] $6.2648\times10^8\,{\rm s}^{-1}$ for $J = 3/2$ and $6.2649\times10^8\,{\rm s}^{-1}$ for $J = 1/2$. Note that, owing to the spherical symmetry of the atom, all the 2P states decay at the same rate, independent of m_L (or more properly, the states at fixed J decay at the same rate, independent of m_J). Hooray for first-order perturbation theory!

15.2.4.2 Angular Distribution

Using the golden rule it is easy to go a bit further and work out the angular distribution of spontaneous decay. To do this we will use the same matrix element (15.37), except that we will consider the transition to a final state of definite $\mathbf{k}$. The density of states (15.42) is correspondingly modified to

$$\rho(E) = \frac{\omega_{\rm eg}^2\mathscr{V}}{8\pi^3\hbar c^3}\,d\Omega, \tag{15.51}$$

where we have added a solid-angle factor $d\Omega/4\pi$ for emission into this solid-angle element, but there is no other orientation dependence here because the electromagnetic vacuum is isotropic. We have also removed a factor of two that came from summing over two polarizations; we will handle this sum directly. The modified spontaneous-decay rate (15.44) is then

$$d\Gamma = \sum_\lambda \frac{\omega_{\rm eg}^3|\hat{\varepsilon}_\lambda\cdot\mathbf{d}_{\rm eg}|^2}{8\pi^2\epsilon_0\hbar c^3}\,d\Omega, \tag{15.52}$$

[3] https://www.nist.gov/pml/atomic-spectra-database

where $\lambda \in \{1, 2\}$ is a polarization index, and we are explicitly summing over the two independent polarizations.

To proceed it simplifies things to assume a particular form for the dipole operator. For example, for the 2P–1S decay in hydrogen, as we noted above, only the z-component of the dipole operator is nonvanishing, so that we can write

$$d\Gamma = \sum_\lambda |\hat{\varepsilon}_\lambda \cdot \hat{z}|^2 \frac{\omega_{\text{eg}}^3 |\mathbf{d}_{\text{eg}}|^2}{8\pi^2 \epsilon_0 \hbar c^3}\, d\Omega. \tag{15.53}$$

To carry out the polarization sum, note that $\hat{\varepsilon}_1$, $\hat{\varepsilon}_2$, and $\hat{k}$ form an orthonormal basis, and since we are summing over the two possible polarizations we may assume the polarization vectors to be real (i.e., we will sum over the two possible *linear* polarizations). Thus, in tensor notation,

$$\sum_\lambda |\hat{\varepsilon}_\lambda \cdot \hat{z}|^2 = \sum_\lambda \text{Tr}\Big[\hat{\varepsilon}_\lambda \otimes \hat{\varepsilon}_\lambda \cdot \hat{z} \otimes \hat{z}\Big] = \text{Tr}\Big[\Big(1 - \hat{k} \otimes \hat{k}\Big) \cdot \hat{z} \otimes \hat{z}\Big] = 1 - \big(\hat{k} \cdot \hat{z}\big)^2 = 1 - \cos^2\theta = \sin^2\theta, \tag{15.54}$$

and so the angular decay rate (15.53) becomes

$$\boxed{\frac{d\Gamma}{d\Omega} = \frac{\omega_{\text{eg}}^3 |\mathbf{d}_{\text{eg}}|^2}{8\pi^2 \epsilon_0 \hbar c^3} \sin^2\theta.}$$

(spontaneous decay rate, angular distribution) (15.55)

The angular dependence is the characteristic $\sin^2\theta$ radiation distribution from a linear dipole. Integrating this decay density over all angles gives a factor of $8\pi/3$, which recovers the total rate (15.44).

15.2.4.3 Temperature Dependence

An alternate calculation of the spontaneous-decay rate will allow us to take advantage of linear-response theory and infer the temperature dependence of the decay rate. Starting with Fermi's golden rule in the form (15.9)

$$\Gamma_{\mathsf{i}\to\mathsf{f}} = \frac{2\pi}{\hbar} |V_{\mathsf{fi}}|^2\, \delta(E_{\mathsf{fi}}), \tag{15.56}$$

we will again consider the decay from an atomic excited state $|\text{e}\rangle$ to a lower state $|\text{g}\rangle$. However, to correctly track energy conservation, we should also include initial and final field states $|I\rangle$ and $|F\rangle$, with a sum over all possible final field states:

$$\Gamma_{\mathsf{i}\to\mathsf{f}} = \frac{2\pi}{\hbar} \sum_F |\langle \text{g}\, F|V|\text{e}\, I\rangle|^2\, \delta(E_\text{g} + E_F - E_\text{e} - E_I). \tag{15.57}$$

Using the integral representation of the delta function, this becomes

$$\Gamma_{\mathsf{i}\to\mathsf{f}} = \frac{1}{\hbar^2} \sum_F \int_{-\infty}^{\infty} d\tau\, |\langle \text{g}\, F|V|\text{e}\, I\rangle|^2\, e^{i\omega_{\text{eg}}\tau} e^{i(E_I - E_F)\tau/\hbar}, \tag{15.58}$$

where $\omega_{\text{eg}} = (E_\text{e} - E_\text{g})/\hbar > 0$ as usual. For the dipole interaction Hamiltonian,

$$\begin{aligned}
\Gamma_{\mathsf{i}\to\mathsf{f}} &= \frac{1}{\hbar^2} \sum_F \int_{-\infty}^{\infty} d\tau \left|\langle\, \mathsf{i}\, |\mathbf{d}|\, \mathsf{f}\,\rangle \cdot \langle I|\boldsymbol{\mathscr{E}}(\mathbf{r})|F\rangle\right|^2 e^{i\omega_{\text{eg}}\tau} e^{i(E_I - E_F)\tau/\hbar} \\
&= \frac{1}{\hbar^2} \sum_F \text{Tr}\left[\mathbf{d}_{\text{ge}} \otimes \mathbf{d}_{\text{eg}} \cdot \int_{-\infty}^{\infty} d\tau\, \boldsymbol{\mathscr{E}}_{IF} \otimes \boldsymbol{\mathscr{E}}_{FI} e^{i\omega_{\text{eg}}\tau} e^{i(E_I - E_F)\tau/\hbar}\right] \\
&= \frac{1}{\hbar^2} \sum_F \text{Tr}\left[\mathbf{d}_{\text{ge}} \otimes \mathbf{d}_{\text{eg}} \cdot \int_{-\infty}^{\infty} d\tau\, \langle I|\boldsymbol{\mathscr{E}}(\mathbf{r},\tau)|F\rangle \otimes \langle F|\boldsymbol{\mathscr{E}}(\mathbf{r},0)|I\rangle\, e^{i\omega_{\text{eg}}\tau}\right] \\
&= \frac{1}{\hbar^2} \text{Tr}\left[\mathbf{d}_{\text{ge}} \otimes \mathbf{d}_{\text{eg}} \cdot \int_{-\infty}^{\infty} d\tau\, \langle I|\boldsymbol{\mathscr{E}}(\mathbf{r},\tau) \otimes \boldsymbol{\mathscr{E}}(\mathbf{r},0)|I\rangle\, e^{i\omega_{\text{eg}}\tau}\right],
\end{aligned} \tag{15.59}$$

where in the second equality we transformed the field operators into the interaction picture (while the dipole operators remain in the Schrödinger picture). The integral here is of the form of a generalized susceptibility tensor for the electric field, encoding the response of the field to forcing by the atomic dipole moment. In fact the field can respond in different ways according to the presence of materials or boundary conditions, which can all be encoded in this correlation function. (Also, to note a technical point, we quantized one mode of the field as a separate object, but in the field operators here there is an implicit sum over all possible modes.)

We derived the decay rate above assuming that the atom and field were in definite initial states. However, the result is linear in a field expectation value, and is thus still valid when averaged over initial field states. The result then applies to any pure or mixed state of the field, such as for a thermal-equilibrium state of the field. Now consider the fluctuation–dissipation theorem in the form (14.42):

$$\frac{\chi_{\mu\nu}(\omega) - \chi^*_{\nu\mu}(\omega)}{e^{\beta\hbar\omega} - 1} = -\frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau \left\langle \tilde{x}_\nu(0)\, \tilde{x}_\mu(\tau)\right\rangle e^{i\omega\tau}. \tag{15.60}$$

To better match the form of the correlation integral in Eq. (15.59), we can invert the signs of ω and τ:

$$\frac{\chi_{\mu\nu}(-\omega) - \chi^*_{\nu\mu}(-\omega)}{1 - e^{-\beta\hbar\omega}} = \frac{i}{\hbar}\int_{-\infty}^{\infty} d\tau \left\langle \tilde{x}_\nu(\tau)\, \tilde{x}_\mu(0)\right\rangle e^{i\omega\tau}. \tag{15.61}$$

At this point it is possible to adapt this formula to the electric field and evaluate the associated susceptibility for the electric field in free space. However, it is sufficient to note that—independent of the details of the susceptibility—the temperature dependence appears as a factor $[1 - e^{-\beta\hbar\omega}]^{-1}$, which reduces to unity in the limit $T \longrightarrow 0$, and that we have already computed the $T = 0$ decay rate. Thus we can modify the decay rate (15.44) by including this factor to incorporate temperature dependence, with the result

$$\Gamma(T) = \frac{1}{1 - e^{-\hbar\omega_{\rm eg}/k_{\rm B}T}} \frac{\omega_{\rm eg}^3 |\mathbf{d}_{\rm ge}|^2}{3\pi\epsilon_0\hbar c^3} = \frac{\Gamma(0)}{1 - e^{-\hbar\omega_{\rm eg}/k_{\rm B}T}}. \tag{15.62}$$

(spontaneous decay rate, thermal equilibrium)

The decay rate increases monotonically with temperature, diverging as $T \longrightarrow \infty$. The extra decay is due to stimulated emission and absorption of real (thermal, in the blackbody sense) photons, reinforcing the vacuum effect of spontaneous decay (which can be interpreted as stimulated emission due to the vacuum field). Note, however, that while the decay is still exponential (albeit at a modified rate), the steady state is *not* $|\mathrm{g}\rangle$, but rather the appropriate thermal (Boltzmann) equilibrium average of $|\mathrm{g}\rangle$ and $|\mathrm{e}\rangle$ (and whatever other states may happen to be around).

15.3 Photoionization

Another nice example of Fermi's golden rule in action is the ionization of the hydrogen atom due to a high-energy laser field. This process is called **photoionization**, but can also be called the **photoeffect**[4] or the **photoelectric effect**[5] (though the latter term also refers to the liberation of electrons from a metal or other bulk material surface). Since the laser must be strong to produce significant ionization, we will assume a classical field of frequency ω. However, since we have the quantized electromagnetic field in hand, we will go ahead and use it, under the assumption that the ''classical'' field is in a coherent state $|\alpha\rangle$. Note that the Fermi golden rule can be applied directly with a truly classical field $\hat{\varepsilon}\mathscr{E}_0 e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}$, but since the interaction varies harmonically in time, the golden rule must be rederived for a time-harmonic perturbation, which amounts to an average over two terms where the energy delta function is shifted by $\pm\hbar\omega$. In any case, the calculation here is a useful example to see how the quantum field works in the classical regime.

[4] A. S. Davydov, *Quantum Mechanics*, 2nd ed, translated by D. ter Haar (Pergamon, 1976), Chapter 12, Section 99, pp. 426-8 (ISBN: 0080204384).

[5] Hans C. O'hanian, *Principles of Quantum Mechanics* (Prentice-Hall, 1990) (ISBN: 0137127952), Section 10.6, pp. 294-8.

We will assume again the electric-dipole interaction

$$V = -\mathbf{d} \cdot \boldsymbol{\mathscr{E}}, \tag{15.63}$$

which means that the atom is sufficiently small that it may be treated as a point dipole on the scale of the field wavelength. On the other hand, we will also assume the atom to achieve a highly ionized state, which means that we will treat the final state as a free-particle state (though not a *relativistic* free particle state, so the final energy should not be *too* high), an idealization called the **Born approximation**.[6] These are somewhat conflicting requirements, as the high ionization energy requires a relatively short wavelength, something we will discuss at the end of the calculation. It is maybe also not obvious that the dipole approximation is compatible with the treatment of an ionized state, which is by definition an extended state. However, it is sufficient for the bound state to satisfy the requirements for the dipole approximation, because the dipole approximation only affects the matrix element of the interaction potential between the bound and ionized states, and the bound state will cut off the matrix-element integral much beyond the length scale a_0.

To better pin down the highly ionizing approximation, recall that the **Rydberg constant** R is defined such that the hydrogen energies are given by (12.188)

$$E_n = -\frac{\alpha^2 m_\mathrm{e} c^2}{2n^2} = -\frac{hcR}{n^2}, \tag{15.64}$$

so that the ionization energy of the 1S state is

$$E_\mathrm{R} = \frac{\alpha^2 m_\mathrm{e} c^2}{2} = hcR = \frac{\hbar^2}{2m_\mathrm{e} a_0^2}. \tag{15.65}$$

Here, the Rydberg energy is $E_\mathrm{R} \approx 13.6\,\mathrm{eV}$ (thus R is the Rydberg energy in wave-number units), and in the last expression $\hbar/a_0$ appears as an effective ''ionization momentum'' for the hydrogen atom. The highly ionizing approximation thus means that $\hbar\omega \gg E_\mathrm{R}$ in terms of energy scales, or in terms of the momentum of the final state, $p \gg \hbar/a_0$.

15.3.1 Density of States

To obtain the density of ionized electron states, note that the idea is the same as in Eq. (15.40) if we discard the factor of 2 for polarizations and interpret the wave-number shell as $k_E = p/\hbar$, and then use $p = \sqrt{2m_\mathrm{e}E}$. Thus,

$$n(E) = \frac{4\pi k_E^3}{3}\frac{\mathscr{V}_{\mathrm{e}^-}}{(2\pi)^3} = \frac{p^3 \mathscr{V}_{\mathrm{e}^-}}{6\pi^2\hbar^3} = \frac{\sqrt{2} m_\mathrm{e}^{3/2} E^{3/2} \mathscr{V}_{\mathrm{e}^-}}{3\pi^2\hbar^3}, \tag{15.66}$$

where $\mathscr{V}_{\mathrm{e}^-}$ is the quantization volume for the electron modes. In any sane setup of the problem this would correspond to the field quantization volume $\mathscr{V}$ (corresponding to a ''bounded universe''), but in the interest of bookkeeping we will keep the two volumes distinct, as this second quantization volume is the only one that will cancel. Now differentiating $n(E)$,

$$\rho(E) = \frac{dn(E)}{dE} = \frac{m_\mathrm{e}\sqrt{2m_\mathrm{e}E}\,\mathscr{V}_{\mathrm{e}^-}}{2\pi^2\hbar^3}, \tag{15.67}$$

we can introduce the angular density of states as in the spontaneous-emission example by introducing $d\Omega/4\pi$:

$$d\rho(E) = \frac{m_\mathrm{e}\sqrt{2m_\mathrm{e}E}\,\mathscr{V}_{\mathrm{e}^-}}{(2\pi\hbar)^3}\,d\Omega. \tag{15.68}$$

[6] The terminology ''Born approximation'' refers to a weak-scattering approximation. As the incident electromagnetic wave moves over the extent of the atom, roughly speaking the amplitude of the wave should decrease as it is converted into an increasing amplitude for electron emission. The assumption of a plane-wave scattered solution is one possible Born approximation; an alternative would be an ionized eigenstate of the Coulomb potential. See C. Bottcher, *Photoionization* (Science Research Council, 1974), `https://www.osti.gov/etdeweb/servlets/purl/4950365`. See also Hans A. Betheand Edwin E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, 1957) (ISBN: 9780306200229) (doi: 10.1007/978-1-4613-4104-8), Sections 7, 9, and 70.

From energy conservation, the final ionized state satisfies $E_{\mathsf{f}} = \hbar\omega - E_{\mathrm{R}} \approx \hbar\omega$, and thus

$$d\rho(E_{\mathsf{f}}) = \frac{m_{\mathrm{e}}\sqrt{2m_{\mathrm{e}}\hbar\omega}\mathscr{V}_{\mathrm{e}^-}}{(2\pi\hbar)^3}\,d\Omega \tag{15.69}$$

in the highly ionized approximation.

15.3.2 Transition Amplitude

The initial and final composite atom–field states are

$$|\,\mathsf{i}\,\rangle = |\mathrm{g},\alpha\rangle, \qquad |\,\mathsf{f}\,\rangle = |\mathbf{p},\alpha\rangle. \tag{15.70}$$

Note that, in the classical regime, the photon number is so large that we will (mostly) neglect the loss of a single photon in the ionization process. Recalling that the coherent state is an eigenstate of the annihilation operator ($a|\alpha\rangle = \alpha|\alpha\rangle$), we can write (at $t = 0$)

$$\begin{aligned} V_{\mathsf{fi}} &= -\langle\mathbf{p},\alpha|\mathbf{d}\cdot\boldsymbol{\mathscr{E}}|\mathrm{g},\alpha\rangle \\ &= \sqrt{\frac{\hbar\omega}{2\epsilon_0\mathscr{V}}}\,\langle\mathbf{p}|\mathbf{d}\cdot\hat{\varepsilon}\,\alpha\,e^{i\mathbf{k}\cdot\mathbf{r}}|\mathrm{g}\rangle \\ &= \sqrt{\frac{\hbar\omega}{2\epsilon_0\mathscr{V}}}\,\langle\mathbf{p}-\hbar\mathbf{k}|\mathbf{d}|\mathrm{g}\rangle\cdot\hat{\varepsilon}\,\alpha, \end{aligned} \tag{15.71}$$

where we used the action of $e^{i\mathbf{k}\cdot\mathbf{r}}$ as a momentum shift operator [Eq. (13.101)]:

$$e^{i\mathbf{k}\cdot\mathbf{r}}|\mathbf{p}\rangle = |\mathbf{p}+\hbar\mathbf{k}\rangle. \tag{15.72}$$

Note that the electric-field matrix element should have yielded a second term corresponding to $a^\dagger$; however, we are neglecting it in the rotating-wave approximation because we only want to consider the photon-absorption process, not stimulated emission. In a more careful accounting of the field state, remember that only matrix elements of the form $\langle n-1|a|n\rangle$ should contribute, because the field is losing one photon in the process in order to conserve energy. In the true classical calculation, this amounts to dropping the nonresonant delta term that can never be satisfied due to energy conservation.

Thus, we have the transition probability

$$|V_{\mathsf{fi}}|^2 = \frac{\langle n\rangle\hbar\omega}{2\epsilon_0\mathscr{V}}\,|\hat{\varepsilon}\cdot\langle\mathbf{p}-\hbar\mathbf{k}|\mathbf{d}|\mathrm{g}\rangle|^2, \tag{15.73}$$

where we have used $\langle n\rangle = \langle a^\dagger a\rangle = |\alpha|^2$ for a coherent state. Then from the golden rule (15.12), the rate of ionization into $d\Omega$ is

$$d\Gamma = \frac{2\pi}{\hbar}\frac{\langle n\rangle\hbar\omega}{2\epsilon_0\mathscr{V}}\left|\hat{\varepsilon}\cdot\langle\mathbf{p}-\hbar\mathbf{k}|\mathbf{d}|\mathrm{g}\rangle\right|^2\frac{m_{\mathrm{e}}\sqrt{2m_{\mathrm{e}}\hbar\omega}\mathscr{V}_{\mathrm{e}^-}}{(2\pi\hbar)^3}\,d\Omega = \frac{\pi^2\langle n\rangle(2m_{\mathrm{e}}\hbar\omega)^{3/2}\mathscr{V}_{\mathrm{e}^-}}{\epsilon_0(2\pi\hbar)^4\mathscr{V}}\left|\hat{\varepsilon}\cdot\langle\mathbf{p}-\hbar\mathbf{k}|\mathbf{d}|\mathrm{g}\rangle\right|^2 d\Omega. \tag{15.74}$$

What we have so far is a fairly general expression for a one-electron atom; what remains is to evaluate the dipole matrix element in the specific case of hydrogen. We are taking $|\mathrm{g}\rangle$ to be the hydrogen 1S state, and we assume the field to have linear polarization, $\hat{\varepsilon} = \hat{z}$. The 1S hydrogen wave function (12.77) is

$$\langle\mathbf{r}|\mathrm{g}\rangle = \langle\mathbf{r}|\psi_0\rangle = \frac{1}{\sqrt{\pi a_0^3}}\,e^{-r/a_0}, \tag{15.75}$$

while the free-particle wave function normalized in the finite volume is of the form (15.38), or

$$\langle\mathbf{r}|\mathbf{p}\rangle = \frac{1}{\sqrt{\mathscr{V}_{\mathrm{e}^-}}}\,e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}. \tag{15.76}$$

Now, to compute the matrix element $\langle \mathbf{p} - \hbar\mathbf{k}|z|\mathrm{g}\rangle$, we will use a trick to simplify it before working out the integral. For a Hamiltonian of the form $H_0 = p^2/2m + V(\mathbf{r})$, then $[\mathbf{r}, H_0] = i\hbar\mathbf{p}/m$, and thus in general we have

$$\begin{aligned}\langle\, \mathsf{f}\,|\mathbf{p}|\,\mathsf{i}\,\rangle &= -\frac{im}{\hbar}\langle\, \mathsf{f}\,|[\mathbf{r}, H_0]|\,\mathsf{i}\,\rangle \\ &= \frac{im}{\hbar}\langle\, \mathsf{f}\,|\Big(H_0\mathbf{r} - \mathbf{r}H_0\Big)|\,\mathsf{i}\,\rangle \\ &= \frac{im}{\hbar}\big(E_\mathsf{f} - E_\mathsf{i}\big)\langle\, \mathsf{f}\,|\mathbf{r}|\,\mathsf{i}\,\rangle \\ &= im\omega_\mathsf{fi}\langle\, \mathsf{f}\,|\mathbf{r}|\,\mathsf{i}\,\rangle,\end{aligned} \tag{15.77}$$

where the two states are assumed to be eigenstates of H_0. Thus,

$$\begin{aligned}\langle \mathbf{p} - \hbar\mathbf{k}|z|\mathrm{g}\rangle &= -\frac{i}{m_\mathrm{e}\omega}\langle \mathbf{p} - \hbar\mathbf{k}|p_z|\mathrm{g}\rangle \\ &= -\frac{ip_z}{m_\mathrm{e}\omega}\langle \mathbf{p} - \hbar\mathbf{k}|\mathrm{g}\rangle \\ &= -\frac{ip\cos\theta}{m_\mathrm{e}\omega}\langle \mathbf{p} - \hbar\mathbf{k}|\mathrm{g}\rangle = -i\sqrt{\frac{2\hbar}{m_\mathrm{e}\omega}}\cos\theta\,\langle \mathbf{p} - \hbar\mathbf{k}|\mathrm{g}\rangle,\end{aligned} \tag{15.78}$$

where in the highly ionizing approximation $p^2 \gg \hbar^2/a_0^2$, so that we have used $\hbar\omega = p^2/2m_\mathrm{e} + E_\mathrm{R} \approx p^2/2m_\mathrm{e}$. Also, we have already mentioned the polarization orientation $\hat{\varepsilon} = \hat{z}$, so that $k_z = \hat{\varepsilon}\cdot\mathbf{k} = 0$, and thus we used $p_z - \hbar k_z = p_z$ in the second equality of Eqs. (15.78). We have additionally used $p_z - \hbar k_z \approx p_z$, to be justified shortly. To be definite, we will assume the propagation direction $\mathbf{k}$ of the optical field lies along the $\hat{x}$ direction; then we are labeling the outgoing direction of the ionized electron (i.e., $\mathbf{p}$) by the polar coordinates (θ, ϕ). Since we have introduced these orientations, it will soon be handy to note that

$$(\mathbf{p} - \hbar\mathbf{k})^2 = p^2 + (\hbar k)^2 - 2\hbar\mathbf{k}\cdot\mathbf{p} = p^2 + (\hbar k)^2 - 2\hbar kp\sin\theta\cos\phi. \tag{15.79}$$

Here the photon momentum $\hbar k$ is small compared to the final electron momentum, as we can see by calculating

$$\frac{\hbar k}{p} = \frac{\hbar\omega}{pc} \approx \frac{p^2/2m_\mathrm{e}}{pc} = \frac{p}{2m_\mathrm{e}c} = \frac{v}{2c} \ll 1, \tag{15.80}$$

where $v = p/m_\mathrm{e}$ is the ejection speed of the electron. Thus the combination $(\mathbf{p} - \hbar\mathbf{k})^2$ is of the order of p^2 (that is, there is not any substantial cancellation of the vectors). So, we will be able to make the approximation

$$(\mathbf{p} - \hbar\mathbf{k})^2 + \frac{\hbar^2}{a_0^2} \approx p^2\left(1 - \frac{v}{c}\sin\theta\cos\phi\right) \tag{15.81}$$

since again $p^2 \gg \hbar^2/a_0^2$.

In the matrix element (15.78) we still need to compute a projection of the 1S state into the momentum representation, of the form

$$\begin{aligned}\langle \mathbf{p}|\mathrm{g}\rangle &= \frac{1}{\sqrt{\pi a_0^3\mathscr{V}_{\mathrm{e}^-}}}\int d^3r\, e^{-i\mathbf{p}\cdot\mathbf{r}/\hbar}\, e^{-r/a_0} \\ &= \frac{1}{\sqrt{\pi a_0^3\mathscr{V}_{\mathrm{e}^-}}}\int_0^\infty dr\, r^2\,\frac{4\pi\sin pr/\hbar}{pr/\hbar}\, e^{-r/a_0} \\ &= \frac{1}{\sqrt{\pi a_0^3\mathscr{V}_{\mathrm{e}^-}}}\frac{8\pi\hbar^4}{a_0(p^2 + \hbar^2/a_0^2)^2} \\ &= \frac{\sqrt{\pi}8\hbar^4}{\sqrt{a_0^5\mathscr{V}_{\mathrm{e}^-}}(p^2 + \hbar^2/a_0^2)^2}.\end{aligned} \tag{15.82}$$

More specifically, we should shift this in momentum to

$$\begin{aligned}\langle \mathbf{p}-\hbar\mathbf{k}|\mathrm{g}\rangle &= \frac{\sqrt{\pi}8\hbar^4}{\sqrt{a_0^5\mathscr{V}_{\mathrm{e}^-}}[(\mathbf{p}-\hbar\mathbf{k})^2+\hbar^2/a_0^2]^2} \\ &\approx \frac{\sqrt{\pi}8\hbar^4}{\sqrt{a_0^5\mathscr{V}_{\mathrm{e}^-}}\,p^4[1-(v/c)\sin\theta\cos\phi]^2} \\ &\approx \frac{\sqrt{\pi}2\hbar^2}{\sqrt{a_0^5\mathscr{V}_{\mathrm{e}^-}}\,m_{\mathrm{e}}^2\omega^2[1-(v/c)\sin\theta\cos\phi]^2}.\end{aligned} \tag{15.83}$$

where we used Eq. (15.81), and then $\hbar\omega \approx p^2/2m_{\mathrm{e}}$. Thus, we have the matrix element

$$\langle \mathbf{p}-\hbar\mathbf{k}|z|\mathrm{g}\rangle = -i\sqrt{\frac{8\pi}{\mathscr{V}_{\mathrm{e}^-}}}\left(\frac{\hbar}{m_{\mathrm{e}}\omega a_0}\right)^{5/2}\frac{\cos\theta}{[1-(v/c)\sin\theta\cos\phi]^2} \tag{15.84}$$

after putting Eq. (15.83) into Eq. (15.78).

15.3.3 Ionization Rate and Cross-Section

With the expression (15.84) for the matrix element, the transition rate (15.74) into angle $d\Omega$ becomes

$$d\Gamma = \frac{16e^2\hbar^6\langle n\rangle}{\pi\epsilon_0 a_0^5(2m_{\mathrm{e}}\hbar\omega)^{7/2}\mathscr{V}}\frac{\cos^2\theta}{[1-(v/c)\sin\theta\cos\phi]^4}\,d\Omega. \tag{15.85}$$

Note that at this point $\mathscr{V}_{\mathrm{e}^-}$ has cancelled, but the quantization volume for the electromagnetic field has not. It is conventional to express the transition rate in terms of a **cross-section** σ, defined such that

$$\Gamma = \sigma \times (\text{photon flux}). \tag{15.86}$$

Intuitively, a photon flux is a rate of incident photons per unit area; the cross section has dimensions of area, and when multiplied by the photon flux, results in a rate of ionization. It is as if the atom "catches" all of the photons that impinge on the cross-sectional area, and converts the caught photons into escaped electrons (though the cross-section does not correspond directly to any physical area of the atom). The photon flux is, on average, the photon density times the propagation speed, or $\langle n\rangle c/\mathscr{V}$. Thus, the cross-section (per unit solid angle) is

$$\frac{d\sigma}{d\Omega} = \frac{16e^2\hbar^6}{\pi\epsilon_0 c a_0^5(2m_{\mathrm{e}}\hbar\omega)^{7/2}}\frac{\cos^2\theta}{[1-(v/c)\sin\theta\cos\phi]^4} \tag{15.87}$$

This expression simplifies somewhat if we define the (angular) frequency corresponding to the ionization energy E_{R},

$$\omega_{\mathrm{R}} := \frac{E_{\mathrm{R}}}{\hbar} = \frac{\hbar}{2m_{\mathrm{e}}a_0^2}, \tag{15.88}$$

in which case we find

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{8}{\pi\epsilon_0}\frac{e^2}{m_{\mathrm{e}}c}\frac{\omega_{\mathrm{R}}^{5/2}}{\omega^{7/2}}\frac{\cos^2\theta}{[1-(v/c)\sin\theta\cos\phi]^4}} \tag{15.89}$$

(differential photoionization cross-section)

Note that electrons are primarily kicked out along the polarization direction of the electric field ($\theta = 0$ or $\theta = \pi$), which is sensible. The angular factor in the denominator represents a small correction to the angular distribution, as a result of the photon momentum; it favors the $\mathbf{k}$ and $-\mathbf{k}$ directions. Remember that the smallness of this correction is related to the validity of the dipole approximation. We could have made a stricter dipole approximation $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$ in Eqs. (15.71), which is equivalent to $\lambda \gg a_0$. In this case the derivation would carry through with $\mathbf{p}-\hbar\mathbf{k}$ replaced by $\mathbf{p}$, which is equivalent to setting $v/c = 0$ in Eq. (15.81). In this case the angular factor in the denominator would be absent.

Integrating the differential cross-section over all angles gives a factor of $4\pi/3$ if we ignore the v/c denominator factor, and thus the *total* cross section is approximately

$$\sigma = \frac{32}{3\epsilon_0}\frac{e^2}{m_e c}\frac{\omega_R^{5/2}}{\omega^{7/2}}. \qquad (15.90)$$
(total photoionization cross-section)

[Keeping the velocity dependence to linear order through the integration leads to an extra overall factor $(1 + 3\pi v/4)$ in the cross-section.] Interestingly, the cross-section decreases with frequency, which says that ionization is in some sense more difficult with increasing frequency. This is due to the transition amplitude (the density of states has the opposite behavior), because the ionized states become an increasingly poor match to the hydrogen ground state.

Interestingly, it is possible to obtain an improved expression in closed form for the total cross section by using a true ionized wave function of the Coulomb potential, rather than a plane wave. The resulting expression may be written[7]

$$\sigma = 2\pi\sqrt{\frac{\omega_R}{\omega}}\sigma_{\text{plane}}\frac{e^{-4s\cot^{-1}s}}{1-e^{-2\pi s}}, \qquad s := \sqrt{\frac{\omega_R}{\omega-\omega_R}}, \qquad (15.91)$$

where σ_{plane} is the cross section from Eq. (15.90).

In deriving the cross-section here, recall that we assumed highly ionizing radiation, so that $p^2 \gg \hbar^2/a_0^2$, where $\hbar\omega \approx p^2/2m_e$. Equivalently, this reads $\hbar\omega \gg E_R$—we can ignore the binding energy of the electron compared to the ionized-state energy. This is the same as the plane-wave approximation, which allowed us to use plane waves for the ionized states. We further assumed $\lambda = 2\pi c/\omega \gg a_0$, which is the dipole approximation (or long-wavelength approximation). Together, these two assumptions constrain the range of valid photon energies to

$$E_R \ll \hbar\omega \ll \frac{hc}{a_0}. \qquad (15.92)$$

Putting in numbers, this energy range is

$$E_R \approx 13.6\,\text{eV} \ll \hbar\omega \ll 23.4\,\text{keV}, \qquad (15.93)$$

or converting these energies to wavelengths,

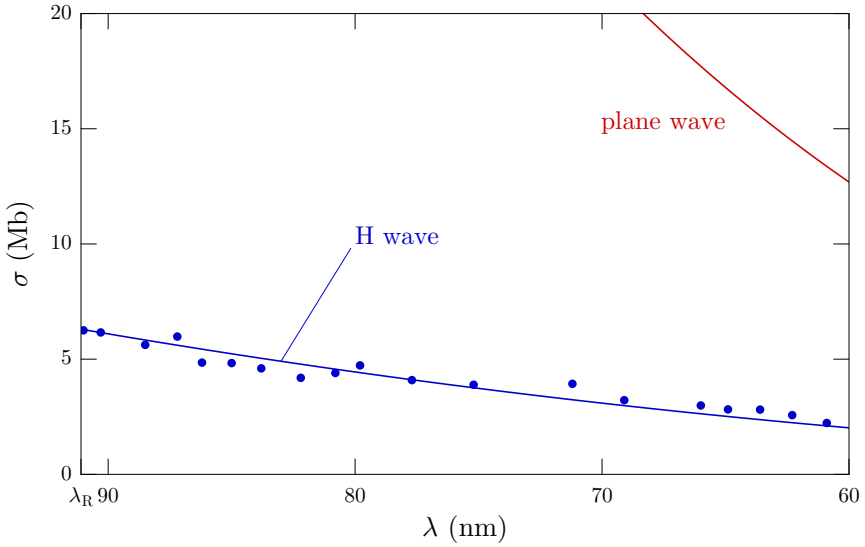
$$53\,\text{pm} \ll \lambda \ll \lambda_R \approx 91.1\,\text{nm}, \qquad (15.94)$$

where $\lambda_R = hc/E_R$ is the wavelength corresponding to the hydrogen ionization limit. The light here ranges from the vacuum ultraviolet to x-rays (''hard'' x-rays).

To illustrate the validity of the approximations here, the plot below shows experimental measurements[8] of the hydrogen ionization cross section, with the simple approximate cross section based on assuming plane-wave ionized states [Eq. (15.90), labeled ''plane wave''], as well as the improved cross section based on the ionized hydrogen wave function [Eq. (15.91), labeled ''H wave''].

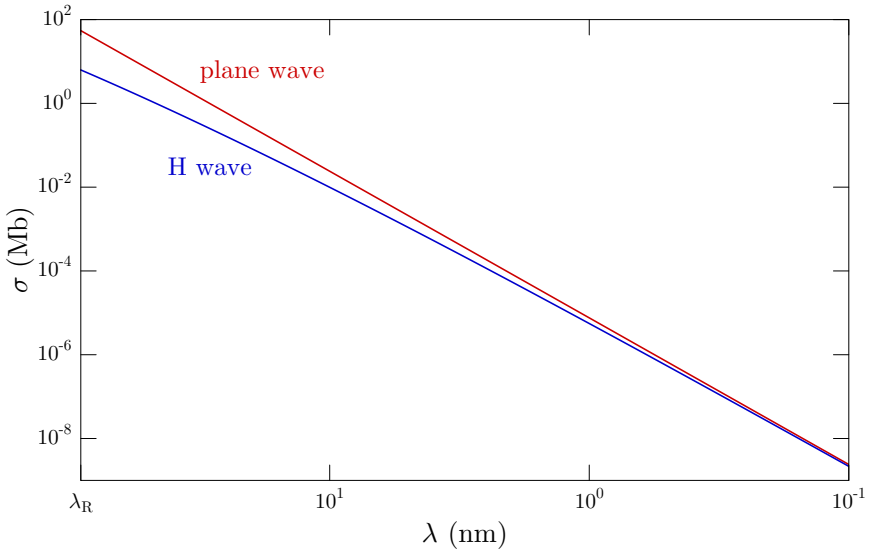
[7] Hans A. Bethe and Edwin E. Salpeter, *op. cit.*, Eqs. (71.7) and (69.3). This book also discussed the plane-wave approximation, of course, but also treats relativistic effects and gives expressions for atoms beyond hydrogen.

[8] Data from H. P. Palenius, J. L. Kohl, and W. H. Parkinson, ''Absolute measurement of the photoionization cross section of atomic hydrogen with a shock tube for the extreme ultraviolet,'' *Physical Review A* **13**, 1805 (1976) (doi: 10.1103/PhysRevA.13.1805).



The cross section is given in Mb (megabarns, where $1\,\text{barn} = 10^{-28}\,\text{m}^2$, as in "the broad side of a barn"). Note that the wavelength in the horizontal axis decreases from left to right, to mimic the trend of decreasing cross section with photon frequency. The experimental measurements were taken in the low-energy regime just above the ionization threshold, so the requirement $\lambda \ll \lambda_R \approx 91\,\text{nm}$ for the plane-wave approximation to hold is not satisfied. Not surprisingly, the data agree much better with the improved cross-section calculation.

To better compare the two approximate cross-sections, they are both plotted logarithmically over a much wider range of wavelengths in the plot below.



Note that they tend to converge in the limit of small wavelength, although the right-hand side of this graph is where the constraint $\lambda \gg 53\,\text{pm}$ is no longer satisfied, and relativistic corrections should be incorporated. Nevertheless, it is possible to see that the plane-wave approximation is improving for smaller λ: while the plane-wave cross section (15.90) is a pure $\lambda^{7/2}$ power law, the improved cross section crosses over to a λ^4 scaling at larger wavelengths close to the ionization limit.

15.4 The Continuum in the Resolvent Formalism

One cool application of the resolvent formalism is that it directly connects Fermi's golden rule to the exponential decay of states. [9] To see this connection, let's start by considering an eigenstate $|\psi_0\rangle$ of H_0 coupled to a continuum by a potential V, and define the projector for this state and the complementary projector,

$$P = |\psi_0\rangle\langle\psi_0|, \qquad Q = 1 - P, \tag{15.95}$$

respectively.[10] As in perturbation theory (Chapter 12), we can set up a time-independent, perturbed Hamiltonian

$$H = H_0 - V, \tag{15.96}$$

with perturbed and unperturbed resolvents,

$$G(z) = \frac{1}{z - H} = \frac{1}{z - H_0 + V}, \qquad G_0(z) = \frac{1}{z - H_0}, \tag{15.97}$$

respectively. These resolvents are connected by the formula [Eq. (12.9)]

$$G(z) = G_0(z) + \lambda G_0(z) V G(z). \tag{15.98}$$

The idea is to partition this relation into parts that refer to $|\psi_0\rangle$ and to its coupling to the rest of Hilbert space. By eliminating the coupling, a closed expression for the matrix element $\langle\psi_0|G(z)|\psi_0\rangle$ will result. This matrix element will describe the modification of $|\psi_0\rangle$ due to the coupling, including decay to the continuum. Note that this "$P + Q$" projector formalism is made to easily generalize to a *set* of decaying states that define the subspace of P. This could correspond, for example, to a set of states in a metastable potential well that are all decaying to the exterior. This generalization will basically require that V is diagonal on P's subspace (i.e., any couplings among the decaying states should have already been accounted for in H_0), as we will note below.

Again, the projection PGP of the perturbed resolvent onto $|\psi_0\rangle$'s subspace is what we ultimately seek. To compute this, we can start by applying P to both sides of Eq. (15.98), we can use the fact that P and Q are projectors, so that $P^2 = P$ and $Q^2 = Q$ (and $PQ = QP = 0$), that $[H_0, P] = 0$, and that the identity is $(P + Q) = 1$ to compute this as

$$\begin{aligned} PGP &= PG_0P + PG_0VGP \\ &= PG_0P + PG_0PV(P+Q)GP \\ &= PG_0P + (PG_0P)(PVP)(PGP) + (PG_0P)(PVQ)(QGP) \\ &= PG_0P\big[1 + (PVP)(PGP) + (PVQ)(QGP)\big]. \end{aligned} \tag{15.99}$$

We can see from this expression that PGP is related to QGP, which describes the coupling of $|\psi_0\rangle$ to the continuum. We will thus need an expression for QGP too. Using similar manipulations as in Eqs. (15.99), we find

$$\begin{aligned} QGP &= QG_0VGP \\ &= QG_0QV(P+Q)GP \\ &= (QG_0Q)(QVP)(PGP) + (QG_0Q)(QVQ)(QGP). \end{aligned} \tag{15.100}$$

[9] The classic references are Marvin L. Goldberger and Kenneth M. Watson, *Collision Theory* (Wiley, 1964), Chapter VIII (ISBN: 0486435075); and Albert Messiah, *Quantum Mechanics* (Wiley, 1958), Section XXI.13 (ISBN: 0486409244). This part of the resolvent formalism is also covered particularly nicely in Claude Cohen-Tannoudji, Jacques Dupont-Roc, and Gilbert Grynberg, *Atom–Photon Interactions: Basic Processes and Applications* (Wiley, 1992), Chapter III (ISBN: 0471625566); and in Paul Roman, *Advanced Quantum Theory: An Outline of the Fundamental Ideas* (Addison–Wesley, 1965), Section 4-5 (ISBN: 0201064952). A brief, but clear treatment in terms of the self-energy operator is in Doron Cohen, "Lecture Notes in Quantum Mechanics," arXiv.org preprint (arXiv: quant-ph/0605180v3) (2008), Section 28.3 (the Born series derivation in Section 15.4.1 follows this treatment).

[10] In treating time-independent perturbation theory (Section 12.3), we used the notations P_0 and Q_0 for these projectors. Since there is no need to distinguish perturbed and unperturbed projectors here, we can dispense with the null subscripts.

Now multiplying through by $(z-H_0)$ on the left, where $(z-H_0)G_0(z)=1$ (even in the presence of P's since $[G_0,P]=[H_0,P]=0$),

$$(z-H_0)(QGP)=(QVP)(PGP)+(QVQ)(QGP). \tag{15.101}$$

Moving both (QGP) factors to the left,

$$(z-H_0-QVQ)(QGP)=(QVP)(PGP), \tag{15.102}$$

and solving for (QGP) gives

$$(QGP)=Q\frac{1}{z-H_0-V}Q(QVP)(PGP). \tag{15.103}$$

Another way to derive the result (15.103) is to iterate the relation (15.100) to obtain a series,

$$\begin{aligned}QGP&=(QG_0Q)(QVP)(PGP)+(QG_0Q)(QVQ)(QG_0Q)(QVP)(PGP)\\&\qquad+(QG_0Q)(QVQ)(QG_0Q)(QVQ)(QGP)\\&=\sum_{n=1}^{\infty}\big[(QG_0Q)(QVQ)\big]^n(PGP)\\&=\sum_{n=0}^{\infty}\big[(QG_0Q)(QVQ)\big]^n(QG_0Q)(QVP)(PGP)\\&=(QGQ)(QVP)(PGP),\end{aligned} \tag{15.104}$$

and in the last step we recognized the Born series $G=G_0+G_0VG_0+\cdots$, which reproduces Eq. (15.103), but showing that the result involves a sum over all perturbation orders.

Now using Eq. (15.103) to eliminate (QGP) in the last expression in Eqs. (15.99),

$$PGP=(PG_0P)\bigg[1+(PVP)(PGP)+(PVQ)\bigg(Q\frac{1}{z-H_0-V}Q\bigg)(QVP)(PGP)\bigg]. \tag{15.105}$$

Defining the **level-shift operator** or **self-energy operator**

$$R(z):=V+VQ\frac{1}{z-H_0-V}QV=V+VQG(z)QV, \tag{15.106}$$
(level-shift operator)

we can rewrite this expression as

$$PGP=(PG_0P)\Big[1+(PRP)(PGP)\Big]. \tag{15.107}$$

Collecting the PGP factors on the left,

$$\Big[1-(PG_0P)(PRP)\Big]PGP=(PG_0P), \tag{15.108}$$

and then solving for PGP, we have

$$PGP=\frac{1}{1-(PG_0P)(PRP)}(PG_0P). \tag{15.109}$$

Note that $P(z-H_0)P$ commutes with PRP because they are proportional to P (for P representing a subspace, this is still possible if V does not cause transitions on P's subspace, i.e., V is diagonal on this subspace). Thus the (PG_0P) factor is like multiplying by $(z-PH_0P)$ on the right in the denominator, which cancels the (PG_0P). Thus, we have

$$PG(z)P=P\frac{1}{z-H_0-R(z)}P, \tag{15.110}$$
(partitioned resolvent)

after pulling P's outside the inverse function. The level-shift operator appears as an effective potential that modifies H_0 due to the coupling to the other states in Hilbert space.

15.4.1 Born-Series Derivation

There is a more direct but less general alternate derivation of Eq. (15.110) that may make it more intuitive. First, let's make the simplifying assumption that $PVP = QVQ = 0$—that is, V only causes transitions between the P and Q subspaces, not within them. Then using the Born series (12.11) for $G(z)$, and inserting identities $(P + Q) = 1$, we find

$$\begin{aligned} PG(z)P &= P\Big(G_0 + G_0VG_0 + G_0VG_0VG_0 + \cdots\Big)P \\ &= PG_0P + PG_0(P+Q)V(P+Q)G_0P + PG_0(P+Q)V(P+Q)G_0(P+Q)V(P+Q)G_0P + \cdots \\ &= PG_0P + PG_0(PVQ)G_0(QVP)G_0P + PG_0(PVQ)G_0(QVP)G_0(PVQ)G_0(QVP)G_0P + \cdots \\ &= PG_0P + (PG_0P)(P\Sigma P)(PG_0P) + (PG_0P)(P\Sigma P)^2(PG_0P) + \cdots , \end{aligned} \tag{15.111}$$

defining the operator

$$\Sigma(z) := VQG_0QV \approx PR(z)P. \tag{15.112}$$

Note that on the P subspace, this operator is just the level-shift operator,

$$P\Sigma(z)P \approx PR(z)P, \tag{15.113}$$

expanded to second order in V—that is, where $G(z)$ is replaced by $G_0(z)$ in Eq. (15.106). Then the last series in Eqs. (15.111) same form as the Born expansion for a resolvent PG_0P with potential PRP, and thus resumming the geometric series gives

$$PG(z)P = (PG_0P)\frac{1}{1-(P\Sigma P)(PG_0P)} = P\frac{1}{z - H_0 - \Sigma(z)}P. \tag{15.114}$$

At this second-order level, we can see from the third line in Eqs. (15.111) that the terms in the resolvent expansion represent processes that make increasingly more transitions between the P and Q subspaces, where only even-order processes contribute due to the assumption that $PVP = QVQ = 0$. However, within this assumption, the series resummation (15.114) is *exact*. The approximate identification (15.113) tells us that Eqs. (15.110) and (15.114) correspond to different resummations of the series (15.111). The level-shift operator $R(z)$ as an effective potential already sums over transition processes at all orders, whereas $\Sigma(z)$ only accounts for double transitions. The use of $R(z)$ can thus facilitate *nonperturbative* approximate solutions.

15.4.2 Action of the Level-Shift Operator

We will now want to study the evolution of the perturbed state, in the process illustrating the action of the level-shift operator. To do so the main object of study is the retarded Green function

$$\langle\psi_0|G^+(E)|\psi_0\rangle \equiv G^+_{00}(E) = P\frac{1}{E - E_0 - R^+_{00}(E) + i0^+}P \tag{15.115}$$

corresponding to $|\psi_0\rangle$. Thus, we will correspondingly want the level-shift operator just above the real axis:

$$R^+(E) = V + VQ\frac{1}{E - H + i0^+}QV. \tag{15.116}$$

Using the identity (Problem 13.11)

$$\frac{1}{x \pm i0^+} = \mathscr{P}\frac{1}{x} \mp i\pi\delta(x), \tag{15.117}$$

we obtain

$$R^+(E) = V + \mathscr{P}VQ\frac{1}{E - H}QV - i\pi VQ\delta(E - H)QV, \tag{15.118}$$

which can be rewritten

$$R^+(E) = V + \hbar\Delta(E) - \frac{i\hbar}{2}\Gamma(E),$$

(decomposiiton of level-shift operator) (15.119)

in terms of the (Hermitian) operators $\Delta(E)$ and $\Gamma(E)$, defined by

$$\hbar\Delta(E) := \mathscr{P}VQ\frac{1}{E-H}QV$$
$$\hbar\Gamma(E) := 2\pi VQ\delta(E-H)QV,$$

(level-shift operator, real and imaginary components) (15.120)

representing the real and imaginary parts of $R^+(E)$.

According to Eq. (15.115) the pole at $E = E_0$ has then shifted to

$$\begin{aligned} E &= E_0 + R^+_{00}(E) - i0^+ \\ &= E_0 + V_{00} + \hbar\Delta_{00}(E) - \frac{i\hbar}{2}\Gamma_{00}(E), \end{aligned} \tag{15.121}$$

after dropping the $-i0^+$ compared to the presumably finite $-i\Gamma_{00}(E)/2$. Note that this result is valid to all orders, but is still implicit in E. In the case of a small shift, to a first approximation we can replace E by E_0 on the right-hand side to obtain the explicit expression

$$E \approx E_0 + V_{00} + \hbar\Delta_{00}(E_0) - \frac{i\hbar}{2}\Gamma_{00}(E_0) \tag{15.122}$$

for the shifted pole. Given that the energy eigenstate determines the time evolution of the unperturbed state via

$$|\psi_0(t)\rangle = |\psi_0\rangle\, e^{-iE_0t/\hbar}, \tag{15.123}$$

the perturbed state evolves in the same way according to the shifted pole:

$$|\psi(t)\rangle = |\psi\rangle\, e^{-iEt/\hbar} = |\psi\rangle\, e^{-i[E_0+V_{00}+\hbar\Delta_{00}(E_0)]t/\hbar}\, e^{-\Gamma_{00}(E_0)\,t/2}. \tag{15.124}$$

In particular, the norm (probability) of this state decays exponentially at the rate $\Gamma_{00}(E_0)$:

$$\langle\psi(t)|\psi(t)\rangle = e^{-\Gamma_{00}(E_0)\,t}. \tag{15.125}$$

The V_{00} gives a first-order energy shift exactly as expected from ordinary perturbation theory, and the $\hbar\Delta_{00}(E_0)$ gives higher-order shifts (at all higher orders, but not the exactly correct shift unless E_0 is replaced by E). A more formal demonstration of the state decay starts with the expression [Eq. (13.44)]

$$U(\tau,0) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, e^{-iE\tau/\hbar}\, G^+(E) \qquad (\tau > 0) \tag{15.126}$$

for the forward evolution operator. The integral can be evaluated as a (clockwise) contour just above the real axis, closing around the lower half-plane, which picks up the shifted pole (15.122) to give

$$U(\tau,0) = e^{-i[E_0+V_{00}+\hbar\Delta_{00}(E_0)]\tau/\hbar} e^{-i\Gamma_{00}(E_0)\tau/2}, \tag{15.127}$$

in agreement with the aboveheuristic argument. This is the so-called **pole approximation**, which although it leads to an accurate result, is not technically correct in the presence of a continuum that leads to a branch cut along the positive real axis. The contour cannot be simply completed around the lower half-plane because the crossing of the branch cut must be handled carefully. A more circuitous contour can be used instead, and the extra components lead to nonexponential corrections to the decay at long times.

As for the decay rate, the relevant matrix element of the decay operator can be written

$$\begin{aligned} \Gamma_{00}(E_0) &= \frac{2\pi}{\hbar}\langle\psi_0|VQ\delta(E-H)QV|\psi_0\rangle \\ &= \frac{2\pi}{\hbar}\sum_{\alpha\neq 0}|V_{\alpha 0}|^2\delta(E_0-E_\alpha) \end{aligned} \tag{15.128}$$

after expanding the Q projector. This is the same as the prediction from Fermi's golden rule [Eq. (15.9)]

$$\Gamma_{\mathsf{i}\to\mathsf{f}} \approx \frac{2\pi}{\hbar}|V_{\mathsf{fi}}|^2\,\delta(E_{\mathsf{fi}}), \tag{15.129}$$

except that now the result is summed over (integrated over, in the case of a continuum) all possible final states, as is sensible anyway for the delta function. Also the decay operator can give a more accurate result by using more accurate value for E for the argument in $\Gamma_{00}(E)$.

Finally, the shifted energy is given by the real part of Eq. (15.121):

$$\begin{aligned}\mathrm{Re}[E] &= E_0 + V_{00} + \hbar\Delta_{00}(E)\\ &= E_0 + V_{00} + \mathscr{P}\langle\psi_0|VQ\frac{1}{E-H_0-V}QV|\psi_0\rangle.\end{aligned} \tag{15.130}$$

At this point we can use

$$Q\frac{1}{E-H_0-V}Q = Q\frac{1}{1-G_0(E)QVQ}G_0(E)Q = \sum_{n=0}^{\infty}[G_Q V]^n G_Q, \tag{15.131}$$

where we are again using the shorthand $G_Q := QG_0(E)Q$. Then the energy shift becomes

$$\begin{aligned}\mathrm{Re}[E] &= E_0 + V_{00} + \sum_{n=0}^{\infty}\mathscr{P}\langle\psi_0|V(G_Q V)^n G_Q V|\psi_0\rangle\\ &= E_0 + V_{00} + \sum_{n=1}^{\infty}\mathscr{P}\langle\psi_0|V(G_Q V)^n|\psi_0\rangle.\end{aligned} \tag{15.132}$$

This matches up with the energy shift (12.253) from Wigner–Brillouin perturbation theory,

$$E = E_0 + \sum_{n=1}^{\infty}\langle\psi_0|V(G_Q V)^{n-1}|\psi_0\rangle \tag{15.133}$$

(with $\lambda = 1$) to all orders. Thus, the implicit energy shift is exact (somewhat less so in the pole approximation). Note that the resolvent gives an explicit prescription for handling the singularities from the $QG_0(E)Q$ in an energy integral; this is consistent with the sum over $\alpha \neq 0$ from the Q projectors, which avoids divergences at E_0, but also avoids issues with branch cuts.

15.5 Exercises

Problem 15.1

In the treatment of multipole radiation (Section 7.4.4), we saw that sources couple to the electromagnetic field via the interaction potential (7.212)

$$V = -\int d^3r\, \mathbf{j}(\mathbf{r}) \cdot \mathscr{A}(\mathbf{r}), \tag{15.134}$$

where $\mathscr{A}(\mathbf{r})$ is the vector potential and $\mathbf{j}(\mathbf{r})$ is the current density. In the dipole (or long-wavelength) approximation, we assume the atom to be well localized, with a current density of the form

$$\mathbf{j} = -\frac{e}{m_\mathrm{e}} \mathbf{p}\, \delta^3(\mathbf{r} - \mathbf{r}_\mathrm{A}), \tag{15.135}$$

where r_A is the atom's location, and assuming only one electron (with *kinetic* momentum $\mathbf{p}$) is interacting with the field. In this case the interaction potential becomes

$$V = \frac{e}{m_\mathrm{e}} \mathbf{p} \cdot \mathscr{A}(\mathbf{r}_\mathrm{A}). \tag{15.136}$$

Since there is both a momentum operator and a position, in principle this interaction should be symmetrized; however, in the dipole approximation the position refers to the atomic center of mass, not the electron position, so that $\mathbf{p}$ and $\mathscr{A}(\mathbf{r}_\mathrm{A})$ commute.

Show using Fermi's golden rule that this form of the atom–field interaction leads to an expression for the spontaneous decay rate to the expression that we derived using the $V = -\mathbf{d} \cdot \mathscr{E}$ interaction. In particular, note that in Coulomb gauge, $\mathscr{E} = -\partial_t \mathscr{A} = i\omega \mathscr{A}$, and thus you can use

$$\mathscr{A}_\mathbf{k}(\mathbf{r}, t) = i\hat{\varepsilon} \sqrt{\frac{\hbar}{2\omega\epsilon_0 \mathscr{V}}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a + \mathrm{H.c.} \tag{15.137}$$

as the expression for a quantized mode of the vector potential. To handle the electron momentum operator, use $\mathbf{p}(t) = m_\mathrm{e}\dot{\mathbf{r}}(t)$ and evaluate the relevant matrix element of this expression in the interaction picture.

Note that the equivalence between the two interaction potentials comes out fairly straightforwardly in this problem. In fact these two interactions are related by a unitary transformation called the **Power–Zienau transformation**. In other calculations, the equivalence between the two interactions is not as straightforward, and has caused a fair amount of confusion over the years.

Problem 15.2

Use Fermi's golden rule to rederive the rate of spontaneous decay for an atom in

(a) 2D electromagnetism.

(b) 1D electromagnetism.

By "nD" electromagnetism, I mean n spatial dimensions, but still allowing for two distinct polarizations for each $\mathbf{k}$. This is an artificial statement, because fundamentally there are three spatial dimensions, so physically this problem will correspond to something like an atom in a 2D or 1D ideal cavity or waveguide, with dimensions so small that mode excitations are suppressed along all but two or one of the spatial dimensions.

Thus, set up these problems as follows. Start with the same quantum electric field as before, quantized in the box of volume $\mathscr{V} = LA$, where A is a quantization area (formerly represented by L^2). Now for the 2D problem we will keep L fixed and small, while letting $A \longrightarrow \infty$ later in the problem, so only do the mode count with those dimensions. Neglecting the mode count in the L direction amounts to assuming that the energy gap to the next mode is so high that other modes won't influence the

spontaneous decay rate. At the end of the problem, your result should be dimensionally correct and still depend on L. The same goes for the 1D problem, but the result will depend on A (with $L \longrightarrow \infty$).

Problem 15.3

Consider a magnetic dipole transition, coupled via the dipole interaction $V = -\boldsymbol{\mu} \cdot \mathbf{B}$.

(a) Adapt the electric-dipole calculation to write down an expression for the spontaneous decay rate Γ on this transition.

(b) Use your result to compute a numerical value for the decay rate (and the lifetime $\tau = 1/\Gamma$) for the $1\mathrm{S}(F = 1)$ hyperfine states to $1\mathrm{S}(F = 0)$.

Note that the magnetic moment $\boldsymbol{\mu}$ here is approximately the electron's magnetic moment, since there is no orbital part ($L = 0$) and the nuclear moment is much weaker. Then use $\mathbf{F} = \mathbf{S} + \mathbf{I}$, decompose the excited and ground states into eigenstates of S_z and I_z (a Clebsch–Gordan coefficient or two will come in handy), and compute the matrix element directly. Also, note that there are multiple excited states, but by symmetry they decay at the same rate, so just pick one (say $m_F = 0$).

(c) Recompute the quantities from (b) at temperature $T = 25\,^\circ\mathrm{C}$.

Chapter 16

Scattering and Collisions

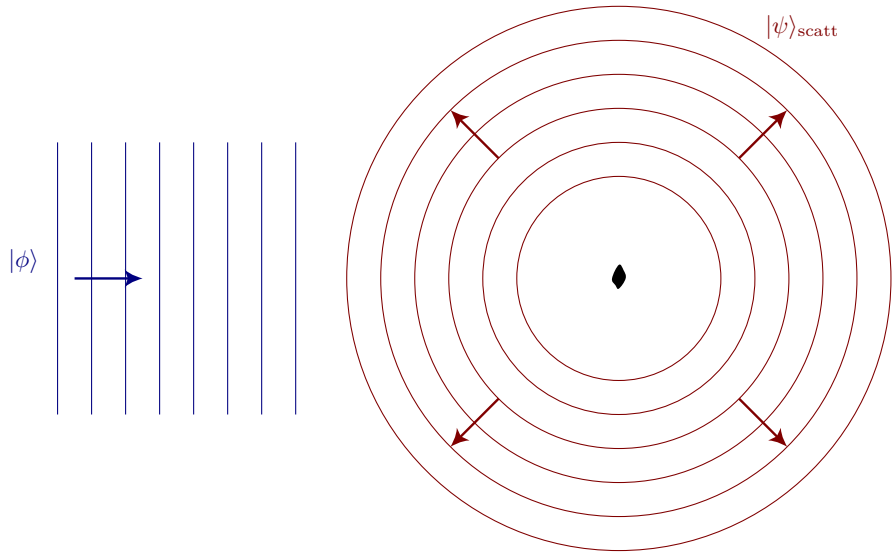
16.1 Scattering Setup

The theory of scattering deals with the impact of a particle with some fixed object, represented by some reasonably localized potential $V(\mathbf{r})$. The same theory applies to the collision of one particle with another. In this case one particle of mass m is the ''incident'' particle, and we know from our study of the hydrogen atom that the ''scatterer'' particle can be treated as fixed if we replace m by the reduced mass μ.

In quantum mechanics we can envision a scattering process in terms of a state of the form

$$|\psi\rangle = |\phi\rangle + |\psi\rangle_{\text{scatt}}, \tag{16.1}$$

where the total state $|\psi\rangle$ comprises an incident wave $|\phi\rangle$ and a scattered wave $|\psi\rangle_{\text{scatt}}$, shown schematically below.



A huge simplification occurs for a localized scattering potential, where $V(\mathbf{r}) \longrightarrow 0$ as $r \longrightarrow \infty$ (really the potential must fall off more quickly than $1/r$). This is because, far away from the center of the scattering potential, the state can be represented in terms of asymptotic free-particle states. That is, in the position representation, we can make the *ansatz* that the wave function has the asymptotic form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + f(\Omega)\frac{e^{ikr}}{r} \tag{16.2}$$

(3D scattering equation, far-field limit)

in three dimensions, where the incoming state is a plane wave of wave vector $\mathbf{k}$, and the scattered state is an outgoing spherical wave. The angular factor $f(\Omega)$ is the **scattering amplitude**, and it accounts for the

possibility that there may be more scattering in some directions than others. Note that for the units to work out, the scattering amplitude must have dimensions of length. The squared modulus of the scattering amplitude is called the **differential cross-section**

$$\frac{d\sigma}{d\Omega} := |f(\Omega)|^2, \tag{16.3}$$
(differential cross-section)

More precisely and generally, the differential cross section $d\sigma$ is defined as the ratio of the rate of scattering into $d\Omega$ [the number of particles scattering into $d\Omega$ per unit time, here, $(\hbar k/m)|f(\Omega)|^2\,d\Omega$, corresponding to the probability current density (2.125) $\mathbf{j}(\mathbf{r}) = (\hbar|\psi|^2/m)\nabla(kr)$ integrated over $d\Omega$] to the incident particle flux (here, $\hbar k/m$). The **cross-section** or **total cross-section** is its angular integral:

$$\sigma = \int d\Omega\,\frac{d\sigma}{d\Omega} = \int d\Omega\,|f(\Omega)|^2. \tag{16.4}$$
(cross-section)

The cross-section thus has dimensions of area, as does the differential cross-section (alternatively, area per steradian). We saw the cross section before in the treatment of photoionization (Section 15.3.3), and as mentioned there a customary unit for the cross-section is the barn, as in "the broad side of a barn", where $1\,\text{barn} = 10^{-28}\,\text{m}^2$. Intuitively, an incoming plane wave represents the probability flux of a single particle, or a number flux in a stream of particles. The cross-section represents an effective area that intercepts the incoming stream, and the product of the incident flux and the cross-section gives the scattering rate.

16.1.1 Partial-Wave Expansion

The main problem in scattering theory is then to somehow connect the incoming and scattered waves in the scattering state (16.2), the problem being that the waves may be much more complicated than the asymptotic forms deep in the potential region. A direct and instructive approach is to require consistency of the incoming and outgoing solutions on some boundary. We did exactly this boundary matching in one-dimensional scattering when we analyzed the square-barrier potential (Section 2.6).

We talked before (Section 8.1.2) about the solution of the free particle in spherical coordinates, and it is useful to relate the asymptotic scattered wave to that solution. The energy, eigenfunctions corresponding to $E = \hbar^2k^2/2m$, were

$$\psi_{\ell m}(\mathbf{r}) = j_\ell(kr)Y_\ell^m(\theta,\phi), \tag{16.5}$$

where the $j_\ell(r)$ are the spherical Bessel functions of the first kind. The spherical Bessel functions of the second kind, $y_\ell(r)$, are also solutions of the Schrödinger equation. Recalling the small-argument asymptotics for both kinds of spherical Bessel functions,

$$j_\ell(r) \approx \frac{r^\ell}{(2\ell+1)!!}, \qquad y_\ell(r) \approx -\frac{(2\ell-1)!!}{r^{\ell+1}}, \tag{16.6}$$

we rejected the $y_\ell(r)$ because they diverged at the origin, and thus could not be part of a representation of regular wave functions. However, now we can entertain the possibility of using them, because now we don't need them at the origin.

To see why we'd like to broaden the scope of our eigenfunctions to include the former *functios non gratos*, consider the **spherical Hankel functions** of the first and second kind, defined respectively by

$$\begin{aligned} h_\ell^{(1)}(x) &:= j_\ell(x) + iy_\ell(x) \\ h_\ell^{(2)}(x) &:= j_\ell(x) - iy_\ell(x). \end{aligned} \tag{16.7}$$

The large-r asymptotics are given by

$$h_\ell^{(1)}(kr) \sim \frac{e^{ikr - i\ell\pi/2}}{ikr}, \qquad h_\ell^{(2)}(kr) \sim -\frac{e^{-ikr + i\ell\pi/2}}{ikr}, \tag{16.8}$$

where we see that $h_\ell^{(1)}(kr)$ corresponds to an *outgoing* spherical wave, and $h_\ell^{(2)}(kr)$ is the *ingoing* counterpart. The scattered solution should be represented by the outgoing functions $h_\ell^{(1)}(kr)$, so we can write the scattered wave as

$$\psi_{\text{scatt}}(\mathbf{r}) = \sum_{\ell m} c_{\ell m} h_\ell^{(1)}(kr)\, Y_\ell^m(\theta,\phi),$$

(scattered wave, partial wave expansion) (16.9)

valid beyond some radius R that bounds the region of nonvanishing potential (alternately, it is asymptotically valid for large r where the potential becomes vanishingly small. This series is called the **partial-wave expansion** of the scattered solution, which is a decomposition of the scattered into components corresponding to different angular-momentum eigenfunctions. Similar to the notation for hydrogen-atom states, the $\ell = 0$ partial wave is called the **S-wave**, the $\ell = 1$ waves are **P-wave** solutions, the $\ell = 2$ are **D-waves**, and so on. Using the large-r asymptotics (16.8), the partial wave expansion becomes

$$\psi_{\text{scatt}}(\mathbf{r}) \sim \frac{1}{ik} \sum_{\ell m} c_{\ell m} e^{-i\ell\pi/2} Y_\ell^m(\theta,\phi) \frac{e^{ikr}}{r}, \tag{16.10}$$

which will generally be the more useful form for analyzing the scattering solutions. Note that this explicitly matches the form of the scattered wave—the last term of Eq. (16.2)—that we assumed at the start, and so the scattered amplitude is everything here other than the e^{ikr}/r factor.

16.1.1.1 Spherically Symmetric Scattering Potential

In the case of a purely radial scattering potential $V(r)$, the partial-wave expansion simplifies considerably. Given an incident plane wave, the problem is axially symmetric about the incoming wave vector $\mathbf{k}$, which we will take as the pole of the spherical coordinate system. In this case the scattered wave must be independent of ϕ, which fixes $m = 0$ for every partial wave. Asymptotically, we then have

$$\psi_{\text{scatt}}(\mathbf{r}) \sim \frac{1}{ik} \sum_{\ell} c_\ell Y_\ell^0(\theta,0) \frac{e^{ikr - i\ell\pi/2}}{r} \tag{16.11}$$

for the scattered wave.

The incident plane wave also has a partial-wave expansion, as we have seen before [Eq. (7.233)],

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi \sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}}\, j_\ell(kr)\, Y_\ell^0(\theta,0), \tag{16.12}$$

where as above θ is the angle between $\mathbf{k}$ and $\mathbf{r}$. The spherical Bessel function $j_\ell(kr)$ here is best thought of as a linear combination of the outgoing wave $h_\ell^{(1)}(kr)$ and the ingoing wave $h_\ell^{(2)}(kr)$—the plane wave extending over all space (sensibly) contains both ingoing and outgoing components. Using Eqs. (16.7) and (16.8), the plane wave in the far field is

$$e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{2\pi}{ik} \sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}}\, Y_\ell^0(\theta,0) \left(\frac{e^{ikr - i\ell\pi/2}}{r} - \frac{e^{-ikr + i\ell\pi/2}}{r} \right). \tag{16.13}$$

Note the corresponding constraint $m = 0$ and lack of dependence on ϕ in this expression. The other considerable simplification that we get in a spherically symmetric potential is that angular momentum is conserved, here meaning that the potential causes no transitions between states of different ℓ or m. Thus, by comparison to Eq. (16.13) we can think of the total wave function as

$$\psi(\mathbf{r}) = \frac{2\pi}{ik} \sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}}\, Y_\ell^0(\theta,0) \left(\frac{e^{ikr - i\ell\pi/2}}{r} e^{2i\delta_\ell} - \frac{e^{-ikr + i\ell\pi/2}}{r} \right). \tag{16.14}$$

That is, the total state is a superposition of incoming and outgoing waves, but the incoming components must exactly match the corresponding components of the plane wave (16.13), because the scattering wave

(16.11) is purely outgoing. The total state (16.14) also has components with the same amplitude as their ingoing counterparts, due to conservation of angular momentum. We must consider the possibiility of a different phase of the outgoing components compared to the plane wave, however, so we introduce a phase shift of $2\delta_\ell$ for the ℓth partial wave. In the absence of a scattering potential, then clearly $\delta_\ell = 0$.

Then if we take the assumed form of the scattering state (16.2) and rewrite it in terms of the scattered state,

$$\psi_{\text{scatt}}(\mathbf{r}) = f(\Omega)\frac{e^{ikr}}{r} = \psi(\mathbf{r}) - e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{16.15}$$

then the scattered wave appears as the difference between the incident plane wave and the total wave. Putting in Eqs. (16.13) and (16.14) into this expression, the ingoing components cancel by design, leaving

$$f(\Omega)\frac{e^{ikr}}{r} = \frac{2\pi}{ik}\sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}}\, Y_\ell^0(\theta,0)\frac{e^{ikr-i\ell\pi/2}}{r}\big(e^{2i\delta_\ell}-1\big), \tag{16.16}$$

or after simplifying,

$$f(\Omega) = \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\, Y_\ell^0(\theta,0)\, e^{i\delta_\ell}\sin\delta_\ell. \tag{16.17}$$
(scattering amplitude)

The scattering amplitude is highly determined, without knowing any details of the radial dependence of the potential. Squaring the modulus and integrating over all angles, we obtain

$$\sigma = \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell \tag{16.18}$$
(total cross-section)

for the total cross section in spherical symmetry. Note that the phase shifts δ_ℓ are *everything* here, controlling how much is scattered into each partial wave. The phase shift δ_ℓ has an extra contribution as a phase in the differential cross-section—the squared modulus of Eq. (16.17)—by modifying the interferences between the different partial waves and thus controlling the θ-dependence of the angular scattered distribution. But these phases are absent in the total cross section, which sums over the angular distribution into an incoherent sum over the partial waves.

16.1.1.2 Hard-Sphere Scattering

One of the simpler examples of partial-wave analysis in action is the hard-sphere potential, defined by

$$V(r) = \begin{cases} 0, & r > a \\ \infty, & r < a, \end{cases}, \tag{16.19}$$

representing an impenetrable sphere of radius a. Here the ingoing and outgoing waves are connected by the Dirichlet boundary condition on the surface of the sphere.

To apply the boundary condition, we need the exact (not asymptotic) expression for the total state. For the scattered component, we can compare the asymptotic scattered wave (16.16) to the asymptotics of the Hankel functions (16.8). Then the exact scattering solution in spherical symmetry is

$$\psi_{\text{scatt}}(\mathbf{r}) = 4\pi i\sum_{\ell=0}^{\infty} i^\ell\sqrt{\frac{2\ell+1}{4\pi}}\, Y_\ell^0(\theta,0)\, h_\ell^{(1)}(kr)\, e^{i\delta_\ell}\sin\delta_\ell. \tag{16.20}$$

For the incident wave, we can use the exact plane wave expansion (16.12),

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 4\pi\sum_{\ell=0}^{\infty} i^\ell\sqrt{\frac{2\ell+1}{4\pi}} j_\ell(kr) Y_\ell^0(\theta,0). \tag{16.21}$$

Putting these components together, the total scattering state is

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + \psi_{\text{scatt}}(\mathbf{r}) = 4\pi i \sum_{\ell=0}^{\infty} i^\ell \sqrt{\frac{2\ell+1}{4\pi}} Y_\ell^0(\theta,0)\Big[j_\ell(kr) + h_\ell^{(1)}(kr)\, i e^{i\delta_\ell}\sin\delta_\ell\Big]. \tag{16.22}$$

To satisfy the boundary condition $\psi(r=a)=0$, the bracketed quantity must vanish, so that

$$e^{i\delta_\ell}\sin\delta_\ell = i\frac{j_\ell(ka)}{h_\ell^{(1)}(ka)}. \tag{16.23}$$

Substituting this expression into Eq. (16.17) gives an exact solution for the scattering amplitude.

For a more intuitive result, consider instead the square of the condition (16.23),

$$\sin^2\delta_\ell = \frac{j_\ell^2(ka)}{|h_\ell^{(1)}(ka)|^2}, \tag{16.24}$$

which is the relevant quantity for the total cross-section (16.18). Now suppose we consider the limit of $k \longrightarrow 0$ (zero incident energy). Using the short-range expansions (16.6)

$$j_\ell(r) \approx \frac{r^\ell}{(2\ell+1)!!}, \qquad y_\ell(r) \approx -\frac{(2\ell-1)!!}{r^{\ell+1}}, \tag{16.25}$$

to leading order this quantity becomes

$$\sin^2\delta_\ell \approx \frac{(ka)^{2\ell}/[(2\ell+1)!!]^2}{[(2\ell+1)!!]^2/(ka)^{2(\ell+1)}} = \frac{(ka)^{2(2\ell+1)}}{[(2\ell+1)!!]^4} \tag{16.26}$$

In the limit of small k, the $\ell=0$ term dominates the others, with a contribution

$$\sin^2\delta_0 = (ka)^2 + O(k^3). \tag{16.27}$$

Putting this into the total cross-section (16.18), we find

$$\sigma(k\to 0) = 4\pi a^2 \tag{16.28}$$
(hard sphere, zero-energy cross-section)

in the limit of low-energy scattering.

There are two interesting things to note in the above analysis. The first is that intuitively, the cross-section represents an area that intercepts the incident probability flux to produce the scattered field which radiates probability at a certain rate. The classical result is $\sigma = \pi a^2$, the area of a disc of radius a, at any energy which is certainly reasonable. The low-energy quantum-mechanical result is four times this, and is in fact the total area of the sphere. Intuitively, diffraction effects allow the incoming wave to ''see'' more of the sphere than we might naïvely expect.

The second interesting result is that in the limit of zero incident energy, *scattering only occurs into the S-wave*. This turns out to be true even when the potential is not spherically symmetric, and we will revisit this effect in more generality when we study scattering from a delta potential in Section 16.2.3.2. We can also see from Eqs. (16.26) that at low but nonzero energies, the lower-order partial waves are more important than higher-order ones, so that with increasing energy the S-wave is present, then the P-wave turns on and so on. Note that for the low-energy collision of two identical fermions in the same spin state, Pauli exclusion rules out S-wave scattering, in which case the lowest-energy scattering is into the P-wave (which turns off as $E \longrightarrow 0$).

16.1.1.3 Scattering Length

In the low-energy regime of scattering we saw in the hard-sphere example above that the scattering is S-wave, or spherically symmetric. Another way to say this is that the scattering amplitude reduces to a constant. Specifically, from Eq. (16.17), we have

$$f(\Omega) = \lim_{k\to 0}\frac{1}{k}\, e^{i\delta_0}\sin\delta_0 = \lim_{k\to 0}\frac{i}{k}\frac{j_\ell(ka)}{h_\ell^{(1)}(ka)} = \lim_{k\to 0}\frac{i}{k}\frac{1}{(-i/ka)} \tag{16.29}$$

after using Eqs. (16.23) and (16.6), and thus

$$f(\Omega) = -a. \tag{16.30}$$
(scattering amplitude, hard sphere)

In this case the value of the constant scattering amplitude is the negative radius of the hard sphere. Recalling the asymptotic form (16.2) of the scattered state,

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} + f(\Omega)\frac{e^{ikr}}{r}, \tag{16.31}$$

in the limit $k \longrightarrow 0$, this reduces to

$$\psi_{E\to 0}(\mathbf{r}) \approx 1 - \frac{a}{r}. \tag{16.32}$$
($E \to 0$ asymptotic state)

This says that in the zero-energy limit, the *asymptotic* total wave function satisfies the correct Dirichlet boundary condition at $r = a$.

Even in more general problems, where the radius a does not appear, it is conventional and useful to *define* a constant a such that the asymptotic zero-crossing in Eq. (16.32) holds at zero energy. This constant a is called the **scattering length** a, and it fully characterizes the scattering in the S-wave regime in that $f = -a$, and $\sigma = 4\pi a^2$. For some potentials it can work out that $a < 0$, and thus the scattering length may not correspond to a literal zero-crossing of the true asymptotic scattered wave; rather, it may just be the zero-crossing of the asymptotic part of the wave, extrapolated back towards (through) the scattering origin.

Returning to the scattered solution from Eqs. (16.16) and (16.17), we can write

$$\psi_{\text{scatt}}(\mathbf{r}) = f(\Omega)\frac{e^{ikr}}{r} = \frac{e^{ikr}}{kr}\, e^{i\delta_0} \sin\delta_0. \tag{16.33}$$

To be consistent with our desired form (16.32) this scattered state should match up with the second term, and so

$$-\frac{a}{r} = \lim_{k\to 0} \frac{e^{ikr}}{kr}\, e^{i\delta_0} \sin\delta_0. \tag{16.34}$$

Simplifying the right-hand side in this limit (where also $\delta_0 \longrightarrow 0$), we see that it is sensible to take

$$a := -\lim_{k\to 0} \frac{\delta_0}{k} \tag{16.35}$$

as the definition for the scattering length in terms of the S-wave phase shift.[1] The S-wave phase shift is an observable, so this gives one method for empirically determining the scattering length.

16.2 T-Matrix

As an introduction above, we studied scattering in terms of eigenfunction analysis. But there are more powerful operator methods to handle scattering. These methods fall under the moniker of ''formal scattering theory,'' and we will explore them now. [2]

[1] Definitions of the scattering length often include a trigonometric function like $\tan\delta_0$ in place of δ_0, as an artifact of the derivation. But since δ_0 must be small for small k (arbitrarily long wavelength), those definitions are equivalent to this one.

[2] For a brief history of formal scattering theory, see Marvin L. Goldberger and Kenneth M. Watson, *Collision Theory* (Wiley, 1964), p. 173 (intro to Chapter 5) (ISBN: 0486435075). This is one of the definitive works on scattering theory. Formal scattering theory is also covered nicely in the more famous advanced texts on quantum mechanics, such as J. J. Sakurai and Jim Napolitano, *Modern Quantum Mechanics*, 2nd ed. (Cambridge, 2017), (ISBN: 9781108422413), or Eugen Merzbacher, *Quantum Mechanics*, 3rd ed. (Wiley, 1998) (ISBN: 0471887021). A terse but very clear treatment can be found in Doron Cohen, ''Lecture Notes in Quantum Mechanics,'' (arXiv: quant-ph/0605180v3) (2008). Another excellent set of notes is Robert G. Littlejohn, ''Notes 38: The Lippmann-Schwinger Equation and Formal Scattering Theory'' (2021), available at `https://bohr.physics.berkeley.edu/classes/221/notes/greensfuns.pdf`.

Recall that in the setup of time-independent perturbation theory in Chapter 12, we had a perturbed Hamiltonian

$$H = H_0 + V, \tag{16.36}$$

where we have dispensed with the bookkeeping parameter λ. In terms of H and H_0 we defined, respectively, perturbed and unperturbed resolvents

$$G(z) := \frac{1}{z - H}, \qquad G_0(z) := \frac{1}{z - H_0}, \tag{16.37}$$

which were related by

$$G(z) = G_0(z) + G_0(z)VG(z). \tag{16.38}$$

This is an implicit equation and not a direct solution for $G(z)$ in terms of $G_0(z)$. However, iterating it yielded the Born series

$$G = G_0 + G_0VG_0 + G_0VG_0VG_0 + G_0VG_0VG_0VG_0 + \cdots . \tag{16.39}$$

Now suppose that in Eq. (16.38), G_0 appeared in place of G on the right-hand side. The result would be a simple solution for G in terms of G_0. Things are unfortunately not so simple, but if we want to write such an equation, but in terms of some *other* operator $T(z)$, we could imagine that

$$G(z) =: G_0(z) + G_0(z)T(z)G_0(z). \tag{16.40}$$

Using the conjugate $G = G_0 + GVG_0$ of Eq. (16.38) in place of G on the right-hand side of Eq. (16.38) leads to

$$G = G_0 + G_0VG_0 + G_0VGVG_0, \tag{16.41}$$

whereupon comparison with Eq. (16.40) shows that we should define

$$T(z) := V + VG(z)V. \tag{16.42}$$
(T-operator)

With the identification $VG(z) = T(z)\,G_0(z)$, this definition reads

$$T(z) = V + VG_0(z)\,T(z). \tag{16.43}$$

This can be iterated in the usual way, or the Born series (16.39) can be put directly into the definition (16.42) to yield the expansion

$$T(z) = V + VG_0(z)V + VG_0(z)VG_0(z)V + \cdots . \tag{16.44}$$
(T-operator expansion)

The operator in Eqs. (16.42) or (16.44) is the **transition operator**, or **T-operator** (or more commonly, **T-matrix**, referring to an expression in a relevant representation). In the above definition, the T-matrix is something like a corrected potential in terms of which Eq. (16.40) is an explicit expression of G in terms of G_0, which is known, in principle.

16.2.1 Lippmann–Schwinger Equation

The unperturbed eigenvalue condition can be written $(E - H_0)|\phi\rangle = 0$, we can add it to the perturbed condition $E|\psi\rangle = H|\psi\rangle$ to read

$$E|\psi\rangle = (E - H_0)|\phi\rangle + H|\psi\rangle. \tag{16.45}$$

Then writing H in terms of H_0 and rearranging,

$$(E - H_0)|\psi\rangle = (E - H_0)|\phi\rangle + V|\psi\rangle. \tag{16.46}$$

Multiplying through again by $G_0(E)$, we find

$$|\psi\rangle = |\phi\rangle + G_0(E)V|\psi\rangle. \tag{16.47}$$

To avoid problems with singularities, the energy is typically bumped to just above the real axis, as

$$|\psi\rangle = |\phi\rangle + G_0^+(E)V|\psi\rangle, \tag{16.48}$$
(Lippmann–Schwinger equation)

where as before [Eq. (13.35)], the retarded Green operator (here unperturbed) is

$$G_0^+(E) = G_0(E + i0^+) = \frac{1}{E - H_0 + i0^+}. \tag{16.49}$$

The choice of the retarded (vs. advanced) Green function here corresponds to outgoing boundary conditions on the scattered wave (see Section 13.2.2.1). More traditionally, Eq. (16.48) is written in the position representation as

$$\psi(\mathbf{r}) = \phi(\mathbf{r}) + \int d\mathbf{r}'\, G_0^+(\mathbf{r}, \mathbf{r}'; E)\, V(\mathbf{r}')\, \psi(\mathbf{r}'),$$
(Lippmann–Schwinger equation) (16.50)

in which it appears as an integral equation for $\psi(\mathbf{r})$ (i.e., it is the integral-equation counterpart to the Schrödinger differential equation). Equations (16.48) and (16.50) are both forms of what is called the **Lippmann–Schwinger equation**,[3] which is the basis for the formal theory of scattering. Note that Eq. (16.38) for $G(z)$ and Eq. (16.43) for $T(z)$ have a similar structure to Eq. (16.48) if $z = E + i0^+$, and for this reason Eqs. (16.38) and (16.43) are informally called (operator) Lippmann–Schwinger equations as well.

As usual, the difficulty in using the implicit formula (16.48) is the lack of knowledge about the perturbed solution $|\psi\rangle$. But we can of course iterate the equation,

$$|\psi\rangle = |\phi\rangle + G_0^+(E)V|\phi\rangle + G_0^+(E)VG_0^+(E)V|\phi\rangle + \cdots, \tag{16.51}$$

obtaining an operator series acting on the incident state. Comparison to the T-operator expansion (16.44) shows that we can rewrite the series in terms of the T-operator as[4]

$$|\psi\rangle = |\phi\rangle + G_0^+(E)\, T^+(E)|\phi\rangle,$$
(Lippmann–Schwinger equation with T-operator) (16.52)

where $T^+(E) := T(E + i0^+)$, as for the retarded Green operator. This equation illustrates why T is the "transition operator." In the second (scattering) term, the incoming state $|\phi\rangle$ makes a transition to a scattered state via $T^+(E)$, and then propagates away from the scatterer via $G_0^+(E)$.

The exact evaluation of the T-operator is not in general possible, but if the series (16.44) is truncated, then Eq. (16.48) is an approximate but explicit equation that is useful for analyzing the scattered wave. The truncation the T-operator after the nth term in Eq. (16.44) in this context is called the ***n*th Born approximation**.[5] Thus, in the **first Born approximation**, we would make the replacement $T^+(E) \approx V$ in Eq. (16.48), while in the **second Born approximation**, we would make the replacement $T^+(E) \approx V + G_0^+(E)VG_0^+(E)$. In the first Born approximation, which reads

$$|\psi\rangle \approx |\phi\rangle + G_0^+(E)V|\phi\rangle, \tag{16.53}$$

the incident wave scatters from the potential V, and then propagates away via G_0^+. The second Born approximation,

$$|\psi\rangle \approx |\phi\rangle + G_0^+(E)V|\phi\rangle + G_0^+(E)VG_0^+(E)V|\phi\rangle, \tag{16.54}$$

[3] B. A. Lippmann and Julian Schwinger, "Variational Principles for Scattering Processes. I," *Physical Review* **79**, 469 (1950) (doi: 10.1103/PhysRev.79.469).

[4] Equation (16.51) is sometimes also written $|\psi\rangle = \Omega^+(E)|\phi\rangle$ in terms of the **Møller scattering operator** $\Omega^+(E) = 1 + G_0^+(E)\, T^+(E) = 1/[1 + G_0^+(E)V]$, which also satisfies $G(z) = \Omega(z)G_0(z)$, after C. Møller, "General Properties of the Characteristic Matrix in the Theory of Elementary Particles I," *Det Kongelige Danske Videnskabernes Selskab. Matematisk–Fysiske Meddelelser* **23**, 1 (1945), available at `http://gymarkiv.sdu.dk/MFM/kdvs/mfm%2020-29/mfm-23-1.pdf`. See Robert G. Littlejohn, op. cit., p. 7.

[5] After the development of an iteration method based on an integral similar to that in Eq. (16.50) by Max Born, "Quantenmechanik der Stoßvorgänge [Quantum Mechanics of Collision Processes]," *Zeitschrift für Physik* **38**, 803–827 (1926) (doi: 10.1007/BF01397184); see Eqs. (6.2) and (6.3).

includes an extra term representing the scattering of the incoming wave from V, free propagation via G_0^+ (assuming H_0 gives free-particle evolution), scattering by a *second* interaction with V, and then free propagation away. Correspondingly, the nth Born approximation amounts to an n-fold interaction with the scattering potential, interspersed with free propagation, and then propagation away from the scatterer.

16.2.2 Scattering in One Dimension

As a simple application of the T-matrix formalism, we can revisit the problem of reflections at a barrier potential in one dimension from Section 2.6, in order to treat the problem in more generality. We will need the free-space Green function in one dimension, which reads (Problem 13.8)

$$G_0^+(x, x_0; E) = \frac{m}{i\hbar p_E} e^{ip_E|x-x_0|/\hbar} = \frac{1}{i\hbar v_E} e^{ik_E|x-x_0|}, \tag{16.55}$$

where the momentum is $p_E = \sqrt{2mE}$, and we can define the corresponding wave number $k_E = p_E/\hbar = \sqrt{2mE}/\hbar$ and velocity $v_E = p_E/m = \sqrt{2E/m}$ to absorb some of the constants. Now starting with the Lippman–Schwinger equation (16.48), put into the position representation by an inner product with $\langle x|$, we have we can write

$$\langle x|\psi\rangle = \langle x|\phi\rangle + \int dx_0 \, \langle x|G_0^+(E)|x_0\rangle\langle x_0|T^+(E)|\phi\rangle, \tag{16.56}$$

after inserting a second position identity. As before, the incident wave is a plane wave,

$$|\phi\rangle = \sqrt{2\pi\hbar}|p_E\rangle = \sqrt{2\pi}|k_E\rangle, \tag{16.57}$$

but normalized to unit amplitude, in that $\langle x|\phi\rangle = e^{ip_E x/\hbar}$. Here, we are also reducing the factors of $\hbar$ by changing to a scaled momentum (wave number) $k_E = p_E/\hbar$, in terms of which the momentum eigenstates may be similarly scaled as $|p_E\rangle = |k_E\rangle/\sqrt{\hbar}$. Then Eq. (16.56) becomes

$$\begin{aligned}
\psi(x) &= e^{ik_E x} + \frac{\sqrt{2\pi}}{i\hbar v_E} \int dx_0 \, e^{ik_E|x-x_0|}\langle x_0|T^+(E)|k_E\rangle \\
&= e^{ik_E x} + \frac{\sqrt{2\pi}}{i\hbar v_E} \int dx_0 \int dk \, e^{ik_E|x-x_0|}\langle x_0|k\rangle\langle k|T^+(E)|k_E\rangle \\
&= e^{ik_E x} + \frac{1}{i\hbar v_E} \int dk \, \langle k|T^+(E)|k_E\rangle \int dx_0 \, e^{ik_E|x-x_0|} e^{ikx_0}.
\end{aligned} \tag{16.58}$$

We assume the potential $V(x)$ to be nonvanishing over some compact region about $x = 0$. The interpretation of the component waves is simpler outside this region. In particular, the asymptotic wave function in the forward ($x > x_0$) region is

$$\begin{aligned}
\psi(x \to +\infty) &= e^{ik_E x} + \frac{1}{i\hbar v_E} \int dk \, \langle k|T^+(E)|k_E\rangle \int dx_0 \, e^{ik_E x} e^{i(k-k_E)x_0} \\
&= e^{ik_E x} - \frac{2\pi i}{\hbar v_E} e^{ik_E x}\langle k_E|T^+(E)|k_E\rangle,
\end{aligned} \tag{16.59}$$

where for the purposes of asymptotics we are ignoring the change in the phase dependence of $e^{ik_E|x-x_0|}$ at $x = x_0$, and we have also used the integral representation of the delta function. Similarly, the asymptotic wave function in the backward ($x < x_0$) region is

$$\begin{aligned}
\psi(x \to -\infty) &= e^{ik_E x} + \frac{1}{i\hbar v_E} \int dk \, \langle k|T^+(E)|k_E\rangle \int dx_0 \, e^{-ik_E x} e^{i(k+k_E)x_0} \\
&= e^{ik_E x} - \frac{2\pi i}{\hbar v_E} e^{-ik_E x}\langle -k_E|T^+(E)|k_E\rangle.
\end{aligned} \tag{16.60}$$

The second term on the right-hand side of Eq. (16.60) represents the reflected wave, while the entire right-hand side of Eq. (16.59) represents the transmitted wave. Thus, we can read off the reflected and transmitted amplitudes

$$r = -\frac{2\pi i}{\hbar}\frac{\langle -k_E|T^+(E)|k_E\rangle}{v_E}, \qquad \tau = 1 - \frac{2\pi i}{\hbar}\frac{\langle k_E|T^+(E)|k_E\rangle}{v_E},$$

(scattering amplitudes, one dimension) (16.61)

respectively. Again, we see the T-matrix inducing transitions from the incident state $|k_E\rangle$ to the scattered states $|\pm k_E\rangle$.

16.2.2.1 Example: Delta Scatterer

As a simple illustration of the scattering amplitudes (16.61), consider a delta scatterer in one-dimension,

$$V(x) = \beta\delta(x), \tag{16.62}$$

called a **contact potential** due to its zero range in the context of collisions. In the first Born approximation, we can evaluate the T-matrix element as

$$\begin{aligned}\langle -k_E|T^+(E)|k_E\rangle &\approx \langle -k_E|V(x)|k_E\rangle \\ &= \beta\langle -k_E|\delta(x)|k_E\rangle \\ &= \beta\int dx\,\langle -k_E|\delta(x)|x\rangle\langle x|k_E\rangle \\ &= \beta\langle -k_E|x=0\rangle\langle x=0|k_E\rangle \\ &= \frac{\beta}{2\pi},\end{aligned} \tag{16.63}$$

in which case we obtain the reflection amplitude

$$r \approx -\frac{2\pi i}{\hbar v_E}\langle -k_E|V(x)|k_E\rangle = -\frac{im\beta}{\hbar^2 k_E}, \tag{16.64}$$

which matches the first-order expansion (in β) of the exact result (2.161). In the second Born approximation, we have an additional contribution that is second order in the potential:

$$\begin{aligned}\langle -k_E|T^+(E)|k_E\rangle &\approx \langle -k_E|V(x)|k_E\rangle + \langle -k_E|V(x)G_0^+(E)V(x)|k_E\rangle \\ &= \frac{\beta}{2\pi} + \beta^2\int dx\int dx'\,\langle -k_E|x\rangle\langle x|\delta(x)G_0^+(E)\delta(x')|x'\rangle\langle x'|k_E\rangle \\ &= \frac{\beta}{2\pi} + \beta^2\langle -k_E|x=0\rangle G_0^+(0,0;E)\langle x=0|k_E\rangle \\ &= \frac{\beta}{2\pi} + \frac{\beta^2}{2\pi}\frac{m}{i\hbar^2 k_E} \\ &= \frac{\beta}{2\pi}\left(1 - \frac{im\beta}{\hbar^2 k_E}\right).\end{aligned} \tag{16.65}$$

Thus, the reflection amplitude becomes

$$r \approx -\frac{im\beta}{\hbar^2 k_E} + \left(-\frac{im\beta}{\hbar^2 k_E}\right)^2 \tag{16.66}$$

in this approximation. Now we see the pattern in in the Born expansion: Each successive accompanied by another factor $G_0^+(0,0;E) = -im\beta/\hbar^2 k_E$, so that the exact reflection amplitude is given by the series expansion

$$r = -\frac{im\beta}{\hbar^2 k_E} + \left(-\frac{im\beta}{\hbar^2 k_E}\right)^2 + \left(-\frac{im\beta}{\hbar^2 k_E}\right)^3 + \cdots. \tag{16.67}$$

This is a geometric series, which is readily summed to obatin

$$r = \frac{-im\beta/\hbar^2 k_E}{1 + im\beta/\hbar^2 k_E} = \frac{1}{i\hbar^2 k_E/m\beta - 1} \tag{16.68}$$

in agreement with the exact result (2.161).

A more direct trick to obtain the exact reflection amplitude is to appeal to the Lippmann–Schwinger equation in the first form (16.48), which in the position representation reads

$$\psi(x) = \phi(x) + \int dx'\, G_0^+(x, x'; E)\, V(x')\, \psi(x'). \tag{16.69}$$

Putting in the delta potential and evaluating the integral and Green function, we have

$$\begin{aligned} \psi(x) &= \phi(x) + \beta \int dx'\, G_0^+(x, x'; E)\, \delta(x')\, \psi(x') \\ &= e^{ik_E x} + \beta\, G_0^+(x, 0; E)\, \psi(0) \\ &= e^{ik_E x} + \frac{m\beta}{i\hbar^2 k_E}\, e^{ik_E|x|}\, \psi(0). \end{aligned} \tag{16.70}$$

Now setting $x = 0$, we can solve for $\psi(0)$, which becomes

$$\psi(0) = \frac{\phi(0)}{1 - m\beta/i\hbar^2 k_E}, \tag{16.71}$$

with $\phi(0) = 1$ in our normalization of the input state Now because of continuity, and because $V(x) = 0$ for $x \neq 0$, we can write $\psi(0) = \tau = 1 + r$, so that the reflection coefficient becomes

$$r = \psi(0) - 1 = \frac{m\beta/i\hbar^2 k_E}{1 - m\beta/i\hbar^2 k_E} = \frac{1}{i\hbar^2 k_E/m\beta - 1}, \tag{16.72}$$

in agreement with the summation of the Born series. Note that this trick is specific to the delta potential, where $\psi(0)$ is already in the far-field asymptotic regime.

16.2.3 Scattering in Three Dimensions

As in the one-dimensional case, to handle scattering in three dimensions we can start with the Lippmann–Schwinger equation in the form (16.56):

$$\langle \mathbf{r}|\psi\rangle = \langle \mathbf{r}|\phi\rangle + \int d\mathbf{r}_0\, \langle \mathbf{r}|G_0^+(E)|\mathbf{r}_0\rangle \langle \mathbf{r}_0|T^+(E)|\phi\rangle. \tag{16.73}$$

The free-particle Green function in three dimensions is is [Eq. (13.57)]

$$G^+(\mathbf{r}, \mathbf{r}_0; E) = -\frac{m}{2\pi\hbar^2}\, \frac{e^{ik_E|\mathbf{r}-\mathbf{r}_0|}}{|\mathbf{r} - \mathbf{r}_0|}, \tag{16.74}$$

and we can take the input state to be a plane wave $e^{i\mathbf{k}_0\cdot\mathbf{r}}$ in the $\mathbf{p}_0 = \hbar\mathbf{k}_0$ direction,

$$|\phi\rangle = (2\pi\hbar)^{3/2}|\mathbf{p}_0\rangle = (2\pi)^{3/2}|\mathbf{k}_0\rangle, \tag{16.75}$$

with the magnitude taken to be $k_0 = k_E$. Putting both of these expressions into Eq. (16.73) gives the Lippmann–Schwinger equation in three dimensions:

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_0\cdot\mathbf{r}} - \frac{m\sqrt{2\pi}}{\hbar^2} \int d\mathbf{r}_0\, \frac{e^{ik_E|\mathbf{r}-\mathbf{r}_0|}}{|\mathbf{r} - \mathbf{r}_0|} \langle \mathbf{r}_0|T^+(E)|\mathbf{k}_0\rangle. \tag{16.76}$$

This is still an exact relation, but it is more convenient to go into the far field region ($r \gg r_0$) with respect to the compact region of the scatterer [$V(\mathbf{r}_0) \neq 0$], over which the $\mathbf{r}_0$ integral ranges. This amounts to the approximation

$$\begin{aligned} |\mathbf{r} - \mathbf{r}_0| &= \sqrt{(\mathbf{r} - \mathbf{r}_0)^2} \\ &\approx \sqrt{r^2 - 2\mathbf{r}\cdot\mathbf{r}_0} \\ &= r\sqrt{1 - 2\mathbf{r}\cdot\mathbf{r}_0/r^2} \\ &\approx r - \hat{r}\cdot\mathbf{r}_0, \end{aligned} \tag{16.77}$$

and defining the scattered wave vector $\mathbf{k}_\Omega := k_E\hat{r}$, we have the far-field scattering expression

$$\psi(\mathbf{r}) \approx e^{i\mathbf{k}_0\cdot\mathbf{r}} - \frac{m\sqrt{2\pi}}{\hbar^2}\frac{e^{ik_E r}}{r}\int d\mathbf{r}_0\, e^{i\mathbf{k}_\Omega\cdot\mathbf{r}_0}\langle\mathbf{r}_0|T^+(E)|\mathbf{k}_0\rangle. \tag{16.78}$$

Using $\langle\mathbf{k}_\Omega|\mathbf{r}_0\rangle = e^{i\mathbf{k}_\Omega\cdot\mathbf{r}_0}/(2\pi)^{3/2}$, we can eliminate the remaining integral to obtain

$$\psi(\mathbf{r}) \approx e^{i\mathbf{k}_0\cdot\mathbf{r}} - \frac{4\pi^2 m}{\hbar^2}\frac{e^{ik_E r}}{r}\langle\mathbf{k}_\Omega|T^+(E)|\mathbf{k}_0\rangle. \tag{16.79}$$

To match the original scattering *ansatz* (16.2), we can rewrite this result in the form

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_0\cdot\mathbf{r}} + f(\mathbf{k}_0,\mathbf{k}_\Omega)\frac{e^{ik_E r}}{r}, \tag{16.80}$$

(3D scattering equation, far-field limit)

in terms of the scattering amplitude

$$f(\mathbf{k}_0,\mathbf{k}_\Omega) = -\frac{4\pi^2 m}{\hbar^2}\langle\mathbf{k}_\Omega|T^+(E)|\mathbf{k}_0\rangle, \tag{16.81}$$

(scattering amplitude)

which appears here in terms of the on-shell T-matrix ("on-shell" because $k_\Omega = k_0$ for energy conservation). The scattering amplitude acts to modulate the angular dependence of the scattered spherical wave, giving the amplitude for an input wave vector $\mathbf{k}_0$ to be scattered into the output wave $\mathbf{k}_\Omega$. Remember that all these wave vectors have the same magnitude, $|\mathbf{k}_0| = |\mathbf{k}_\Omega| = k_E = \sqrt{2mE}/\hbar$, because scattering from a time-independent scattering potential is purely elastic.

16.2.3.1 Symmetries of the Scattering Amplitude

The scattering amplitude has some symmetry properties related to the underlying scattering problem, and it is interesting to review them.[6] First, recall the parity operator (Section 2.4), which is unitary and involutive ($\Pi^{-1} = \Pi = \Pi^\dagger$), which reflects the position operator via

$$\Pi\mathbf{r}\Pi = -\mathbf{r}. \tag{16.82}$$

If the scattering potential is parity symmetric, then it is unchanged under the change $\mathbf{r} \longrightarrow -\mathbf{r}$,

$$\Pi V(\mathbf{r})\Pi = V(\mathbf{r}), \tag{16.83}$$

or that is, the parity operator commutes with the potential, $[\Pi, V(\mathbf{r})] = 0$. Since Π commutes with p^2 as well, it follows that Π also commutes with H_0, H, and thus $G_0(z)$ and $G(z)$, and by extension, the T-operator. In terms of the scattering amplitude (16.81),

$$f(\mathbf{k}_0,\mathbf{k}_\Omega) = -\frac{4\pi^2 m}{\hbar^2}\langle\mathbf{k}_\Omega|T^+(E)|\mathbf{k}_0\rangle, \tag{16.84}$$

[6] See Robert G. Littlejohn, op. cit.

we can insert parity operators to see that

$$\langle \mathbf{k}_\Omega | T^+(E) | \mathbf{k}_0 \rangle = \langle \mathbf{k}_\Omega | \Pi \big(\Pi T^+(E) \Pi \big) \Pi | \mathbf{k}_0 \rangle = \langle -\mathbf{k}_\Omega | T^+(E) | -\mathbf{k}_0 \rangle. \tag{16.85}$$

Thus, in the case of a parity-symmetric scattering potential, the scattering amplitude satisfies

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = f(-\mathbf{k}_0, -\mathbf{k}_\Omega). \tag{16.86}$$
(parity symmetry)

That is, if an incident wave $\mathbf{k}_0$ is scattered to $\mathbf{k}_\Omega$, then under a parity transform, the mirror-image wave $-\mathbf{k}_0$ is scattered to $-\mathbf{k}_\Omega$, which is sensible.

A second symmetry is time-reversal symmetry, which is represented by the time-reversal (conjugation) operator C (Problem 1.20), defined by $\langle \mathbf{r} | C | \psi \rangle = \langle \mathbf{r} | \psi \rangle^*$ (and specific to the position representation, see Problem 2.15). The treatment of time reversal is a bit more subtle because of the antiunitary antilinear property of C, which says that $C^\dagger C = 1$, but in the sense that $\langle \varphi | C^\dagger C | \psi \rangle = \langle \varphi | \psi \rangle^* = \langle \psi | \varphi \rangle$. Proceeding by inserting conjugation pairs, we obtain

$$\begin{aligned}
\langle \mathbf{k}_\Omega | T^+(E) | \mathbf{k}_0 \rangle &= \langle \mathbf{k}_\Omega | C^\dagger C T^+(E) | \mathbf{k}_0 \rangle^* \\
&= \langle \mathbf{k}_\Omega | C^\dagger C T^+(E) C^\dagger C | \mathbf{k}_0 \rangle \\
&= \langle \mathbf{k}_\Omega | C^\dagger T^-(E) | -\mathbf{k}_0 \rangle \\
&= \Big[\big(\langle \mathbf{k}_\Omega | C^\dagger \big) T^-(E) | -\mathbf{k}_0 \rangle \Big]^* \\
&= \langle -\mathbf{k}_\Omega | T^-(E) | -\mathbf{k}_0 \rangle^* \\
&= \langle -\mathbf{k}_0 | T^+(E) | -\mathbf{k}_\Omega \rangle.
\end{aligned} \tag{16.87}$$

Some comments on the above steps are in order. At the third equality, we are using the operator conjugation rule $C^\dagger Q C = Q^\dagger$ and that $C|\mathbf{k}\rangle = |-\mathbf{k}\rangle$, which follows from the position representation $\langle \mathbf{r} | \mathbf{k} \rangle \propto e^{-i\mathbf{k}\cdot\mathbf{r}}$. At the fourth equality, we are changing the $C^\dagger$ operator so that it acts to the left. Recall that for an ordinary (linear) operator, we can freely allow it to operate to the left or right, $\langle \phi | Q | \psi \rangle \equiv \langle \phi | Q \psi \rangle = \langle Q \phi | \psi \rangle$ (provided both operations are sensible). But for an antilinear operator such as C, taking the default direction of operation to be to the right,

$$\langle \phi | C | \psi \rangle \equiv \langle \phi | C \psi \rangle = \langle C\psi | \phi \rangle^* \equiv \Big[\big(\langle \psi | C \big) | \phi \rangle \Big]^*. \tag{16.88}$$

That is, changing the direction of operation should be accompanied by complex conjugation of the whole inner product.

In terms of the scattering amplitude, the result of Eqs. (16.87) reads

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = f(-\mathbf{k}_\Omega, -\mathbf{k}_0). \tag{16.89}$$
(time-reversal symmetry/microscopic reversibility/reciprocity)

This property, also called **microscopic reversibility** and the **reciprocity relation**, says that the reversed output wave $-\mathbf{k}_\Omega$ scatters to the reversed input wave $-\mathbf{k}_0$. This property is independent of the details of the potential.

In the case that *both* parity symmetry and time-reversal symmetry hold, we can combine Eq. (16.86) and (16.89) to find

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = f(\mathbf{k}_\Omega, \mathbf{k}_0). \tag{16.90}$$
(parity+time symmetry/detailed balance)

This property is known as **detailed balance**, in the particular context of elastic scattering from potentials. In statistical mechanics, detailed balance is an important underlying principle, stating that there is a symmetry in the forward and backward transition rates between two states, which is crucial for the existence of an equilibrium state. As an example, Einstein's rate-equation treatment of the interaction of an atom with a

radiation field[7] used this principle in the form $B_{12} = B_{21}$ where B_{12} is the rate of stimulated absorption from the radiation field, causing the atomic-state transition $|1\rangle \longrightarrow |2\rangle$, and B_{21} is the rate of stimulated emission into the radiation field, causing the inverse atomic-state transition $|2\rangle \longrightarrow |1\rangle$. Since the excited state $|2\rangle$ also decays spontaneously (irreversibly) to $|1\rangle$ via spontaneous emission, a corollary to detailed balance is that there can never be an equilibrium population inversion (larger probability amplitude in $|2\rangle$ than $|1\rangle$) in a two-level atom due to a radiation field.

16.2.3.2 Example: 3D Delta Scatterer

To illustrate the above results, we will return to the delta scatterer, but in three dimensions:

$$V(\mathbf{r}) = \beta\delta^3(\mathbf{r}). \tag{16.91}$$

Before proceeding it's worth emphasizing that this is not *just* a simple model potential, but one that applies whenever the length scale associated with the potential is small. Small compared to what? The incident wave itself contains the other length scale—the de Broglie wavelength. Thus, if d represents a diameter length scale for a more general $V(\mathbf{r})$, we should be able to approximate it well by Eq. (16.91) provided $\lambda \sim 1/k_E \gg d$. This is the regime of small k_E, or equivalently the *zero-energy limit* of scattering. This presupposes that the scattering potential $V(\mathbf{r})$ vanishes asymptotically as $r \longrightarrow \infty$, and falls off sufficiently quickly—this would break down for $V \sim 1/r$, for example—in which case β would represent the integral of V over all space.

In the first Born approximation, we can treat the 3D delta potential in much the same was as in the 1D case:

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = -\frac{4\pi^2 m}{\hbar^2}\langle\mathbf{k}_\Omega|V|\mathbf{k}_0\rangle = -\frac{4\pi^2 m\beta}{\hbar^2}\langle\mathbf{k}_\Omega|\delta^3(\mathbf{r})|\mathbf{k}_0\rangle = -\frac{4\pi^2 m\beta}{\hbar^2}\langle\mathbf{k}_\Omega|\mathbf{r}=0\rangle\langle\mathbf{r}=0|\mathbf{k}_0\rangle = -\frac{m\beta}{2\pi\hbar^2}. \tag{16.92}$$

The important result here is that the scattering amplitude is *independent of angle*—the scattered wave is an isotropic spherical wave. In the language of the partial-wave expansion, this is *pure S-wave scattering*, and again this is generically true for low-energy scattering (even for anisotropic scattering potentials, which are still effectively delta-scatterers in the long-wavelength limit). That low-energy scattering is 1e only for more general potentials also follows from Eq. (16.78), where the exponential factor $e^{i\mathbf{k}_\Omega\cdot\mathbf{r}} \approx 1$ because $k_E r_0 \ll 1$, and thus the angular dependence ($\mathbf{k}_\Omega$) drops out of the scattered wave.

In the low-energy (S-wave) regime of scattering from an arbitrary, localized potential, we see that the scattering amplitude reduces to a constant. As we saw before in Section 16.1.1.3, it is conventional to identify this constant, zero-energy scattering amplitude in terms of the **scattering length** a, such that $f = -a$. In the delta-scatterer case the scattering length is given in Eq. (16.92) as

$$a = \frac{m\beta}{2\pi\hbar^2}, \tag{16.93}$$

but it is worth reiterating that the scattering length is a more fundamental, general, and useful concept beyond this specific example. In terms of the scattering length, in the $E \longrightarrow 0$ limit, we still have the asymptotic scattering state (16.80) reduce to

$$\psi_{E\to 0}(\mathbf{r}) \approx 1 - \frac{a}{r}, \tag{16.94}$$

and from Eq. (16.4), the total cross-section becomes

$$\sigma = 4\pi a^2, \tag{16.95}$$

all as if scatterer were a hard sphere of radius a.

[7] A. Einstein, "Zur Quantentheorie der Strahlung," *Physikalische Zeitschrift* **18**, 121 (1917), translation "On the Quantum Theory of Radiation" by Alfred Engel appears in *The Collected Papers of Albert Einstein, Volume 6, The Berlin Years: Writings, 1914-1917* (Princeton University Press, 1997) p. 200 (ISBN: 0691017344).

16.2.3.3 Regularized Delta Potential

The conclusions above about the scattering length representing the scattered wave in the low-energy limit hold more generally, even though we derived the scattering wave function in the first Born approximation. We will demonstrate that this holds to all orders, and in doing so address some technical complications that arise for contact potentials.

In the second Born approximation, we would evaluate a matrix element of the form

$$\langle \mathbf{k}_\Omega | V G_0^+(E) V | \mathbf{k}_0 \rangle = \beta^2 \langle \mathbf{k}_\Omega | \mathbf{r}=0 \rangle G_0^+(0,0;E) \langle \mathbf{r}=0 | \mathbf{k}_0 \rangle. \tag{16.96}$$

Here we went ahead and tried to evaluate it naïvely by inserting a couple of position identities, just like in the 1D case where this method worked out fine. Here, however, it does not, because the Green function diverges as $1/|\mathbf{r}-\mathbf{r}_0|$ as $\mathbf{r}, \mathbf{r}_0 \longrightarrow 0$. This is not so much a symptom of having two delta functions in the same matrix element, but rather of having a delta function act on a $1/r$ wave function—a problem absent from the 1D case. Although the results as we have stated them so far are okay, the divergent matrix element here says that the 3D delta well is pathological (Problem 16.3), so we will have to treat it carefully.

The solution is to modify the potential to avoid problems with $1/r$ wave functions. The delta potential (16.91) is defined more explicitly to act in the position representation as multiplication by a delta function:

$$\langle \mathbf{r} | V(\mathbf{r}) | \psi \rangle = \beta \delta^3(\mathbf{r}) \psi(\mathbf{r}) = \beta \delta^3(\mathbf{r}) \psi(0). \tag{16.97}$$

A generalization (or, more properly, *regularization*) of this contact potential is the **regularized contact pseudopotential**[8,9]

$$\langle \mathbf{r} | V(\mathbf{r}) | \psi \rangle = \beta \delta^3(\mathbf{r}) \frac{\partial}{\partial r} \big[r \psi(\mathbf{r}) \big] \tag{16.98}$$

(regularized contact pseudopotential)

To see how this funny-looking potential helps things, first note that if ψ is regular at $r = 0$, then the factor of r have cancelling effects when multiplied by the delta function. More explicitly, suppose we give a Laurent expansion of ψ about $r = 0$,

$$\psi(\mathbf{r}) \sim \frac{\psi_{-1}}{r} + \psi_0 + \psi_1 r + \cdots \tag{16.99}$$

where the coefficients ψ_n are angular functions. When the pseudopotential (16.98) acts on this series, we see that

$$\begin{aligned} \delta^3(\mathbf{r}) \frac{\partial}{\partial r} \big[r \psi(\mathbf{r}) \big] &= \delta^3(\mathbf{r}) \frac{\partial}{\partial r} \big[\psi_{-1} + \psi_0 r + \psi_1 r^2 + \cdots \big] \\ &= \delta^3(\mathbf{r}) \frac{\partial}{\partial r} \big[\psi_0 + 2\psi_1 r + \cdots \big] \\ &= \delta^3(\mathbf{r})\, \psi_0, \end{aligned} \tag{16.100}$$

and so what survives is ψ_0, just as it would for a regular wave function, and it ignores the singular part ψ_{-1} if it is present. The action of this pseudopotential is justified because the $1/r$ behavior of the Green function near the origin is an unphysical idealization because it ignores the effects of the true, underlying potential at short range.

[8] Here "pseudopotential" refers to an idealized potential that is intended to reproduce important results of exact potentials, here in the far field. The ordinary delta potential serves in this capacity too, but the pseudopotential (16.98) is the better (regularized) version.

[9] Yvan Castin, "Bose-Einstein Condensates in Atomic Gases: Simple Theoretical Results," in *Coherent Atomic Matter Waves: Les Houches Session LXXII*, R. Kaiser, C. Westbrook, and F. David, Eds. (Springer, 2001), p. 1 (doi: 10.1007/3-540-45338-5_1) (arXiv: cond-mat/0105058). This pseudopotential is attributed to Fermi, who reduced an arbitrary scattering potential at short range to a finite-radius-sphere approximation delta function interacting with the sphere-averaged wave function, regularized explicitly in terms of the scattering length. This approach more directly accounts for the effect of the potential at short ranges, so that a $1/r$ potential never arises. Enrico Fermi, "Sul Moto dei Neutroni nelle Sostanze Idrogenate," ("Motion of Neutrons in Hydrogenous Substances") *La Ricerca Scientifica*, **7**, 13(1936) reprinted in Enrico Fermi, *Note e Memorie. Volume I, Italia 1921-1938*, p. 943, with translation by G. M. Temmer on p. 980. See also Kerson Huang, *Statistical Mechanics*, 2nd ed. (Wiley, 1987) pp. 231–8.

The regularized potential (16.98) thus cures the problem we encountered in the second Born approximation, but rather than sum the Born series we will find the exact solution more directly, as in the 1D case. Going back to the Lippmann–Schwinger equation (16.50) in the position representation, we can put in the regularized potential (16.98) and then the Green function

$$\begin{aligned}\psi(\mathbf{r}) &= \phi(\mathbf{r}) + \int d\mathbf{r}'\, G_0^+(\mathbf{r},\mathbf{r}';E)\, V(\mathbf{r}')\, \psi(\mathbf{r}') \\ &= \phi(\mathbf{r}) + \beta\, G_0^+(\mathbf{r},0;E)\, \left[\frac{\partial}{\partial r}\big[r\psi(\mathbf{r})\big]\right]_{\mathbf{r}=0} \\ &= e^{i\mathbf{k}_0\cdot\mathbf{r}} - \frac{m\beta}{2\pi\hbar^2}\,\frac{e^{ik_E r}}{r}\,\left[\frac{\partial}{\partial r}\big[r\psi(\mathbf{r})\big]\right]_{\mathbf{r}=0} \\ &= e^{i\mathbf{k}_0\cdot\mathbf{r}} - a\,\frac{e^{ik_E r}}{r}\bar{\psi}(0),\end{aligned} \tag{16.101}$$

where we used (16.93) for the scattering length a, and

$$\bar{\psi}(0) := \left[\frac{\partial}{\partial r}\big[r\psi(\mathbf{r})\big]\right]_{\mathbf{r}=0}. \tag{16.102}$$

Now multiplying through by r, differentiating with respect to r, and setting $r = 0$, we find

$$\bar{\psi}(0) = e^{i\mathbf{k}_0\cdot\mathbf{r}} - ik_E a\, e^{ik_E r}\bar{\psi}(0), \tag{16.103}$$

and then

$$\bar{\psi}(0) = 1 - ik_E a\bar{\psi}(0) \tag{16.104}$$

after setting $\mathbf{r} = 0$. This has the solution

$$\bar{\psi}(0) = \frac{1}{1+ik_E a}, \tag{16.105}$$

so that the scattering wave function (16.101) becomes

$$\psi(\mathbf{r}) = e^{i\mathbf{k}_0\cdot\mathbf{r}} - \frac{a}{1+ik_E a}\,\frac{e^{ik_E r}}{r}.$$

(exact scattering solution for regularized delta potential) (16.106)

Then the scattering amplitude is

$$f(\mathbf{k}_0,\mathbf{k}_\Omega) = -\frac{a}{1+ik_E a}, \tag{16.107}$$

which is still angle-independent and thus reflects pure S-wave scattering. The scattering length of this wave is the limit of this scattering amplitude as $k_E \longrightarrow 0$, which is still a, consistent with the first-order approximate solution.

16.2.3.4 Scattering in Dilute, Quantum Atomic Gases

One important application of the contact pseudopotential (16.98) is to the understanding of quantum dilute bosonic atomic gases. In the dilute regime, the density is low and the atoms are typically in the far field of any other atom. To summarize this collision interaction potential, we can change to a more standard notation for this subject, replacing β by g. To summarize, we have the potential

$$\langle\mathbf{r}|V(\mathbf{r})|\psi\rangle = g\,\delta^3(\mathbf{r})\frac{\partial}{\partial r}\big[r\psi(\mathbf{r})\big], \qquad g = \frac{4\pi\hbar^2 a}{m}.$$

(atom–atom pseudopotential) (16.108)

Here, the expression for g in terms of the scattering length a is given by Eq. (16.93), which reads $a = mg/2\pi\hbar^2$. But in a collision process, the m here should be interpreted as the reduced mass for one of

the atoms, which is $\mu = m/2$ for identical atoms of mass m. Making this replacement leads to the quoted expression for g in terms of the scattering length, which can be measured in other experiments (e.g., photoassociation experiments). The applications of this contact pseudopotential are discussed later in the context of second quantization beginning in Section 20.6.3.1.

16.3 S-Matrix

The T-matrix formalism above analyzed the scattering process in terms of energy eigenstates, in the spirit of the resolvent operator and static perturbation theory. However, scattering can be viewed in a complementary way as a dynamical process, where an incoming state $|\,\mathsf{i}\,\rangle$ interacts with a scattering potential in the form of time evolution, and ends up in a final state $|\,\mathsf{f}\,\rangle$. This scattering $|\,\mathsf{i}\,\rangle \longrightarrow |\,\mathsf{f}\,\rangle$ transition is then similar in spirit to time-dependent perturbation theory. Formally the time evolution in the scattering process takes place in the form of the ***S*-operator**

$$S := \lim_{T\to\infty} \tilde{U}(T/2, -T/2) \equiv \tilde{U}(+\infty, -\infty), \tag{16.109}$$
(S-operator)

which is just the evolution operator from the distant past to the distant future. As in time-dependent perturbation theory, treating the evolution operator in the interaction picture is a convenience to suppress phase factors associated with the asymptotic H_0 evolution. (As before, $|\,\mathsf{i}\,\rangle$ and $|\,\mathsf{f}\,\rangle$ are static reference states, not really associated with any picture.) The transition from the input state to the scattered state is represented in terms of the ***S*-matrix**[10]

$$S_{\mathsf{fi}} = \lim_{T\to\infty} \langle\,\mathsf{f}\,|\tilde{U}(T/2, -T/2)|\,\mathsf{i}\,\rangle. \tag{16.110}$$
(S-matrix)

Typically $|\,\mathsf{i}\,\rangle$ and $|\,\mathsf{f}\,\rangle$ are taken to be eigenstates of H_0, which in turn is often taken to be the Hamiltonian for a free particle.

The S-matrix is the fundamental observable in a scattering experiment, being the recipe for mapping input states to outputs, unlike the T-matrix, which is more of a tool for calculation. The S-matrix and T-matrix are closely connected, however, as we will now argue.[11] First, recall that time-dependent Green functions are related by a Fourier transform to the resolvent operator by [Eq. (13.43)]

$$G^{\pm}(\tau, 0) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, e^{-iE\tau/\hbar}\, G^{\pm}(E), \tag{16.111}$$

where $G\pm(E) := G(E \pm i0^+)$, and the retarded and advanced Green operators are defined by [Eq. (13.38)]

$$G^{\pm}(\tau, 0) := \pm U(\tau, 0)\,\Theta(\pm\tau). \tag{16.112}$$

The full time-evolution operator thus involves both Green operators:

$$\begin{aligned} U(\tau, 0) &= G^{+}(\tau, 0) - G^{-}(\tau, 0) \\ &= \frac{1}{2\pi i}\int_{-\infty}^{\infty} dE\, e^{-iE\tau/\hbar}\Big[G^{-}(E) - G^{+}(E)\Big]. \end{aligned} \tag{16.113}$$

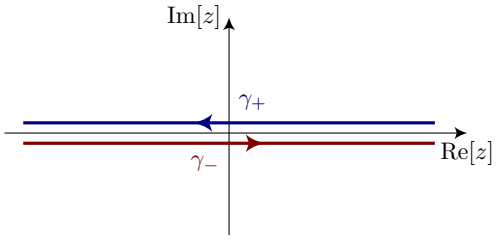
[10] John A. Wheeler, ''On the Mathematical Description of Light Nuclei by the Method of Resonating Group Structure,'' *Physical Review* **52**, 1107 (1937) (doi: 10.1103/PhysRev.52.1107); W. Heisenberg, *Zeitschrift für Physik* **120**, 513, 673 (1943) ''Die „beobachtbaren Größen" in der Theorie der Elementarteilchen'' (doi: 10.1007/978-3-642-70078-1_44); Werner Heisenberg, ''Der mathematische Rahmen der Quantentheorie der Wellenfelder,'' *Zeitschrift für Naturforschung* **1**, 608 (1946) (doi: 10.1515/zna-1946-11-1202); C. Møller, *op. cit.*

[11] Here we are following Claude Cohen-Tannoudji, Jacques Dupont-Roc, and Gilbert Grynberg, *Atom–Photon Interactions: Basic Processes and Applications* (Wiley, 1992), pp. 222-9 (ISBN: 0471625566).

We can rewrite this in terms of a single resolvent if we integrate over two contours γ_+ and γ_-, so that

$$U(\tau,0) = \frac{1}{2\pi i}\int_{\gamma_+ + \gamma_-} dz\, e^{-iz\tau/\hbar}\, G(z), \tag{16.114}$$

where the contours are the infinitesimally displaced real axis in either direction, as shown below.



Note that γ_+ is the only contour that contributes for $\tau > 0$, while γ_- is the only contribuor for $\tau < 0$. Now recalling that the evolution operator transforms from the interaction picture back to the Schrödinger picture via $\tilde{U}(t,t_0) = U_0(0,t)\,U(t,t_0)\,U_0(t_0,0)$, we can write the S-matrix as

$$S_{\mathsf{fi}} = \lim_{\tau\to\infty} \langle\, \mathsf{f}\,|e^{iE_{\mathsf{f}}\tau/2\hbar}\, U(\tau/2,-\tau/2)\, e^{iE_{\mathsf{i}}\tau/2\hbar}|\,\mathsf{i}\,\rangle. \tag{16.115}$$

Using Eq. (16.114) to replace the evolution operator with a contour integral, we will assume $\tau > 0$ so that we only need the γ_+ contour, and thus

$$S_{\mathsf{fi}} = \lim_{\tau\to\infty} \frac{e^{i(E_{\mathsf{i}}+E_{\mathsf{f}})\tau/2\hbar}}{2\pi i}\int_{\gamma_+} dz\, e^{-iz\tau/\hbar}\,\langle\, \mathsf{f}\,|G(z)|\,\mathsf{i}\,\rangle. \tag{16.116}$$

From Eq. (16.40) we have the perturbed resolvent in terms of the T-operator,

$$G(z) = G_0(z) + G_0(z)\,T(z)\,G_0(z), \tag{16.117}$$

which gives the resolvent matrix elements

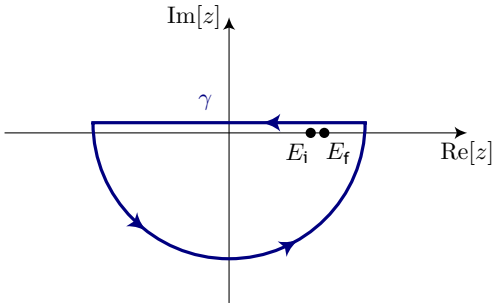
$$\langle\, \mathsf{f}\,|G(z)|\,\mathsf{i}\,\rangle = \frac{\delta_{\mathsf{if}}}{z-E_{\mathsf{i}}} + \frac{T_{\mathsf{fi}}(z)}{(z-E_{\mathsf{f}})(z-E_{\mathsf{i}})}, \tag{16.118}$$

with

$$T_{\mathsf{fi}}(z) = V_{\mathsf{fi}} + \langle\, \mathsf{f}\,|VG(z)V|\,\mathsf{i}\,\rangle \tag{16.119}$$

giving the relevant T-matrix element.

Now we need to work out the contour integral (16.116), with Eqs. (16.118) and (16.119) in the integrand. We will proceed by making a simplifying assumption, and then go back to justify that the possible complications don't change the result. Namely, we will assume that the only poles in the integrand that we need to worry about are the ones explicitly in Eq. (16.118) at E_{i} and E_{f}. (Namely, we are assuming that $\langle\, \mathsf{f}\,|VG(z)V|\,\mathsf{i}\,\rangle$ is completely regular, which may not necessarily be true.) Proceeding for new under this assumption, because of the exponential factor $e^{-iz\tau/\hbar}$ for $\tau > 0$, we should close the contour around the lower half-plane, as shown below.



Applying the residue theorem gives the result

$$\begin{aligned} S_{\mathsf{fi}} &= \lim_{\tau\to\infty} e^{i(E_\mathsf{i}+E_\mathsf{f})\tau/2\hbar}\left[\delta_{\mathsf{fi}}\, e^{-iE_\mathsf{i}\tau/\hbar} + \frac{T^+_{\mathsf{fi}}(E_\mathsf{i})\, e^{-iE_\mathsf{i}\tau/\hbar}}{E_\mathsf{i}-E_\mathsf{f}} + \frac{T^+_{\mathsf{fi}}(E_\mathsf{f})\, e^{-iE_\mathsf{f}\tau/\hbar}}{E_\mathsf{f}-E_\mathsf{i}}\right] \\ &= \lim_{\tau\to\infty}\left[\delta_{\mathsf{fi}}\, e^{-iE_{\mathsf{if}}\tau/2\hbar} + \frac{T^+_{\mathsf{fi}}(E_\mathsf{i})\, e^{-iE_{\mathsf{if}}\tau/2\hbar} - T^+_{\mathsf{fi}}(E_\mathsf{f})\, e^{iE_{\mathsf{if}}\tau/2\hbar}}{E_{\mathsf{if}}}\right]. \end{aligned} \tag{16.120}$$

Note that we have written $T^+_{\mathsf{fi}}(E_\mathsf{i})$, which displaces the T-matrix just above the real line, as consistent with the setup of the integral, which involved the retarded Green operator $G^+(E)$ via the choice of γ_+ contour. Then the exponential factor in the δ_{if} term is unity for $E_\mathsf{i} = E_\mathsf{f}$, which is enforced by the Kronecker delta. In the other terms we separate the complex exponentials into sines and cosines to obtain

$$S_{\mathsf{fi}} = \delta_{\mathsf{fi}} + \lim_{\tau\to\infty}\left[\Big(T^+_{\mathsf{fi}}(E_\mathsf{i}) - T^+_{\mathsf{fi}}(E_\mathsf{f})\Big)\frac{\cos(E_{\mathsf{if}}\tau/2\hbar)}{E_{\mathsf{if}}} - i\Big(T^+_{\mathsf{fi}}(E_\mathsf{i}) + T^+_{\mathsf{fi}}(E_\mathsf{f})\Big)\frac{\sin(E_{\mathsf{if}}\tau/2\hbar)}{E_{\mathsf{if}}}\right]. \tag{16.121}$$

The cosine factor has finite amplitude at any $E_{\mathsf{if}} \neq 0$ and oscillates arbitrarily rapidly as $\tau \longrightarrow \infty$; we should replace it by its zero average value (in the sense of its action under an integral over E_{fi}), including at $E_{\mathsf{fi}} = 0$ (in the sense of a Cauchy principal value). The sine factor is the finite-time delta funciton [Eq. (13.77)]

$$\delta_\tau(E_{\mathsf{fi}}) := \frac{\sin(E_{\mathsf{fi}}\tau/2\hbar)}{\pi E_{\mathsf{fi}}}, \tag{16.122}$$

so that as $\tau \longrightarrow \infty$, we have

$$S_{\mathsf{fi}} = \delta_{\mathsf{fi}} - 2\pi i T^+_{\mathsf{fi}}(E_\mathsf{i})\,\delta(E_{\mathsf{if}}). \tag{16.123}$$

(S-matrix and T-matrix)

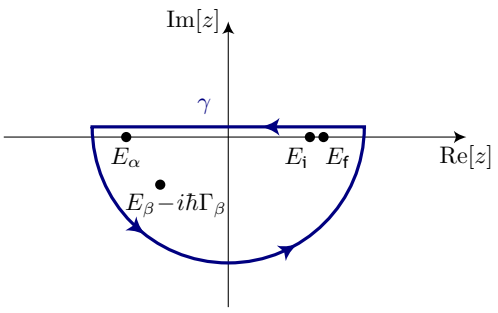
This important result relates the S- and T-matrices. This also matches and extends the third-order result (13.86) from our perturbation-theory analysis,

$$\tilde{K}_{\mathsf{fi}}(t) \approx \langle\, \mathsf{f}\,|\,\mathsf{i}\,\rangle - 2\pi i\left[V_{\mathsf{fi}} + \sum_k \frac{V_{\mathsf{f}k}V_{k\mathsf{i}}}{E_\mathsf{i}-E_k+i0^+} + \sum_{jk}\frac{V_{\mathsf{f}j}V_{jk}V_{k\mathsf{i}}}{(E_\mathsf{i}-E_j+i0^+)(E_\mathsf{i}-E_k+i0^+)}\right] e^{iE_{\mathsf{fi}}t/2\hbar}\,\delta_t(E_{\mathsf{fi}}). \tag{16.124}$$

To match these, this expression should be shifted backward in time by $t/2$ to remove the phase factor, and then the delta function emerges as $t \longrightarrow \infty$. In the scattering expression (16.123), the Born series (16.44) for $T(z)$ and expansion into identities gives the potential matrix elements and the energy denominators (at least in the case of a discrete spectrum).

Now we should go back and justify in the derivation of Eq. (16.123) that the result is really valid in the face of any additional complications in the contour integral.

1. First, there is the possibility of other (isolated) poles inside the contour associated with the resolvent in the T-matrix (16.119), corresponding to an eigenstate of H, say at energy E_α, as shown in the diagram below.



The isolated pole E_α corresponds to a bound state, and in the context of a scattering problem, should be far away from E_i and E_f, which are in the continuum (and thus located on a branch cut, which we will discuss separately below). The contribution from this pole to the S-matrix integral (16.116) will be of the form

$$\lim_{\tau\to\infty} \frac{e^{i(E_\mathsf{i}+E_\mathsf{f})\tau/2\hbar}}{2\pi i} e^{-iE_\alpha\tau/\hbar} \frac{\mathrm{Res}[T_\mathsf{fi}(E_\alpha)]}{(E_\alpha - E_\mathsf{f})(E_\alpha - E_\mathsf{i})}. \tag{16.125}$$

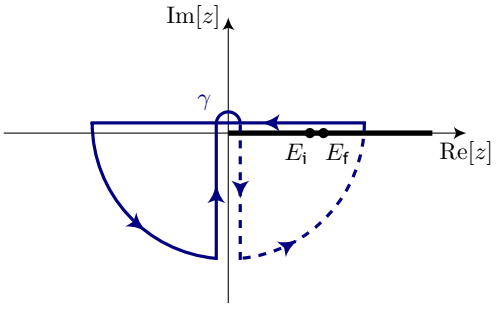
Again, since E_α is far from the initial and final-state energies, the energy denominator makes the function overall small, and the exponentials oscillate arbitrarily rapidly in E_i, E_f, and E_α in the limit $\tau \longrightarrow \infty$, and the function can be replaced by its zero average value. Such poles will thus not contribute to the result (16.123).

2. Recall that the energy-domain Green operators can be written in the integral form [Eq. (13.39)]

$$G^\pm(E) = \frac{1}{i\hbar}\int_{-\infty}^{\infty} d\tau\, e^{i[E+(\mathrm{sgn}\tau)i0^+]\tau/\hbar}\, G^\pm(\tau,0). \tag{16.126}$$

Since the matrix elements of $G^\pm(\tau,0)$ are well-behaved, the exponential factor $e^{iE\tau/\hbar}$ guarantees convergence of the integral for E everywhere in the upper half of the complex plane. However, this is not guaranteed in the lower half-plane, and so we should consider the possibility of poles there, which would be located at $E = E_\beta - i\hbar\Gamma_\beta$, as shown in the diagram above. Such a pole will vanish for the same reason as the E_α above, with the addition that the exponential factor will be modified according to $e^{-iE_\alpha\tau/\hbar} \longrightarrow e^{-iE_\beta\tau/\hbar}e^{-\Gamma_\beta\tau}$, so that the rapid oscillation will also be damped to zero at large τ.

3. In the case of a scattering problem, the energies E_i and E_f should be part of a continuum, and thus there will be a branch cut along the positive real axis of the complex plane. We have to be careful about crossing such a cut with a contour, because in doing so the contour passes onto the next Riemann sheet. The way to handle this is to modify the contour as shown below, so that an extra pair of lines along the negative real axis returns the contour to the first Riemann sheet; besides this new section, the contour is the same as the great lower semicircle from before.



The new hairpin in the contour is intended to be contracted to be just on either side of the negative imaginary axis. Since there is no pole at the origin (the zero energy state is part of the continuum), the contribution of the hairpin's semicircle vanishes in this limit. The contributions of the two linear sections of the hairpin have the additional contributions to Eq. (16.116) of the form

$$\lim_{\tau\to\infty} \frac{\hbar\, e^{i(E_\mathsf{i}+E_\mathsf{f})\tau/2\hbar}}{2\pi} \int_0^{-\hbar\Gamma} d\Gamma\, e^{-\Gamma\tau}\, \langle\, \mathsf{f}\,|G(i\hbar\Gamma)|\,\mathsf{i}\,\rangle, \tag{16.127}$$

where we set $z = -i\hbar\Gamma$. But because of the exponential factor $e^{-\Gamma\tau}$, this contribution also vanishes in the $\tau \longrightarrow \infty$ limit.

Thus, any irregular behavior of $G(z)$ does not affect the main result (16.123).

16.3.1 Optical Theorem

An important result follows from the relation (16.123) between the S- and T-matrices.[12] Taking that equation and replacing the input and output states by plane waves, $|\,\mathsf{i}\,\rangle \longrightarrow |\mathbf{k}\rangle$ and $|\,\mathsf{f}\,\rangle \longrightarrow |\mathbf{k}'\rangle$, respectively, gives

$$S_{\mathbf{k}'\mathbf{k}} = \langle \mathbf{k}'|\mathbf{k}\rangle - 2\pi i \langle \mathbf{k}'|T^+(E_\mathbf{k})|\mathbf{k}\rangle\, \delta(E_\mathbf{k} - E_{\mathbf{k}'}), \tag{16.128}$$

where the plane-wave energy is $E_\mathbf{k} = \hbar^2 k^2/2m$. The S-matrix, represents the scattering amplitude from the input $|k\rangle$ to the output $|k\rangle'$ on the same energy shell. Since the input must scatter into *some* output state (i.e., the total output probability must equal the input probability), so the S-matrix is unitary on the energy shell in the sense that

$$\int d\mathbf{k}''\, S^*_{\mathbf{k}'\mathbf{k}''} S_{\mathbf{k}''\mathbf{k}} = \langle \mathbf{k}'|\mathbf{k}\rangle = \delta^3(\mathbf{k} - \mathbf{k}'), \tag{16.129}$$

in the case of delta-normalized states (as appropriate for plane waves). Putting Eq. (16.128) into this unitarity integral gives

$$\begin{aligned}\int d\mathbf{k}''\, S^*_{\mathbf{k}'\mathbf{k}''} S_{\mathbf{k}''\mathbf{k}} = \langle \mathbf{k}'|\mathbf{k}\rangle - 2\pi i\Big[\langle \mathbf{k}'|T^+(E_\mathbf{k})|\mathbf{k}\rangle\, \delta(E_\mathbf{k} - E_{\mathbf{k}'}) - \text{c.c.}\Big] \\ +4\pi^2 \int d\mathbf{k}''\, \langle \mathbf{k}'|T^-(E_\mathbf{k})|\mathbf{k}''\rangle\, \delta(E_{\mathbf{k}''} - E_{\mathbf{k}'})\, \langle \mathbf{k}''|T^+(E_\mathbf{k})|\mathbf{k}\rangle\, \delta(E_\mathbf{k} - E_{\mathbf{k}''}).\end{aligned} \tag{16.130}$$

In the last term $\delta(E_{\mathbf{k}''} - E_{\mathbf{k}'})$ replaced by $\delta(E_\mathbf{k} - E_{\mathbf{k}'})$ due to the presence of the other delta function, Then equating the right-hand expressions in Eqs. (16.129) and (16.130), we find

$$2\pi i\Big[\langle \mathbf{k}|T^+(E_\mathbf{k})|\mathbf{k}\rangle - \text{c.c.}\Big] = 4\pi^2 \int d\mathbf{k}''\, \langle \mathbf{k}|T^-(E_\mathbf{k})|\mathbf{k}''\rangle\, \langle \mathbf{k}''|T^+(E_\mathbf{k})|\mathbf{k}\rangle\, \delta(E_\mathbf{k} - E_{\mathbf{k}''}). \tag{16.131}$$

Here, we have dropped the overall $\delta(E_\mathbf{k} - E_{\mathbf{k}'})$, which serves only to enforce the on-shell constraint; to compensate, we have now enforced this explicitly by setting $\mathbf{k}' = \mathbf{k}$.

Now recalling Eq. (16.81),

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = \frac{4\pi^2 m}{\hbar^2} \langle \mathbf{k}_\Omega|T^+(E)|\mathbf{k}_0\rangle, \tag{16.132}$$

we can change the matrix elements to scattering amplitudes, with the result

$$4\pi \text{Im} f(\mathbf{k}, \mathbf{k}) = \frac{\hbar^2}{m} \int d\mathbf{k}''\, \big|f(\mathbf{k}'', \mathbf{k})\big|^2\, \delta(E_\mathbf{k} - E_{\mathbf{k}''}). \tag{16.133}$$

To handle the delta function, we use the identity

$$\delta[g(x)] = \sum_{x_0 \in g^{-1}(0)} \frac{\delta(x - x_0)}{|g'(x_0)|}, \tag{16.134}$$

where the sum is over the (isolated) zeros of $g(x)$. In the case at hand, $g(k) = \hbar^2(k^2 - k'^2)/2m$, so that

$$\delta(E_k - E_{k''}) = \frac{m}{\hbar^2 k} \delta(k - k''), \tag{16.135}$$

so that we now have a delta function in terms of *magnitudes* of the wave vectors. With this relation and moving the 4π, Eq. (16.133) becomes

$$\begin{aligned}\text{Im} f(\mathbf{k}, \mathbf{k}) &= \frac{\hbar^2}{4\pi m} \frac{m}{\hbar^2 k} \int d\mathbf{k}''\, \big|f(\mathbf{k}, \mathbf{k}'')\big|^2\, \delta(k - k'') \\ &= \frac{1}{4\pi k} \int dk''\, k''^2 \int d\Omega''\, \big|f(\mathbf{k}, \mathbf{k}'')\big|^2\, \delta(k - k'') \\ &= \frac{k}{4\pi} \int d\Omega''\, \frac{d\sigma}{d\Omega''},\end{aligned} \tag{16.136}$$

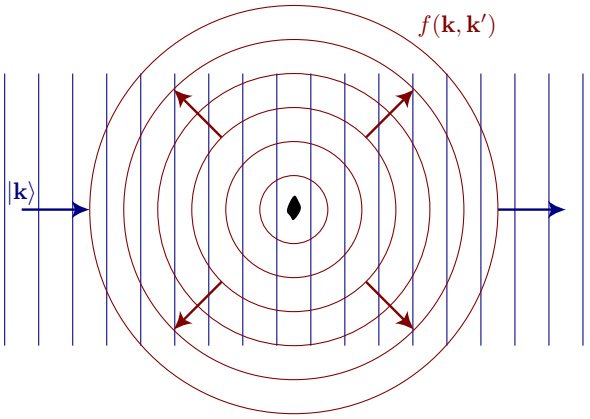
[12] An alternate proof can be based on the partial wave expansion (see Problem 16.1).

where in the last step we have identified $|f(\mathbf{k}'', \mathbf{k})|^2$ with $d\sigma/d\Omega''$. The angular just gives the total cross section and thus we arrive at the important relation

$$\mathrm{Im} f(\mathbf{k}, \mathbf{k}) = \frac{k}{4\pi}\,\sigma, \tag{16.137}$$
(optical theorem)

which is known as the **optical theorem**.[13]

To understand the physical content of the optical theorem, recall the setup, shown below. An input plane wave $\mathbf{k}$ is incident on a scattering potential, which scatters into a spherical wave with angular amplitude $f(\mathbf{k}, \mathbf{k}')$ in the $\mathbf{k}'$ direction.



The input wave zooms on through the potential, which makes it seem like the scattered wave is generated out of thin air. But to conserve probability, any probability that is scattered into the spherical wave must be *depleted* from the input wave. The way this works out is that the plane wave and spherical wave *destructively interfere* in the region to the right of the scatterer, which reduces the outgoing amplitude of the input wave. The right-hand side of the optical theorem (16.137) represents the *total* scattering probability, proportional to the integrated square of the scattering amplitude $f(\mathbf{k}, \mathbf{k}')$. The left-hand side came from the cross terms from squaring the S-matrix, and thus represented products (interferences between) the incident and scattered waves. In the language of the fluctuation–dissipation theorem (Section 14.3), the scattering amplitude is a scattering response function, and intuitively its imaginary part represents a loss or dissipation (in this case the loss of amplitude from the ingoing wave). Specifically, what appears is the imaginary part of $f(\mathbf{k}, \mathbf{k})$, which is the amplitude for scattering into the same plane-wave mode as the input wave, which is what allows the destructive interference even asymptotically far to the right.

16.3.2 *S*-Matrix in One Dimension

As a simple example of an S-matrix, let's work out the case of scattering in one dimension. Using the one-dimensional scattering amplitudes (16.61),

$$r = -\frac{2\pi i}{\hbar}\,\frac{\langle -k_E|T^+(E)|k_E\rangle}{v_E}, \qquad \tau = 1 - \frac{2\pi i}{\hbar}\,\frac{\langle k_E|T^+(E)|k_E\rangle}{v_E}, \tag{16.138}$$

we can write the relevant T-matrix elements as

$$\langle -k_E|T^+(E)|k_E\rangle = -\frac{\hbar v_E}{2\pi i}\,r, \qquad \langle k_E|T^+(E)|k_E\rangle = \frac{\hbar v_E}{2\pi i}\,(1-\tau), \tag{16.139}$$

where the wave energy E is parameterized by any of $v_E = p_E/m = \sqrt{2E/m} = \hbar k_E/m$. For definiteness, we need to fix the orientation of the scattering process, so we will choose $k_E > 0$ (corresponding to wave incident from $-\infty$).

[13] Eugene Feenberg, "The Scattering of Slow Electrons by Neutral Atoms," *Physical Review* **40**, 40 (1932) (doi: 10.1103/PhysRev.40.40).

Now we can use the S–T-matrix relation (16.128),

$$S_{k'k} = \langle k'|k\rangle - 2\pi i \langle k'|T^+(E_k)|k\rangle\, \delta(E_k - E_{k'}), \tag{16.140}$$

where we are tidying up the notation a bit by dropping the subscript from k_E. The delta function here can be written in k-space as

$$\delta(E_k - E_{k'}) = \frac{m}{\hbar^2 k}\big[\delta(k-k') + \delta(k+k')\big] = \frac{m}{\hbar^2 k}\big[\langle k|k'\rangle + \langle k|{-k'}\rangle\big], \tag{16.141}$$

where we are summing over both possible roots of $E_k - E_{k'}$ [note that we didn't need to do this before in the 3D case of Eq. (16.135), because there the integral already included the sum over roots]. Then the S-matrix becomes

$$\begin{aligned} S_{k'k} &= \langle k'|k\rangle - \frac{2\pi i m}{\hbar^2 k}\big[\langle k|k'\rangle + \langle k|{-k'}\rangle\big]\langle k'|T^+(E_k)|k\rangle \\ &= \langle k'|k\rangle - \frac{2\pi i m}{\hbar^2 k}\langle k|k'\rangle\langle k|T^+(E_k)|k\rangle - \frac{2\pi i m}{\hbar^2 k}\langle k|{-k'}\rangle\langle -k|T^+(E_k)|k\rangle \\ &= \langle k'|k\rangle - \langle k|k'\rangle(1-\tau) + \langle k|{-k'}\rangle\, r \\ &= \langle k|k'\rangle\, \tau + \langle k|{-k'}\rangle\, r, \end{aligned} \tag{16.142}$$

giving the superposition of a reflected and transmitted wave. Again, fixing the input wave as the plane wave $|k\rangle$, the S-matrix gives the corresponding amplitudes for the two possible output modes.

To completely characterize the S-matrix, we also need to work out its matrix elements with an input state $|{-k}\rangle$. We can do this by redoing the calculation (16.142), but with $k \longrightarrow -k$:

$$\begin{aligned} S_{k'(-k)} &= \langle k'|{-k}\rangle - \frac{2\pi i m}{\hbar^2 k}\langle -k|k'\rangle\langle -k|T^+(E_k)|{-k}\rangle - \frac{2\pi i m}{\hbar^2 k}\langle -k|{-k'}\rangle\langle k|T^+(E_k)|{-k}\rangle \\ &= \langle k'|{-k}\rangle - \langle -k|k'\rangle(1-\tau') + \langle -k|{-k'}\rangle\, r' \\ &= \langle -k|k'\rangle\, \tau' + \langle -k|{-k'}\rangle\, r'. \end{aligned} \tag{16.143}$$

Here, we have translated the T-matrix elements into the *backward* reflection amplitude r' and transmission amplitude τ' via

$$\langle k|T^+(E)|{-k}\rangle = -\frac{\hbar v_E}{2\pi i}\, r', \qquad \langle -k|T^+(E)|{-k}\rangle = \frac{\hbar v_E}{2\pi i}\,(1-\tau') \tag{16.144}$$

[cf. Eqs. (16.144)].

To put the entire S-matrix together from Eqs. (16.142) and (16.143), first note that the various S-matrix elements are accompanied by inner-product factors of the form $\langle k|k'\rangle$. The S-matrix elements are only nonzero in the case $|k| = |k'|$, but the factors $\langle k|k\rangle = \delta(0)$ are divergent on the energy shell, an artifact of working with a continuum of states. This can be handled, for example by quantizing in a box and working with normalizable states, so that instead $\langle k|k\rangle = 1$; here we will just implicitly regularize the S-matrix by dividing through by the divergent factor (which is the same as working with $S_{k'k}\, dk$). In the representation of $\{|{+k}\rangle, |{-k}\rangle\}$ states, the renormalized S-matrix then reads

$$\frac{(S)}{\langle k|k\rangle} = \begin{bmatrix} \tau & r' \\ r & \tau' \end{bmatrix}. \tag{16.145}$$

(S-matrix, one dimension)

Recalling that the S-matrix is unitary, we can multiply it by its conjugate to obtain

$$\frac{(S^\dagger S)}{|\langle k|k\rangle|^2} = \begin{bmatrix} \tau^* & r^* \\ r'^* & \tau'^* \end{bmatrix}\begin{bmatrix} \tau & r' \\ r & \tau' \end{bmatrix} = \begin{bmatrix} |\tau|^2 + |r|^2 & \tau^* r' + r^* \tau' \\ r'^*\tau + \tau'^* r & |r'|^2 + |\tau'|^2 \end{bmatrix}. \tag{16.146}$$

In order for this to agree with the identity matrix, we must have

$$|r|^2 + |\tau|^2 = |r'|^2 + |\tau'|^2 = 1, \qquad r' = -r^* \frac{\tau^*}{\tau}. \tag{16.147}$$
(Stokes relations)

These are the **Stokes relations** for the scattering problem (i.e., where the potential asymptotically vanishes), and can be compared to more general counterparts [see Problems 2.28 and 2.29]. The first pair of equalities give conservation of probability, while the second relation gives the phase of the backward reflection coefficient r' relative to the forward coefficient r.

The symmetry relations from Section 16.2.3.1 give additional information about the reflection and transmission amplitudes. For example, time reversal symmetry (16.89),

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = f(-\mathbf{k}_\Omega, -\mathbf{k}_0), \tag{16.148}$$

which always holds, says that we can swap the ingoing and outgoing waves, while also reversing their directions, and the total transformation will leave the amplitude invariant. This implies that

$$\tau' = \tau, \tag{16.149}$$
(time-reversal symmetry)

so that there is no need to distinguish between forward and backward transmission amplitudes. (Time-reversal symmetry says nothing about the reflection amplitudes, since it just says that $r = r$ and $r' = r'$.) Parity symmetry (16.86),

$$f(\mathbf{k}_0, \mathbf{k}_\Omega) = f(-\mathbf{k}_0, -\mathbf{k}_\Omega), \tag{16.150}$$

just says the problem is reflection symmetric (invariant under reversing the directions of the waves). This condition further implies

$$r' = r, \tag{16.151}$$
(parity symmetry)

since there should be no distinction at all between forward and backward amplitudes.

16.4 Exercises

Problem 16.1

For a spherically symmetric scattering potential, we had partial-wave expansions for the the scattering amplitude and cross-section [Eqs. (16.17) and (16.17)],

$$\begin{aligned} f(\Omega) &= \frac{\sqrt{4\pi}}{k}\sum_{\ell=0}^{\infty}\sqrt{2\ell+1}\,Y_\ell^0(\theta,0)\,e^{i\delta_\ell}\sin\delta_\ell \\ \sigma &= \frac{4\pi}{k^2}\sum_{\ell=0}^{\infty}(2\ell+1)\sin^2\delta_\ell, \end{aligned} \tag{16.152}$$

respectively. Use these expressions to prove the optical theorem in the form

$$\mathrm{Im}f(\theta=0) = \frac{k}{4\pi}\,\sigma. \tag{16.153}$$

Note that this is a less general result than the proof based on the S-matrix in Section 16.3.1, because spherical symmetry is assumed here.

Problem 16.2

For the 1D scattering problem with a delta scatterer, $V = \beta\,\delta(x)$, show that the exact T operator may be written

$$T^+(E) = \frac{\beta}{1-m\beta/i\hbar^2 k_E}\,\delta(x) = \frac{\beta}{1-\beta\,G_0^+(0,0;E)}\,\delta(x). \tag{16.154}$$

These expressions reinforce the idea of the T operator being a corrected or renormalized version of the scattering potential that accounts for multiple scattering interactions.

Problem 16.3

The basic delta-scattering potential in 3D is

$$V = \beta\delta^3(\mathbf{r}), \tag{16.155}$$

without any regularization for $1/r$ divergent states. Starting with the T-matrix relation (16.43),

$$T^+(E) = V + V\,G_0^+(E)\,T^+(E), \tag{16.156}$$

show that the T-matrix element in the momentum basis may be written

$$\langle\mathbf{k}|T^+(E)|\mathbf{k}'\rangle = \frac{1}{(2\pi)^3}\left(\frac{1}{\beta}-I\right)^{-1} \tag{16.157}$$

in terms of the integral

$$I := \frac{1}{(2\pi)^3}\int d\mathbf{k}\,\frac{1}{E-\hbar^2k^2/2m+i0^+}. \tag{16.158}$$

Then argue that the integral diverges, and thus the scattering amplitude and cross section vanish for the (unregularized) 3D delta scatterer.

This is quite a result, considering the first Born approximation for the scattering amplitude is finite, and the second term in the expansion is divergent. The problem is that the delta potential is an unphysical idealization because it ignores important structure of the scattering potential at short length scales (large k). By cutting off the integral I at large k one can obtain a finite (but cutoff-dependent) result for the scattering amplitude.[14]

[14] Indrajit Mitra, Ananda DasGupta, and Binayak Dutta-Roy, "Regularization and renormalization in scattering from Dirac

delta potentials,'' *American Journal of Physics* **66**, 1101 (1998) (doi: 10.1119/1.19051) regularize the divergence and give what appears to be a finite result for the T-matrix element and scattering cross section in terms of the binding energy of a bound state. However, the binding energies tend to infinity for the 3D delta well, so their results are consistent with the vanishing cross section.

Chapter 17

Quantum Brownian Motion

By this point, we have already seen some examples of how dissipation arises in quantum mechanics. The fluctuation–dissipation theorem (Chapter 14) connects the dissipative part of a generalized susceptibility to a two-time correlation function. We have also seen how transitions to a continuum of states (Chapter 15) are irreversible. Here we will consider an explicit and detailed model for how frictional damping of a quantum particle arises from a purely Hamiltonian description. Elements of both linear-response theory and continuum transitions will reappear here. In particular, both mechanical damping and a fluctuating force will arise from coupling to an environment, yielding the quantum-mechanical analogue of Brownian motion.

17.1 Particle Coupled to a Reservoir

The basic model for a damped particle subdivides into three basic parts; we can write the total Hamiltonian as

$$H = H_{\mathrm{S}} + H_{\mathrm{R}} + H_{\mathrm{SR}}. \tag{17.1}$$
(Caldeira–Leggett Hamiltonian)

The first part is the quantum system to be damped, described by the system Hamiltonian,

$$H_{\mathrm{S}} = \frac{p^2}{2M} + V(q), \tag{17.2}$$
(system Hamiltonian)

which is just a particle of mass M with canonical coordinates p and q in some potential $V(q)$, which is assumed to confine the system to a potential well. The next component of the model is the energy **reservoir**, which functions to soak up energy from the system. In this model this is a collection of N harmonic oscillators (with all $\omega_\alpha > 0$):

$$H_{\mathrm{R}} = \sum_{\alpha=1}^{N} \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 x_\alpha^2 \right). \tag{17.3}$$
(reservoir Hamiltonian)

The reservoir is also commonly called a **heat bath** or an **environment**. The final component is the system–reservoir coupling, which we can write as

$$H_{\mathrm{SR}} = \sum_{\alpha=1}^{N} \left(-c_\alpha x_\alpha q + \frac{c_\alpha^2}{2m_\alpha \omega_\alpha^2} q^2 \right) =: -fq + \frac{1}{2} M \delta\omega^2 q^2.$$
(system–reservoir interaction) (17.4)

The $-c_\alpha x_\alpha q$ terms represent a bilinear coupling between the system and reservoir coordinates; this is of course appropriate for linearizing a weak coupling, but this model can also work for strong damping. The q^2 component has a couple of benefits, although it doesn't in itself represent a coupling to the reservoir. First,

it ensures that the total Hamiltonian is positive definite (provided $V(q) \geq 0$), which rules out the possibility of any unbounded solutions. This follows from considering the potential terms

$$\frac{1}{2}m_\alpha\omega_\alpha^2 x_\alpha^2 - c_\alpha x_\alpha q + \frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2}q^2 = \frac{1}{2}m\omega_\alpha^2\left(x_\alpha - \frac{c_\alpha}{m_\alpha\omega_\alpha^2}q\right)^2. \tag{17.5}$$

Another easy way to see the benefit of the renormalization term is that in the limit of a free particle $V(q) = 0$, the total Hamiltonian must be translationally invariant, which happens provided we make the choice $c_\alpha = m_\alpha\omega_\alpha^2$. A more general manifestation of this same effect is that the coupling to the reservoir will end up modifying the curvature of the potential $V(q)$, and this ''renormalization'' term will end up canceling it.

The model here is a famous one, called the **Caldeira–Leggett model**.[1,2,3] The goal of this model is to study a quantum analogue of a classical particle of the form

$$m\ddot{q} + m\gamma\dot{q} + V'(q) = F(t), \tag{17.6}$$
(classical Langevin equation)

with damping rate γ and a randomly fluctuating external force $F(t)$. This is precisely the model for a particle undergoing Brownian motion (e.g., the random motion of pollen grain in a fluid), and this equation of motion is called the **Langevin equation** in classical mechanics.[4]

In quantum mechanics, where the Hamiltonian is a centerpiece, dissipation is not obviously a natural phenomenon. The approach here it to couple the system to be damped to a reservoir with many degrees of freedom. Of course, in the setup above with coupling to N degrees of freedom, we will not truly achieve irreversible damping except in the limit $N \longrightarrow \infty$ of a continuum of reservoir modes. (For example, if the system is a harmonic oscillator, then the entire system can be decoupled into normal modes, or a set of $N + 1$ independent harmonic oscillators, which is quasiperiodic, and will thus eventually recur). Another common approach is to consider the damped system directly in the Heisenberg picture. The problem here is that a damped equation like $\dot{p} = -\gamma p$, which has a solution like $p = p_0\, e^{-\gamma t}$, is problematic in leading to a commutator $[x, p]$ that damps away to zero, and this can't be. The way to save the commutator is to postulate the addition of a noise operator to the damped equation $\dot{p} = -\gamma p + F_{\text{noise}}(t)$, where the extra noise term is concocted to maintain the commutator at the required constant value. In the model here we will see the damping and noise both arising directly from the coupling to the reservoir.

[1] After A. O. Caldeira and A. J. Leggett, ''Path Integral Approach to Quantum Brownian Motion,'' *Physica A: Statistical Mechanics and its Applications* **121**, 587 (1983) (doi: 10.1016/0378-4371(83)90013-4), who studied the emergence of Brownian motion in this model via a path-integral formulation; they also applied this to the study of the effect of dissipation on quantum tunneling: A. O. Caldeira and A. J. Leggett, ''Influence of Dissipation on Quantum Tunneling in Macroscopic Systems,'' *Physical Review Letters* **46**, 211 (1981) (doi: 10.1103/PhysRevLett.46.211); A. O. Caldeira and A. J. Leggett, ''Quantum Tunnelling in a Dissipative System,'' *Annals of Physics* **149**, 374 (1983) (doi: 10.1016/0003-4916(83)90202-6).

[2] Despite being called the Caldeira–Leggett model, this model was studied previously. See V. B. Magalinskiĭ, ''Dynamical Model in the Theory of the Brownian Motion,'' *Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki* **36**, 1942 (1959) [*Soviet Physics JETP* **9**, 1381 (1959)] (`http://www.jetp.ac.ru/cgi-bin/e/index/e/9/6/p1382?a=list`); I. R. Senitzky, ''Dissipation in Quantum Mechanics. The Harmonic Oscillator,'' *Physical Review* **119**, 670 (1960) (doi: 10.1103/PhysRev.119.670); I. R. Senitzky ''Dissipation in Quantum Mechanics. The Harmonic Oscillator. II,'' *Physical Review* **124**, 642 (1961) (doi: 10.1103/PhysRev.124.642); G. W. Ford, M. Kac, and P. Mazur ''Statistical Mechanics of Assemblies of Coupled Oscillators,'' *Journal of Mathematical Physics* **6**, 504 (1965) (doi: 10.1063/1.1704304); P. Ullersma, ''An exactly solvable model for Brownian motion: I. Derivation of the Langevin equation,'' *Physica* **32**, 27 (1966) (doi: 10.1016/0031-8914(66)90102-9); P. Ullersma, ''An exactly solvable model for Brownian motion: II. Derivation of the Fokker-Planck equation and the master equation,'' *Physica* **32**, 56 (1966) (doi: 10.1016/0031-8914(66)90103-0); P. Ullersma, ''An exactly solvable model for Brownian motion: III. Motion of a heavy mass in a linear chain,'' *Physica* **32**, 74 (1966) (doi: 10.1016/0031-8914(66)90104-2); P. Ullersma, ''An exactly solvable model for Brownian motion: IV. Susceptibility and Nyquist's theorem,'' *Physica* **32**, 90 (1966) (doi: 10.1016/0031-8914(66)90105-4); Robert Zwanzig, ''Nonlinear Generalized Langevin Equations,'' *Journal of Statistical Physics* **9** 215 (1973) (doi: 10.1007/BF01008729).

[3] For further reading, see Peter Hänggi and Gert-Ludwig Ingold, ''Fundamental aspects of quantum Brownian motion,'' *Chaos* **15**, 026105 (2005) (doi: 10.1063/1.1853631); and Heinz-Peter Breuer and Francesco Petruccione, *The Theory of Open Quantum Systems* (Oxford, 2002) (ISBN: 0198520638) (doi: 10.1093/acprof:oso/9780199213900.001.0001).

[4] After P. Langevin, ''Sur la théorie du mouvement brownien,'' *Comptes rendus hebdomadaires des séances de l'Académie des Sciences* **146**, 530 (1908) (`https://gallica.bnf.fr/ark:/12148/bpt6k3100t/f530`).

17.1.1 Heisenberg-Picture Treatment

In the Heisenberg picture, the equation of motion (1.195) for an operator A with no explicit time dependence is

$$\dot{A} = -\frac{i}{\hbar}[A, H]. \tag{17.7}$$

With the Hamiltonian (17.1), this generates the Heisenberg equations

$$\begin{aligned} \dot{q} &= \frac{p}{M} \\ \dot{p} &= -V'(q) - M\delta\omega^2 q + f \end{aligned} \tag{17.8}$$

for the system, and

$$\begin{aligned} \dot{x}_\alpha &= \frac{p_\alpha}{m_\alpha} \\ \dot{p}_\alpha &= -m_\alpha \omega_\alpha^2 x_\alpha + c_\alpha q \end{aligned} \tag{17.9}$$

for the reservoir. Decoupling the system and reservoir equations by eliminating the momenta we have

$$\begin{aligned} M\ddot{q} + V'(q) + M\delta\omega^2 q &= f \\ m_\alpha \ddot{x}_\alpha + m_\alpha \omega_\alpha^2 x_\alpha &= c_\alpha q. \end{aligned}$$

(system and reservoir equations of motion) (17.10)

The next step is to eliminate the reservoir modes by analytically solving their evolution equations, which of course is possible in general because they are harmonic oscillators.

17.1.1.1 Green-Function Solution of Reservoir Modes

Starting with the reservoir-mode equation of motion

$$\ddot{x}_\alpha + \omega_\alpha^2 x_\alpha = \frac{c_\alpha}{m_\alpha} q(t), \tag{17.11}$$

the idea will be to treat $q(t)$ as a given function of time, and to solve the resulting equation. We can first solve the homogeneous version of this equation:

$$\ddot{x}_\alpha + \omega_\alpha^2 x_\alpha = 0. \tag{17.12}$$

This is a harmonic oscillator, so the solutions are sines and cosines; writing the superposition coefficients in terms of initial conditions, the homogeneous solution is

$$x_\alpha(t) = x_\alpha(0)\cos\omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha \omega_\alpha}\sin\omega_\alpha t. \tag{17.13}$$

Now to proceed to the inhomogeneous solution, let's replace the right-hand side of Eq. (17.11) by a delta function:

$$\ddot{x}_\alpha + \omega_\alpha^2 x_\alpha = \delta(t). \tag{17.14}$$

The initial conditions will be that $x = p = 0$ before the impulse at $t = 0$. Integrating this equation of motion across $t = 0$ gives

$$\dot{x}_\alpha(0^+) = \dot{x}_\alpha(0^-) + 1, \tag{17.15}$$

which is the same as saying $p_\alpha(0^+) = m_\alpha$ and $x_\alpha(0^+) = 0$, given the initial conditions. We can then adapt the homogeneous solution (17.13) to write

$$x_\alpha(t) = \frac{1}{\omega_\alpha}\sin\omega_\alpha t \tag{17.16}$$

for $t > 0$. This is the Green-function solution to the equation, which we can write more generally as

$$g(t,t') = \frac{1}{\omega_\alpha}\sin\omega_\alpha(t-t'), \tag{17.17}$$

which solves

$$\ddot{g}(t,t') + \omega_\alpha^2 g(t,t') = \delta(t-t'). \tag{17.18}$$

Since this is a linear ODE, we can multiply by $q(t')c_\alpha/m_\alpha$ to recover Eq. (17.11). In this case the solution is

$$x_\alpha(t) = \frac{c_\alpha}{m_\alpha}\int_0^t dt'\, g(t,t')\, q(t') = \frac{c_\alpha}{m_\alpha\omega_\alpha}\int_0^t dt'\, q(t')\sin\omega_\alpha(t-t'). \tag{17.19}$$

This is only the inhomogeneous part of the solution, obtained by considering the effect of the external force $q(t)$ but with otherwise vanishing initial conditions. The full solution is the superposition of this and the homogeneous solution (17.13):

$$x_\alpha(t) = x_\alpha(0)\cos\omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin\omega_\alpha t + \frac{c_\alpha}{m_\alpha\omega_\alpha}\int_0^t dt'\, q(t')\sin\omega_\alpha(t-t'). \tag{17.20}$$

(reservoir-mode solution)

This gives a formal solution to the reservoir [formal because $q(t)$ is still unknown].

17.1.2 Reservoir Memory and Spectral Density

Returning to the system's equation of motion from Eqs. (17.10),

$$M\ddot{q} + V'(q) + M\delta\omega^2 q = f = \sum_\alpha c_\alpha x_\alpha, \tag{17.21}$$

the next step will be to use the solution (17.20) to decouple the reservoir modes and obtain a closed equation for the system evolution. The result is

$$M\ddot{q} + V'(q) + M\delta\omega^2 q = \sum_\alpha c_\alpha\left(x_\alpha(0)\cos\omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha\omega_\alpha}\sin\omega_\alpha t\right) + \int_0^t dt'\, q(t')\, G(t-t'), \tag{17.22}$$

where the integral in the last term corresponds to the integral in Eq. (17.20), and we have defined the response function

$$G(t) := \sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha}\sin\omega_\alpha t \tag{17.23}$$

as a sum over reservoir Green functions (17.17), weighted by coupling factors c_α^2/m_α. The integral term in Eq. (17.22) is a convolution of the system coordinate with kernel (17.23). It represents a memory effect of the bath, and in particular it represents a ''feedback'' influence of the reservoir on the system, because it only involves the reservoir Green functions (which represent the part of the reservoir dynamics induced by the system). This term will lead to damping, because the memory effect allows the bath to push back on the system in a coherent way.

To facilitate the continuum limit of the bath, it is conventional to define the **spectral density of reservoir modes** by

$$J(\omega) = \frac{\pi}{2}\sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha), \tag{17.24}$$

in terms of which the kernel (17.23) appears as a Fourier transform:

$$G(t) = \frac{2}{\pi}\int_0^\infty d\omega\, J(\omega)\sin\omega t. \tag{17.25}$$

Because we started with a discrete bath, the reservoir spectral density has discrete peaks. We can pass to the continuum limit simply by replacing the spectral density by a continuous function. (Note that the spectral density $J(\omega)$ reflects not just the actual density of the modes, but also how the coupling coefficients c_α^2 scale with frequency.)

17.1.2.1 Reservoir Correlation Functions and the Spectral Density

To go a bit further with the spectral density, we can compare Eq. (17.25) to linear response theory to learn a bit more about it and the response kernel. Because we have an explicit model of the reservoir, we can compute the correlation functions directly. For example, from the reservoir-mode solution (17.20) we can compute the mode commutator

$$[x_\alpha(t), x_\beta(0)] = \frac{[p_\alpha(0), x_\beta(0)]}{m_\alpha\omega_\alpha}\sin\omega_\alpha t = -i\delta_{\alpha\beta}\frac{\hbar}{m_\alpha\omega_\alpha}\sin\omega_\alpha t. \tag{17.26}$$

Given the total reservoir-coupling operator f as defined in Eq. (17.4),

$$f(t) = \sum_\alpha c_\alpha x_\alpha(t), \tag{17.27}$$

we can then compute the total bath correlation function

$$[f(\tau), f(0)] = -i\hbar\sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha}\sin\omega_\alpha\tau = -\frac{2i\hbar}{\pi}\int_0^\infty d\omega\, J(\omega)\sin\omega\tau, \tag{17.28}$$

after rewriting the result in terms of $J(\omega)$ in Eq. (17.24) in the last expression here. Since the result is not an operator, we can write this more generally as a correlation function by applying an expectation value with respect to the (arbitrary) reservoir state, $[f(t), f(0)] = \langle[f(t), f(0)]\rangle$. Then we have the relation

$$\big\langle[f(\tau), f(0)]\big\rangle = -\frac{2i\hbar}{\pi}\int_0^\infty d\omega\, J(\omega)\sin\omega\tau \tag{17.29}$$
(reservoir correlation function)

between the reservoir-memory correlation function, which we now identify as

$$G(\tau) = \frac{i}{\hbar}\big\langle[f(\tau), f(0)]\big\rangle, \tag{17.30}$$

and the spectral mode density. This relation is analogous to the expression (14.13) relating the generalized susceptibility to the correlation function via a Fourier transform in the Kubo linear-response formalism.

Also from the reservoir-mode solution (17.20) we can compute a second two-time correlation function. The anticommutator of the mode solution is

$$[x_\alpha(t), x_\beta(0)]_+ = 2x_\alpha(0)\,x_\beta(0)\cos\omega_\alpha t + \frac{[p_\alpha(0), x_\beta(0)]_+}{m_\alpha\omega_\alpha}\sin\omega_\alpha t + 2\frac{c_\alpha}{m_\alpha\omega_\alpha}\int_0^t dt'\,[q(t'), x_\beta(0)]_+\sin\omega_\alpha(t-t'). \tag{17.31}$$

To compute the correlation function, we must now make an assumption about the state of the reservoir in order to compute the expectation value of this expression. First, we can assume that the reservoir is (initially) in a thermal equilibrium state, which implies for example that $\langle x_\alpha(0)\rangle = \langle p_\alpha(0)\rangle = 0$:

$$\big\langle[x_\alpha(t), x_\beta(0)]_+\big\rangle = 2\delta_{\alpha\beta}\langle x_\alpha^2(0)\rangle\cos\omega_\alpha t + \delta_{\alpha\beta}\frac{\langle[x_\alpha(0), p_\alpha(0)]_+\rangle}{m_\alpha\omega_\alpha}\sin\omega_\alpha t. \tag{17.32}$$

Note that we have dropped the integral term involving $q(t')$, which reflects the modified reservoir evolution due to the action of the system—this amounts to assuming that the system's effect on any particular reservoir mode is small, because of weak coupling, and because there are many reservoir modes to soak up energy from the system. To go further, we need the following expression for the position variance of a harmonic oscillator in thermal equilibrium at temperature T (Problem 10.10):

$$V_x = \langle x_\alpha^2(0)\rangle = \frac{\hbar}{2m_\alpha\omega_\alpha}\coth\left(\frac{\hbar\omega_\alpha}{2k_\text{B}T}\right). \tag{17.33}$$

Additionally, position and momentum are uncorrelated in thermal equilibrium, $C_{xp} = \langle [x_\alpha(0), p_\alpha(0)]_+ \rangle / 2 = 0$, and thus the correlation function becomes

$$\left\langle [x_\alpha(t), x_\beta(0)]_+ \right\rangle = \delta_{\alpha\beta} \frac{\hbar}{m_\alpha \omega_\alpha} \coth\left(\frac{\hbar\omega_\alpha}{2k_{\mathrm{B}}T} \right) \cos\omega_\alpha t. \tag{17.34}$$

Again in terms of the total reservoir-coupling operator f in Eq. (17.27), the total reservoir correlation function is

$$\left\langle [f(\tau), f(0)]_+ \right\rangle = \sum_\alpha \frac{\hbar c_\alpha^2}{m_\alpha \omega_\alpha} \coth\left(\frac{\hbar\omega_\alpha}{2k_{\mathrm{B}}T} \right) \cos\omega_\alpha \tau. \tag{17.35}$$

Rewriting this result in terms of the spectral density (17.24), we obtain the alternate correlation function

$$G_+(\tau) := \left\langle [f(\tau), f(0)]_+ \right\rangle = \frac{2\hbar}{\pi} \int_0^\infty d\omega\, J(\omega) \coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T} \right) \cos\omega\tau.$$

(reservoir correlation function) (17.36)

This relation is analogous to the fluctuation–dissipation theorem (14.48), which relates the imaginary part of a susceptibility to an anticommutator correlation function via a Fourier transform and the same thermal factor.

17.1.2.2 Emergence of Damping

To cast the system equation of motion (17.22) into a more illuminating form, consider the final (integral) term. Integrating by parts changes this term into

$$\begin{aligned} \int_0^t dt'\, q(t')\, G(t-t') &= \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha} \int_0^t dt'\, q(t')\, \sin\omega_\alpha (t-t') \\ &= q(t) \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} - q(0) \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} \cos\omega_\alpha t - \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} \int_0^t dt'\, \dot{q}(t')\, \cos\omega_\alpha (t-t'). \end{aligned} \tag{17.37}$$

Putting the last expression back into Eq. (17.22), several things happen. The first term cancels the $M\delta\omega^2 q$ term on the left-hand side of Eq. (17.22); this is the "renormalization," or the reason for including the $M\delta\omega^2 q 2/2$ component in the system–reservoir interaction Hamiltonian (17.4). The second term in the last expression of Eq. (17.37) has a form similar to the $x_\alpha(0)$ and $p_\alpha(0)$ terms of Eq. (17.22), while the last term has the form of a damping term. With this substitution, Eq. (17.22) becomes

$$M\ddot{q} + M \int_0^t dt'\, \dot{q}(t')\, \Gamma(t-t') + V'(q) = F(t), \tag{17.38}$$

(quantum Langevin equation)

where the external, fluctuating force due the reservoir is

$$F(t) := \sum_\alpha c_\alpha \left[\left(x_\alpha(0) - q(0) \frac{c_\alpha}{m_\alpha \omega_\alpha^2} \right) \cos\omega_\alpha t + \frac{p_\alpha(0)}{m_\alpha \omega_\alpha} \sin\omega_\alpha t \right],$$

(reservoir fluctuating force) (17.39)

and the damping kernel is

$$\Gamma(t) := \frac{1}{M} \sum_\alpha \frac{c_\alpha^2}{m_\alpha \omega_\alpha^2} \cos\omega_\alpha t = \frac{2}{\pi M} \int_0^\infty d\omega\, \frac{J(\omega)}{\omega} \cos\omega t. \tag{17.40}$$

(damping kernel)

The equation of motion in the form (17.38) has the form of a damped, driven particle, albeit with memory in the damping term, which still has the form of a convolution integral (we will see how this memory can go away shortly).

The fluctuating force can again be characterized by its two-time correlation function. For example, the force $F(t)$ is basically the same as the bath operator $f(t)$ except for the presence of the $q(0)$ term in Eq. (17.39).[5] Under the same assumptions, the calculation leading to Eq. (17.29) is not affected by the presence of this term, and so we have

$$\big\langle [F(\tau), F(0)] \big\rangle = -\frac{2i\hbar}{\pi} \int_0^\infty d\omega\, J(\omega) \sin\omega\tau = \frac{\hbar}{i} G(\tau). \tag{17.41}$$
(force correlation function)

The derivation leading to Eq. (17.35) gains an extra term from the presence of $q(0)$, and so

$$\big\langle [F(\tau), F(0)]_+ \big\rangle = \sum_\alpha \frac{\hbar c_\alpha^2}{m_\alpha \omega_\alpha} \coth\!\left(\frac{\hbar\omega_\alpha}{2k_\mathrm{B}T}\right) \cos\omega_\alpha\tau + q^2(0) \sum_\alpha \frac{c_\alpha^4}{m_\alpha^2 \omega_\alpha^4} \cos\omega_\alpha\tau, \tag{17.42}$$

or in terms of the spectral density,

$$\big\langle [F(\tau), F(0)]_+ \big\rangle = \frac{2\hbar}{\pi} \int_0^\infty d\omega\, J(\omega) \coth\!\left(\frac{\hbar\omega}{2k_\mathrm{B}T}\right) \cos\omega\tau + \frac{2q^2(0)}{\pi} \int_0^\infty d\omega\, J^2(\omega) \cos\omega\tau.$$
(force correlation function) (17.43)

The first term here gives the thermal fluctuations of the reservoir, whereas the second represents the influence of the system on the reservoir (i.e., the temperature of the reservoir effectively increases because of the energy lost by the system). Often, the reservoir is large enough that the influence of the system is negligible, in which case the q^2 term is negligible, and this second correlation function reduces to $G_+(\tau)$.

17.1.2.3 Reservoir as a Continuum of Modes

The quantum Langevin equation (17.38) has the form of a damped, driven particle, but as we discussed before, there can be no *true* damping until the reservoir becomes a continuum. To pass over to this limit we simply regard the mode density $J(\omega)$ as a continuous function instead of a discrete combination of delta functions. One important example is the **ohmic reservoir**, characterized by spectral density

$$J(\omega) = M\gamma\omega. \tag{17.44}$$
(ohmic reservoir)

Then in the damping kernel (17.40), reproduced here,

$$\Gamma(t) = \frac{2}{\pi M} \int_0^\infty d\omega\, \frac{J(\omega)}{\omega} \cos\omega t, \tag{17.45}$$

the ohmic frequency dependence leads to

$$\Gamma(t) = \frac{2\gamma}{\pi} \int_0^\infty d\omega \cos\omega t = 2\gamma\delta(t), \tag{17.46}$$

using a variation on the usual integral representation of the delta function (Problem 17.1). Putting this kernel into the quantum Langevin equation (17.38), noting that the time integration only picks up half of the delta function, leads to the more ordinary damped quantum Langevin equation

$$M\ddot{q} + M\gamma\dot{q} + V'(q) = F(t),$$
(quantum Langevin equation, ohmic bath) (17.47)

with no memory in the damping term.

The ohmic reservoir is obviously an idealization, because the mode density diverges at high frequencies, while any physical system should fail to respond in the limit of large frequencies. Because the idealized

[5] For further discussion of this neglected term, see Peter Hänggi, "Generalized Langevin Equations: A Useful Tool for the Perplexed Modeller of Nonequilibrium Fluctuations?" in *Stochastic Dynamics*, Lutz Schimansky-Geier and Thorsten Pöschel, Eds. (Springer, 1997) p. 15 (doi: 10.1007/BFb0105595).

reservoir has arbitrarily large frequencies, it can respond arbitrarily quickly, leading to the instantaneous damping kernel (17.46). In this case it is the low frequency behavior $J(\omega) \sim \omega$ that makes a realistic bath ohmic. More generally, a small-frequency behavior scaling as $J(\omega) \sim \omega^\sigma$ is **sub-ohmic** when $\sigma < 1$ and **super-ohmic** if $\sigma > 1$.[6]

A more realistic model of an ohmic bath is given by

$$J(\omega) = M\gamma \frac{\omega}{1+\omega^2/\Omega^2}, \qquad \text{(ohmic reservoir with Drude cutoff)} \tag{17.48}$$

where Ω represents a frequency beyond which the spectral density drops to zero. This is called a **Drude cutoff** function, named for the Drude model of conductivity (where damped classical electrons respond to an applied ac electric field), where the imaginary part of the conductivity has the same frequency profile. In this case the damping kernel (17.45) becomes

$$\Gamma(t) = \frac{2\gamma}{\pi}\int_0^\infty d\omega\, \frac{\cos\omega t}{1+\omega^2/\Omega^2} = \gamma\Omega\, e^{-\Omega t} \qquad (t \geq 0). \tag{17.49}$$

This shows that within this model, the reservoir has a memory on the time scale Ω^{-1}. If this time scale is short compared to other dynamical time scales, then the idealized ohmic reservoir (17.44) is a good model.

17.1.3 Damped Evolution: Moment Equations

To explore in more detail the system dynamics according to the quantum Langevin equation (17.47), we can work out the equations of motion for the moments, as we did before in Sections 5.5.3 and 6.1. First, writing the QLE (17.47) as a first-order pair, we have

$$\begin{aligned} \dot q &= \frac{p}{M} \\ \dot p &= -\gamma p - V'(q) + F(t). \end{aligned} \tag{17.50}$$

Computing the expectation values of these equations (with respect to both system and reservoir states) gives

$$\begin{aligned} \langle \dot q\rangle &= \frac{\langle p\rangle}{M} \\ \langle \dot p\rangle &= -\gamma\langle p\rangle - \big\langle V'(q)\big\rangle. \end{aligned} \qquad \text{(QLE centroid equations)} \tag{17.51}$$

Note in particular that because $\langle F(t)\rangle = 0$, the fluctuating force does not enter these centroid equations. Proceeding with the variances, defined as usual by

$$\begin{aligned} V_q &= \big\langle q^2\big\rangle - \langle q\rangle^2 \\ V_p &= \big\langle p^2\big\rangle - \langle p\rangle^2 \\ C_{qp} &= \frac{\langle qp+pq\rangle}{2} - \langle q\rangle\langle p\rangle\,, \end{aligned} \tag{17.52}$$

we can work out the equations of motion for the second (noncentered) moments. Two of these second moments are straightforward:

$$\begin{aligned} \frac{d}{dt}\big\langle q^2\big\rangle &= \langle q\dot q + \dot q q\rangle = \frac{\langle qp+pq\rangle}{M} \\ \frac{d}{dt}\langle qp+pq\rangle &= \langle \dot q p + q\dot p + p\dot q + \dot p q\rangle = \frac{2\big\langle p^2\big\rangle}{M} - \gamma\langle qp+pq\rangle - 2\langle qV'(q)\rangle\,. \end{aligned} \tag{17.53}$$

[6] The electromagnetic field, for example, acting as a bath coupled to an atom (dipole–electric field coupling) has a spectral density $J(\omega) \sim \omega^3$, and thus acts as a super-ohmic reservoir. See P. M. V. B. Barone and A. O. Caldeira, "Quantum mechanics of radiation damping," *Physical Review A* **43**, 57 (1991) (doi: 10.1103/PhysRevA.43.57).

However, treating the second momentum moment in the same way, using $d\langle p^2\rangle/dt = \langle p\dot{p} + \dot{p}p\rangle$, leads to the wrong result. The reason for this is rather subtle—it's time for a review of how differential calculus really works.

Let's consider the evolution of variables over a small time interval Δt. To be precise, the notation for the corresponding increment of a dynamical variable is $\Delta p(t) \equiv p(t+\Delta t) - p(t)$. Then the increment of p^2 over this time interval is

$$\begin{aligned}\Delta p^2(t) &= p^2(t+\Delta t) - p^2(t)\\ &= \frac{1}{2}\big[p(t+\Delta t) - p(t)\big]\big[p(t+\Delta t) + p(t)\big] + \frac{1}{2}\big[p(t+\Delta t) + p(t)\big]\big[p(t+\Delta t) - p(t)\big]\\ &= \frac{1}{2}\Delta p(t)\big[p(t+\Delta t) + p(t)\big] + \frac{1}{2}\big[p(t+\Delta t) + p(t)\big]\Delta p(t).\end{aligned} \tag{17.54}$$

At this point, according to the conventional rules of calculus, we would approximate

$$p(t+\Delta t) + p(t) = 2p(t) + \Delta p(t) = 2p(t) + O(\Delta t), \tag{17.55}$$

and then neglect this last $O(\Delta t)$ term in the limit $\Delta t \longrightarrow dt$, in which case we would recover the standard product rule for derivatives, $dp^2/dt = \dot{p}p + p\dot{p}$. But this is precisely the source of the problem: the normal assumption is that $\Delta p(t) \sim \Delta t$, which is justified if $p(t)$ is a smooth, nicely behaved function of time. However, this isn't the case, because from Eq. (17.50), the momentum is driven by the force operator $F(t)$, and from Eq. (17.43), for an ohmic bath $F(t)$ has significant contributions at all frequencies. In particular, the contributions from divergently large frequencies mean that $F(t)$ has significant variation on short time scales (and under certain conditions it is everywhere discontinuous). Anyhow, the correct way to proceed is to keep the usually neglected $(\Delta p)^2$ component of the increment:

$$\Delta p^2(t) = \Delta p(t)\, p(t) + p(t)\, \Delta p(t) + [\Delta p(t)]^2. \tag{17.56}$$

Then using $\Delta p = \dot{p}\,\Delta t + O(\Delta t^2)$ [with Eq. (17.50) for $\dot{p}$] in the last term and working to order Δt,

$$\Delta p^2(t) = \Delta p(t)\, p(t) + p(t)\, \Delta p(t) + F^2(t)\, \Delta t^2. \tag{17.57}$$

Here we ignored other terms in the equation of motion (17.50) for $\dot{p}$, because they give contributions of order Δt^2, which should be neglected, as we noted above. In fact, for the F^2 term here to give a nonvanishing contribution, it must be that $F(t)$ is of order $(\Delta t)^{-1/2}$, a scaling that reveals its singular character in the limit $\Delta t \longrightarrow 0$. Writing this equation of motion as an expectation value, we have

$$\Delta\big\langle p^2(t)\big\rangle = (\Delta p)p + p\Delta p + \big\langle F^2(t)\big\rangle \Delta t^2, \tag{17.58}$$

where now the expectation value $\big\langle F^2(t)\big\rangle$ is of order $1/\Delta t$ in order for the last term to contribute. To obtain this expectation value, we should regard it as the limit

$$\big\langle F^2(t)\big\rangle = \frac{1}{2}\lim_{t'\to t}\big\langle [F(t'), F(t)]_+\big\rangle = \frac{1}{2}\lim_{\tau\to 0}\big\langle [F(\tau), F(0)]_+\big\rangle, \tag{17.59}$$

where in the last step we have taken advantage of the stationarity of the reservoir state. Note that we are also working in terms of the symmetrized correlation function, which is appropriate for this limit, as we saw in the fluctuation–dissipation theorem [see the discussion of Eq. (14.49)]. Now we will assume that the reservoir fluctuations are such that $F(t)$ decorrelates quickly, owing to the contributions at large frequencies. That is, $\langle [F(t), F(0)]_+\rangle \approx 0$ except in a small time interval Δt around $t = 0$. Also, we have already noted that this same correlation function diverges as $1/\Delta t$ within this interval. Thus, $\langle [F(t), F(0)]_+\rangle$ has the character of $\delta(t)$. We may then write

$$\begin{aligned}\big\langle F^2(t)\big\rangle\, \Delta t &= \frac{1}{2}\lim_{\tau\to 0}\big\langle [F(\tau), F(0)]_+\big\rangle \Delta t\\ &\approx \frac{1}{2}\int_{-\infty}^{\infty} d\tau\, \big\langle [F(\tau), F(0)]_+\big\rangle\\ &= \int_0^{\infty} d\tau\, \big\langle [F(\tau), F(0)]_+\big\rangle,\end{aligned} \tag{17.60}$$

taking advantage of the symmetry of the correlation function. Putting this result into Eq. (17.58), dividing by Δt, and taking the limit $\Delta t \longrightarrow 0$ (i.e., $\Delta t \longrightarrow dt$) gives

$$\frac{d}{dt}\langle p^2\rangle \approx \langle \dot{p}p + p\dot{p}\rangle + \int_0^\infty d\tau \left\langle [F(\tau), F(0)]_+ \right\rangle, \tag{17.61}$$

In this treatment, Δt represents a short (finite) time scale compared to the system dynamics of interest, which is why we are justified in taking the limit $\Delta t \longrightarrow 0$ for the system variables. The delta-function nature of the force $F(t)$ is characteristic of white noise (noise with equal power density at all frequencies), and such noise is often referred to as **delta-correlated noise**.

Now we will need to compute the integral over the correlation function; from Eq. (17.43), we will neglect the q^2 term (to account for only the equilibrium reservoir, under the assumption that the reservoir is so large that it is unaffected by the system) to obtain

$$\begin{aligned}
\int_0^\infty d\tau \left\langle [F(\tau), F(0)]_+ \right\rangle &= 2\hbar \int_0^\infty d\omega\, J(\omega) \coth\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right) \delta(\omega) \\
&= \hbar \lim_{\omega\to 0} J(\omega) \coth\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right) \\
&= \hbar M\gamma \lim_{\omega\to 0} \omega \coth\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right) \\
&= 2M\gamma k_{\text{B}}T
\end{aligned} \tag{17.62}$$

for an ohmic reservoir, using the asymptotic expression $x\coth(ax) \sim 1/a$ as $x \longrightarrow 0$. This limit of a quickly decorrelating reservoir thus also amounts to taking the classical, high-temperature limit of the reservoir—the absence of $\hbar$ in the final expression confirms this intuition. Putting this result into Eq. (17.61) and putting in the derivatives gives the proper equation of motion for the second momentum moment:

$$\frac{d}{dt}\langle p^2\rangle = -\langle pV'(q) + V'(q)p\rangle - 2\gamma\langle p^2\rangle + 2M\gamma k_{\text{B}}T. \tag{17.63}$$

Subtracting away the appropriate centroid products of (e.g., $2\langle q\rangle\langle\dot{q}\rangle$ in the case of V_q), we obtain the variance equations

$$\begin{aligned}
\dot{V}_q &= \frac{2C_{qp}}{M} \\
\dot{V}_p &= -\langle pV'(q) + V'(q)p\rangle + 2\langle p\rangle\langle V'(q)\rangle - 2\gamma V_p + 2M\gamma k_{\text{B}}T \\
\dot{C}_{qp} &= \frac{V_p}{M} - \gamma C_{qp} - \langle qV'(q)\rangle + \langle q\rangle\langle V'(q)\rangle\,.
\end{aligned}$$

(QLE variance equations) (17.64)

The moment equations are the same here as for a standard quantum particle in a potential $V(q)$, except that now $\langle\dot{p}\rangle$ in Eqs. (17.51) has a damping term, $\dot{V}_p$ and $\dot{C}_{qp}$ also have similar damping terms, and $\dot{V}_p$ has a temperature-dependent term that tends to increase V_p.

17.1.3.1 Free Particle with Damping

To simplify the problem even more, consider a damped free particle, $V(q) = 0$. A simple check is to look at the equilibrium state from Eq. (17.63), setting $d\langle p^2\rangle/dt = 0$ to obtain

$$\frac{\langle p^2\rangle}{2M} = \frac{k_{\text{B}}T}{2}, \tag{17.65}$$

(equipartition consistency)

which is certainly what we expect from the equipartition theorem.

Another important case is Brownian motion in the limit of strong damping (large γ). In Eqs. (17.64), we can implement the strong-damping limit by assuming that the time-derivative terms are negligibly small compared to the damping terms in the $\dot{V}_p$ and $\dot{C}_{qp}$ equations. In this limit these equations of motion become constraint equations:

$$\begin{aligned} V_p &= M k_{\mathrm{B}} T \\ C_{qp} &= \frac{V_p}{M\gamma} = \frac{k_{\mathrm{B}} T}{\gamma}. \end{aligned} \tag{17.66}$$

Then putting the last expression for C_{qp} into the $\dot{V}_q$ equation gives

$$\dot{V}_q = \frac{2C_{qp}}{M} = \frac{2k_{\mathrm{B}} T}{M\gamma}. \tag{17.67}$$

Thus we see that V_q now evolves independently of V_p and C_{qp}; this decoupling of variables by approximately removing the damping on short time scales is called an **adiabatic elimination** of the V_p and C_{qp}, which are always in approximate equilibrium with respect to V_q.

Equation (17.67) says that V_q increases at a constant rate. This is characteristic of **diffusion**, or random-walk behavior. In particular, the rate of increase of the position variance is called the **diffusion constant** D:

$$V_q =: Dt. \tag{17.68}$$
(diffusion coefficient)

From Eq. (17.67), we can read off the value of the diffusion coefficient:

$$D = \frac{2k_{\mathrm{B}} T}{M\gamma}. \tag{17.69}$$
(Einstein relation)

This is a form of the **Einstein relation** for the diffusion rate.

17.1.3.2 Steady State of the Harmonic Oscillator and the Low-Temperature Limit

The above treatment leading to the temperature-dependent driving term in Eqs. (17.64) relied on a high-temperature approximation and a temporal coarse-graining to tame the fluctuating force. Without this assumption, the problem is that the correlation time of the reservoir can be very long at lower temperatures, and the equations of motion must continue to reflect the memory of the reservoir. This is not so satisfying, since we can't examine the low-temperature (quantum) limit in those equations of motion. However, in the steady-state limit, we can still treat the case of general temperature, because the system time scale is automatically long compared to the reservoir decorrelation time.

To simplify the equations of motion somewhat, let's consider the system to be a harmonic oscillator, with

$$V(q) = \frac{1}{2} M\omega_0^2 q^2 \tag{17.70}$$

In equilibrium, a direct way to handle the steady-state quantities is to appeal to the fluctuation–dissipation theorem in the form (14.49),

$$\langle q^2 \rangle = \frac{\hbar}{2\pi} \int_{-\infty}^{\infty} d\omega \, \mathrm{Im}[\chi(\omega)] \coth\left(\frac{\hbar\omega}{2k_{\mathrm{B}} T}\right), \tag{17.71}$$

after discarding tensor indices. The susceptibility $\chi(\omega)$ represents the frequency-dependent linear response of the system oscillator coordinate q due to the time-dependent force $F(t)$. To compute this susceptibility, we can go back to Eq. (17.47),

$$M\ddot{q} + M \int_0^t dt' \, \dot{q}(t') \, \Gamma(t - t') + V'(q) = F(t), \tag{17.72}$$

and compute the Fourier transform of the entire expression. The convention and notation for the time–frequency Fourier transform is

$$f(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \tilde{f}(\omega)\, e^{-i\omega t}\, d\omega, \qquad \tilde{f}(\omega) = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t}\, dt. \tag{17.73}$$

The Fourier transform of most of Eq. (17.72) is straightforward, with the integral damping term transforming according to a variation of the convolution theorem. In particular, from Eq. (17.40), we can write

$$\Gamma(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, \frac{2J(\omega)}{M\omega}\, e^{-i\omega t}, \tag{17.74}$$

assuming $J(-\omega) = -J(\omega)$. That is, $\Gamma(t)$ and $2J(\omega)/M\omega$ form a Fourier-transform pair, but there is a factor of $1/2$ from the finite upper limit of the integral. Also, in steady state, the t' integral can be treated as being over $(-\infty, t]$ instead of $[0, t]$. In this case, the Fourier transform of the integral term can be written Problem 17.2

$$\int_{-\infty}^{\infty} dt\, e^{i\omega t} \int_{-\infty}^{t} dt'\, \dot{q}(t')\, \Gamma(t-t') = -\frac{i}{M} J(\omega)\, \tilde{q}(\omega). \tag{17.75}$$

Thus, the Fourier transform of Eq. (17.72) is

$$\big(-M\omega^2 - iJ(\omega) + M\omega_0^2\big)\tilde{q}(\omega) = \tilde{F}(\omega), \tag{17.76}$$

or solving for the position amplitude,

$$\tilde{q}(\omega) = \frac{\tilde{F}(\omega)}{M(\omega_0^2 - \omega^2) - iJ(\omega)}. \tag{17.77}$$

Thus we can read off the susceptibility as the frequency-dependent coefficient of the force spectrum:

$$\chi(\omega) = \frac{1}{M(\omega_0^2 - \omega^2) - iJ(\omega)}. \tag{17.78}$$

For the fluctuation–dissipation theorem, we need only the imaginary part:

$$\mathrm{Im}[\chi(\omega)] = \frac{\mathrm{Re}[J(\omega)]}{M^2\big(\omega_0^2 - \omega^2 + \mathrm{Im}[J(\omega)]\big)^2 + \mathrm{Re}[J(\omega)]^2}. \tag{17.79}$$

Thus, Eq. (17.71) becomes

$$V_q = \frac{\hbar}{2\pi}\int_{-\infty}^{\infty} d\omega\, \frac{\mathrm{Re}[J(\omega)]}{M^2\big(\omega_0^2 - \omega^2 + \mathrm{Im}[J(\omega)]\big)^2 + \mathrm{Re}[J(\omega)]^2} \coth\!\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right). \tag{17.80}$$

(equilibrium position variance)

This expression has a nice interpretation: the thermal excitation spectrum from the reservoir (the coth term) is filtered through the system's response function at each frequency, with system damping incorporated via $J(\omega)$, and the resulting position variance is a sum over the filtered fluctuations at all frequencies.

The integral (17.80) obviously can't be carried out without some simplification. We can proceed by assuming an ohmic reservoir, $J(\omega) = M\gamma\omega$, in which case

$$V_q = \frac{\hbar\gamma}{2\pi M}\int_{-\infty}^{\infty} d\omega\, \frac{\omega}{(\omega_0^2 - \omega^2)^2 + (\omega\gamma)^2} \coth\!\left(\frac{\hbar\omega}{2k_{\mathrm{B}}T}\right). \tag{17.81}$$

The system's filtering function is just the usual resonance function for a damped, forced harmonic oscillator. In the limit $T \longrightarrow 0$ we can take $\coth(\hbar\omega/2k_{\mathrm{B}}T) \longrightarrow \operatorname{sgn}\omega$, and the result is

$$V_q = \frac{\hbar\gamma}{\pi M}\int_{0}^{\infty} d\omega\, \frac{\omega}{(\omega_0^2 - \omega^2)^2 + (\gamma\omega)^2}. \tag{17.82}$$

This integral is still difficult; however, it simplifies in the limit of weak damping, $\gamma \ll \omega_0$, where the integrand becomes sharply peaked around $\omega = \omega_0$. In particular we can make the approximation $\omega_0^2 - \omega^2 = (\omega_0 + \omega)(\omega_0 - \omega) \approx 2\omega_0(\omega_0 - \omega)$, set $\omega = \omega_0$ elsewhere, and extend the lower integration limit to $-\infty$, to obtain the weak-damping expression

$$V_q = \frac{\hbar\gamma}{4\pi M\omega_0} \int_{-\infty}^{\infty} d\omega \, \frac{1}{(\omega_0 - \omega)^2 + (\gamma/2)^2}. \tag{17.83}$$

The integral has the value $2\pi/\gamma$, so

$$V_q = \frac{\hbar}{2M\omega_0} \tag{17.84}$$
(weak-damping variance)

This is, of course, the ground-state variance of the (undamped) quantum harmonic oscillator. Two of the variance equations (17.64) in the case of the harmonic oscillator read

$$\begin{aligned} \dot{V}_q &= \frac{2C_{qp}}{M} \\ \dot{C}_{qp} &= \frac{V_p}{M} - \gamma C_{qp} - M\omega_0^2 V_q, \end{aligned} \tag{17.85}$$

and in steady state we then have $C_{qp} = 0$ and $V_p = V_q M^2 \omega_0^2 = \hbar M\omega_0/2$. Thus, the steady-state uncertainty product in the weak-damping limit at zero temperature is

$$V_q V_p = \frac{\hbar^2}{4}. \tag{17.86}$$
(uncertainty product, $T = 0$, $\gamma \ll \omega_0$)

This is the minimum-uncertainty condition, which came from the commutator $[q, p] = i\hbar$. At the beginning of this chapter, we commented that damping in the Heisenberg picture has the potential pitfall that commutators may damp to zero. However, we can see here that the fluctuating force $F(t)$ is sufficient to maintain the uncertainty limit (and thus the canonical commutator), even in the $T \longrightarrow 0$ limit.

17.2 Quantum Master Equation: Damping in the Schrödinger Picture

So far we have stuck to the Heisenberg picture in working with a particle interacting with a bath of harmonic oscillators. Of course, it is also useful to do this in the Schrödinger picture. We already have seen that an interaction of quantum systems induces entanglement, and in this case the state of one system can no longer be represented as a pure state. Since the Schrödinger equation (equivalently, the Schrödinger–von Neumann equation for the density operator) preserved purity as well as energy (in the case of a time-independent Hamiltonian), we will have to develop a more general equation of motion for the local density operator of the quantum system.[7]

In particular we will seed to find an equation of motion of the general form

$$\dot{\rho}(t) = \int_0^t dt' \, \mathcal{L}(t - t') \, \rho(t'),$$
(quantum master equation, schematic form) (17.87)

assuming the interaction with the reservoir is switched on at time $t = 0$, where the **Liouvillian superoperator** generates the evolution of the system density operator ρ (here, "superoperator" means that $\mathcal{L}[\rho]$ must represent things like $[H, \rho]$, and thus must act as an operator that operates on both sides of ρ). The prototype equation (17.87) is called a **quantum master equation**, which is the general evolution equation

[7] For further reading, see Heinz-Peter Breuer and Francesco Petruccione, *op. cit.*; also a good discussion of the quantum master equation (not applied to the Caldeira–Leggett model) can be found in Howard M. Wiseman and Gerard J. Milburn, *Quantum Measurement and Control* (2009) (ISBN: 9780511813948) (doi: 10.1017/CBO9780511813948).

for the local density operator of a system that is in contact with a reservoir. The terminology here comes from the **master equation** of statistical mechanics,[8] which for example takes the form

$$\dot{P}_n = \sum_m (W_{nm} P_m - W_{mn} P_n). \tag{17.88}$$

This equation represents the time-dependent probabilities $P_n(t)$ for a system to be in the nth state, and their evolution via a transition matrix W_{nm} representing the transition rate from state m to state n. A very simple example is exponential decay from state 2 to state 1 at rate γ (e.g., nuclear decay or spontaneous emission), represented by the pair of equations $\dot{P}_2 = -\gamma P_2$ and $\dot{P}_1 = \gamma P_2$. (Master equations like this can of course be generalized to continuous probability distributions and to temporal convolutions to represent memory effects.) Quantum master equations are of course more general in representing evolution of quantum coherences as well as probabilities. Colloquially, quantum master equations are often simply called master equations.

Under certain conditions, the Liouvillian in the quantum master equation (17.87) is local in time, and the more restricted form is

$$\dot{\rho}(t) = \mathcal{L}[\rho(t)].$$

(Markovian quantum master equation, schematic form) (17.89)

A master equation of this form, where the rate of change of ρ at time t only depends on the quantum state at the present time, is called a **Markovian master equation**, and $\rho(t)$ is said to undergo **Markovian evolution**. In the case of quantum Brownian motion, the evolution is only Markovian in the high-temperature limit. We already saw this in the Heisenberg-picture treatment above [Eq. (17.60)], where we had to assume a short decorrelation time for the reservoir in order to carry out the integral over the force correlation function.

17.2.1 Born–Markov Evolution

Starting with the same basic setup of system, reservoir, and interaction, the first order of business is to simplify the equations of motion by transforming to the interaction picture (Section 13.1.1):

$$\begin{aligned} \tilde{\rho}_{\text{SR}}(t) &= e^{i(H_{\text{S}}+H_{\text{R}})t/\hbar} \rho_{\text{SR}}(t) e^{-i(H_{\text{S}}+H_{\text{R}})t/\hbar} \\ \tilde{H}_{\text{SR}}(t) &= e^{i(H_{\text{S}}+H_{\text{R}})t/\hbar} H_{\text{SR}} e^{-i(H_{\text{S}}+H_{\text{R}})t/\hbar}. \end{aligned} \tag{17.90}$$

Here, ρ_{SR} is the total density operator (in the Schrödinger picture) for the system and reservoir. The one complication is that we started with a time-independent Hamiltonian, but now the Hamiltonian is explicitly time-*dependent*, since it now carries along the uncoupled evolution of the system and reservoir. The Schrödinger-von Neumann equation in the interaction picture reads

$$\partial_t \tilde{\rho}_{\text{SR}}(t) = -\frac{i}{\hbar}[\tilde{H}_{\text{SR}}(t), \tilde{\rho}_{\text{SR}}(t)], \tag{17.91}$$

and this can be integrated to give the integral form

$$\tilde{\rho}_{\text{SR}}(t) = \tilde{\rho}_{\text{SR}}(0) - \frac{i}{\hbar}\int_0^t dt' \, [\tilde{H}_{\text{SR}}(t'), \tilde{\rho}_{\text{SR}}(t')]. \tag{17.92}$$

We can then iterate this equation of motion by plugging Eq. (17.92) into the right-hand side of Eq. (17.91), with the result

$$\partial_t \tilde{\rho}_{\text{SR}}(t) = -\frac{i}{\hbar}[\tilde{H}_{\text{SR}}(t), \tilde{\rho}_{\text{SR}}(0)] - \frac{1}{\hbar^2}\int_0^t dt' \, \big[\tilde{H}_{\text{SR}}(t), [\tilde{H}_{\text{SR}}(t'), \tilde{\rho}_{\text{SR}}(t')]\big]. \tag{17.93}$$

[8] The name "master equation" is itself curious. It comes from the paper A. Nordsieck, W. E. Lamb Jr., and G. E. Uhlenbeck, "On the Theory of Cosmic-Ray Showers I. The Furry Model and the Fluctuation Problem," *Physica* **7**, 344 (1940) (doi: 10.1016/S0031-8914(40)90102-1). Here, the authors called an equation of the form (17.88) a "'master' equation," "from which all other equations can be derived" (other equations in the paper, at least). See also the comment on p. 97 of N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, 3rd ed. (Elsevier, 2007) (ISBN: 9780444529657) (doi: 10.1016/B978-0-444-52965-7.X5000-4).

Although this equation of motion is so far exact, note that it is also obtainable in second-order time-dependent perturbation theory (Problem 17.3), and the approximations to come will limit the accuracy of the equation to second order in the system-reservoir coupling.

The goal is now to develop an equation of motion for the system density operator, defined by the partial trace

$$\tilde{\rho}_{\rm S} = {\rm Tr}_{\rm R}[\tilde{\rho}_{\rm SR}] \tag{17.94}$$

over the reservoir degrees of freedom(see Section 10.3.3). The first approximation is the **Born approximation**[9] (weak-coupling approximation) for the reservoir: the reservoir is sufficiently large compared to the system that the system has little influence on it. In this case we can assume that the reservoir is always approximately in a steady state $\rho_{\rm R}$. Additionally we will assume that the total state always approximately factorizes into a product state of the evolving system and the steady reservoir state:

$$\tilde{\rho}_{\rm SR}(t) = \tilde{\rho}_{\rm S}(t) \otimes \tilde{\rho}_{\rm R}. \tag{17.95}$$

Of course, the system–reservoir interaction leads to entanglement and thus lost of purity of the system. This does not seem to be captured by this assumption, but we will see that damping and loss of purity nevertheless happen—this is simply an approximation to the true state to facilitate calculation.

The Born approximation (17.95) allows us to assume

$${\rm Tr}_{\rm R}[\tilde{H}_{\rm SR}(t)\,\tilde{\rho}_{\rm SR}(0)] \approx \rho_{\rm S}(0)\,{\rm Tr}_{\rm R}[\tilde{H}_{\rm SR}(t)\,\tilde{\rho}_{\rm R}] = 0, \tag{17.96}$$

so that the first term on the right-hand side of Eq. (17.93) vanishes. Essentially, this is saying that the effect of the reservoir on the system has no dc component, there are only fluctuations. Any dc component could just be absorbed into $H_{\rm S}$. Explicitly, this means that we should take the system–reservoir interaction potential (17.4), and redefine it to remove any steady component from the reservoir,

$$H_{\rm SR} = \sum_{\alpha=1}^{N} \Big[-c_\alpha\big(x_\alpha - \langle x_\alpha\rangle_{\rm R}\big)q\Big] = -\big(f - \langle f\rangle_{\rm R}\big)q, \tag{17.97}$$

where the R subscripts denote an expectation value with respect to the reservoir state, which has a constant value in the Born approximation. Any part removed here should be absorbed into the system potential, so that Eq. (17.2) should be replaced by

$$H_{\rm S} = \frac{p^2}{2M} + V(q) - \langle f\rangle_{\rm R}\, q + \frac{1}{2}M\delta\omega^2 q^2. \tag{17.98}$$

In moving on, we will simply drop the $\langle f\rangle_{\rm R}$ terms, assuming they have been absorbed into the definitions of other quantities. However, we can here see more explicitly the function of the renormalization (q^2) term in the interaction Hamiltonian (17.4): it was designed precisely to cancel the steady effect of the reservoir interaction on the system.

Thus after the partial trace, Eq. (17.93) becomes

$$\partial_t\tilde{\rho}_{\rm S}(t) \approx -\frac{1}{\hbar^2}\int_0^t dt'\ {\rm Tr}_{\rm R}\big[\tilde{H}_{\rm SR}(t), [\tilde{H}_{\rm SR}(t'), \tilde{\rho}_{\rm S}(t')\otimes\rho_{\rm R}]\big], \tag{17.99}$$

and to proceed we will make a second, related approximation, the **Markov approximation**, which replaces $\tilde{\rho}_{\rm S}(t')$ in the right-hand side by $\tilde{\rho}_{\rm S}(t)$, so that the equation of motion depends only on the quantum state at the current time. The resulting equation of motion is

$$\partial_t\tilde{\rho}_{\rm S}(t) \approx -\frac{1}{\hbar^2}\int_0^t dt'\ {\rm Tr}_{\rm R}\big[\tilde{H}_{\rm SR}(t), [\tilde{H}_{\rm SR}(t'), \tilde{\rho}_{\rm S}(t)\otimes\rho_{\rm R}]\big]. \tag{17.100}$$
(Redfield equation)

[9]The "Born approximation" is a scattering-related term that we saw before in photoionization (Section 15.3). It refers to a weak-scattering approximation that amounts to ignoring any depletion effect of the scattering wave; it carries over by analogy here as a weak-interaction approximation where the reservoir is unaffected.

This equation is called the **Redfield equation**.[10] Again, time evolution of this form, where the rate of change of the system at time t depends *only* on the state of the system at that time, and not on the state in the past, is called Markovian evolution. The Redfield equation is a perfectly good quantum master equation. It is also commonly regarded as Markovian evolution equation, but this isn't really the case—the past state of the system and reservoir are technically buried in the interaction-picture operator $\tilde{H}_{\text{SR}}(t')$. Later, in the specific model of quantum Brownian motion we will have to explicitly remove this implicit dependence on the past state in order to obtain truly Markovian evolution. Also, it's important to note that the Markov approximation is at a similar level of error as the Born approximation, where we assumed a weak coupling with negligible effect on the reservoir. The weakness of the coupling justifies an expansion to lowest nonvanishing order in perturbation theory (Problem 17.3), and changing the time argument of $\tilde{\rho}_{\text{S}}$ in the integral implies further corrections to higher order in the system-reservoir coupling that we are ignoring anyway.

As a next step, the weak system–reservoir coupling means that the evolution due to the coupling is slow compared to the time scales of interest for the system. On the other hand, we assume that the reservoir decorrelates quickly due to its many degrees of freedom. In this case, the main contribution to the integral in Eq. (17.100) comes from $t' \approx t$, and so we do not change things much by extending the lower integration limit to $-\infty$:

$$\partial_t \tilde{\rho}_{\text{S}}(t) \approx -\frac{1}{\hbar^2}\int_{-\infty}^{t} dt' \; \text{Tr}_{\text{R}}\big[\tilde{H}_{\text{SR}}(t), [\tilde{H}_{\text{SR}}(t'), \tilde{\rho}_{\text{S}}(t)\otimes\rho_{\text{R}}]\big]. \tag{17.101}$$

Then shifting the t' variable and reversing its direction, we obtain

$$\partial_t \tilde{\rho}_{\text{S}}(t) \approx -\frac{1}{\hbar^2}\int_{0}^{\infty} dt' \; \text{Tr}_{\text{R}}\big[\tilde{H}_{\text{SR}}(t), \big[\tilde{H}_{\text{SR}}(t-t'), \tilde{\rho}_{\text{S}}(t)\otimes\rho_{\text{R}}\big]\big]. \tag{17.102}$$

This form already hints that two-time correlation functions of $\tilde{H}_{\text{SR}}(t)$ are coming. This observation acts as a further justification of the Markov approximation leading to the Redfield equation (17.100).

17.2.2 Quantum Master Equation for Brownian Motion

To proceed with developing the system evolution equation, we have to make some assumption about the form of the interaction $\tilde{H}_{\text{SR}}(t)$. Typically, this involves factorizing it into a sum over products of system and reservoir operators. However, we already have an explicit interaction if we continue to work with the Calderia–Leggett model (which is indeed a sum over such products). First, transforming Eq. (17.102) back to the Schrödinger picture, we have

$$\partial_t \rho_{\text{S}}(t) = -\frac{i}{\hbar}[H_{\text{S}} + H_{\text{renorm}}, \rho_{\text{S}}(t)] - \frac{1}{\hbar^2}\int_{0}^{\infty} d\tau \, \text{Tr}_{\text{R}}\big[H_{\text{SR}}(0), \big[H_{\text{SR}}(-\tau), \rho_{\text{S}}(t)\otimes\rho_{\text{R}}\big]\big], \tag{17.103}$$

where we are slightly rearranging the previous Hamiltonian from Eqs. (17.1)–(17.4):

$$\begin{aligned}
H &= H_{\text{S}} + H_{\text{R}} + H_{\text{SR}} + H_{\text{renorm}} \\
H_{\text{S}} &= \frac{p^2}{2M} + V(q) \\
H_{\text{R}} &= \sum_{\alpha=1}^{N}\left(\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2}m_\alpha\omega_\alpha^2 x_\alpha^2\right) \\
H_{\text{SR}} &= -q\sum_{\alpha=1}^{N} c_\alpha x_\alpha =: -fq \\
H_{\text{renorm}} &= q^2\sum_{\alpha=1}^{N}\frac{c_\alpha^2}{2m_\alpha\omega_\alpha^2} =: \frac{1}{2}M\delta\omega^2 q^2.
\end{aligned} \tag{17.104}$$

[10] After A. G. Redfield, "On the theory of relaxation processes," *IBM Journal of Research and Development* **1**, 19 (1957) (doi: 10.1147/rd.11.0019)

The main difference is that we are keeping the renormalization term H_{renorm} separate, whereas before we lumped it into the interaction Hamiltonian. Here it is more convenient to think of it as part of the system evolution, because it involves no reservoir operators, and thus it appears in the first term of Eq. (17.103). This is also consistent with thinking of Eq. (17.103) as valid to second order in the interaction, because H_{renorm} is already second order in q (while H_{SR} is only first order in the same operator).

It is the integral term of Eq. (17.103) that really represents the influence of the reservoir, and to study it further we can write it as a superoperator $\mathscr{K}$ acting on ρ_{S} ("superoperator" simply means that it is a linear transformation, but acting on both the left and right of ρ_{S}):

$$\begin{aligned}\mathscr{K}[\rho_{\text{S}}(t)] &:= -\frac{1}{\hbar^2}\int_0^\infty d\tau\, \text{Tr}_{\text{R}}\big[H_{\text{SR}}(0),[H_{\text{SR}}(-\tau),\rho_{\text{S}}(t)\otimes\rho_{\text{R}}]\big] \\ &= -\frac{1}{\hbar^2}\int_0^\infty d\tau\, \text{Tr}_{\text{R}}\big[q(0)f(0),[q(-\tau)f(-\tau),\rho_{\text{S}}(t)\otimes\rho_{\text{R}}]\big].\end{aligned} \tag{17.105}$$

After a bit of algebra, this expression can be rearranged to read (Problem 17.4)

$$\begin{aligned}\mathscr{K}[\rho_{\text{S}}(t)] = &-\frac{1}{2\hbar^2}\int_0^\infty d\tau\, \text{Tr}_{\text{R}}\big[[f(0),f(-\tau)]\rho_{\text{R}}\big]\big[q(0),\big[q(-\tau),\rho_{\text{S}}(t)\big]_+\big] \\ &-\frac{1}{2\hbar^2}\int_0^\infty d\tau\, \text{Tr}_{\text{R}}\big[[f(0),f(-\tau)]_+\rho_{\text{R}}\big]\big[q(0),\big[q(-\tau),\rho_{\text{S}}(t)\big]\big].\end{aligned} \tag{17.106}$$

Then noting the reservoir traces are the expectation values in Eqs. (17.30) and (17.36), with $\big\langle[f(0),f(-\tau)]\big\rangle = \big\langle[f(\tau),f(0)]\big\rangle$ and $\big\langle[f(0),f(-\tau)]_+\big\rangle = \big\langle[f(\tau),f(0)]_+\big\rangle$, we can write

$$\begin{aligned}\mathscr{K}[\rho_{\text{S}}(t)] = &\frac{i}{2\hbar}\int_0^\infty d\tau\, G(\tau)\big[q(0),[q(-\tau),\rho_{\text{S}}(t)]_+\big] \\ &-\frac{1}{2\hbar^2}\int_0^\infty d\tau\, G_+(\tau)\big[q(0),[q(-\tau),\rho_{\text{S}}(t)]\big],\end{aligned} \tag{17.107}$$

where the correlation functions are again

$$\begin{aligned}G(\tau) &= \frac{i}{\hbar}\big\langle[f(\tau),f(0)]\big\rangle = \frac{2}{\pi}\int_0^\infty d\omega\, J(\omega)\sin\omega\tau \\ G_+(\tau) &= \big\langle[f(\tau),f(0)]_+\big\rangle = \frac{2\hbar}{\pi}\int_0^\infty d\omega\, J(\omega)\coth\!\left(\frac{\hbar\omega}{2k_{\text{B}}T}\right)\cos\omega\tau.\end{aligned} \tag{17.108}$$

To proceed with evaluating the integrals here, we can again assume the system evolution to be slow on the decorrelation time scale of the reservoir, so we can approximate the system evolution by its *short-time* dynamics. Working to first order in τ,

$$\begin{aligned}q(-\tau) &= e^{-iH_{\text{S}}\tau/\hbar}qe^{iH_{\text{S}}\tau/\hbar} \\ &\approx q - \frac{i}{\hbar}[H_{\text{S}},q]\,\tau \\ &\approx q - \frac{p\tau}{M}.\end{aligned} \tag{17.109}$$

Note that at this order in τ, contributions from $V(q)$ drop out, and so the dynamics in this regime are effectively *free-particle* dynamics. Within this approximation the reservoir-coupling superoperator becomes

$$\begin{aligned}\mathscr{K}[\rho_{\text{S}}(t)] = &\frac{i}{2\hbar}\big[q,[q,\rho_{\text{S}}(t)]_+\big]\int_0^\infty d\tau\, G(\tau) - \frac{i}{2\hbar M}\big[q,[p,\rho_{\text{S}}(t)]_+\big]\int_0^\infty d\tau\,\tau\, G(\tau) \\ &-\frac{1}{2\hbar^2}\big[q,[q,\rho_{\text{S}}(t)]\big]\int_0^\infty d\tau\, G_+(\tau) + \frac{1}{2\hbar^2 M}\big[q,[p,\rho_{\text{S}}(t)]\big]\int_0^\infty d\tau\,\tau\, G_+(\tau).\end{aligned} \tag{17.110}$$

Thus, the system variables have now been completely decoupled from the correlation-function integrals, and now the evolution is Markovian. Because we are assuming a short decorrelation time, this is essentially the same high-temperature approximation that led to Eq. (17.63) in the Heisenberg picture.

What remains here is to evaluate the four correlation integrals in Eq. (17.110). For the first integral,

$$\int_0^\infty d\tau\, G(\tau) = \frac{2}{\pi}\int_0^\infty d\tau \int_0^\infty d\omega\, J(\omega)\sin\omega\tau, \tag{17.111}$$

we can carry out the τ integral first using the identity (Problem 17.1)

$$\int_0^\infty d\tau \sin\omega\tau = \mathscr{P}\frac{1}{\omega} \tag{17.112}$$

to obtain

$$\int_0^\infty d\tau\, G(\tau) = \frac{2}{\pi}\int_0^\infty d\omega\, \frac{J(\omega)}{\omega}, \tag{17.113}$$

where the principal-value operator does nothing here if we assume that $J(\omega)$ cuts off any dc divergence. Using the original definition (17.24) for the spectral density,

$$J(\omega) = \frac{\pi}{2}\sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha), \tag{17.114}$$

we have

$$\int_0^\infty d\tau\, G(\tau) = \int_0^\infty d\omega\, \frac{1}{\omega}\sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha}\delta(\omega-\omega_\alpha) = \sum_\alpha \frac{c_\alpha^2}{m_\alpha\omega_\alpha^2} = \frac{2H_{\rm renorm}}{q^2}. \tag{17.115}$$

Also, since

$$\big[q,[q,\rho_{\rm S}]_+\big] = [q^2,\rho_{\rm S}], \tag{17.116}$$

then

$$\frac{i}{2\hbar}\big[q,[q,\rho_{\rm S}(t)]_+\big]\int_0^\infty d\tau\, G(\tau) = \frac{i}{\hbar}[H_{\rm renorm},\rho_{\rm S}(t)] \tag{17.117}$$

and so the first term in the superoperator (17.110) cancels the $H_{\rm renorm}$ term in the first-order evolution of Eq. (17.103), as it did in the Heisenberg-picture treatment. Note the importance of this renormalization (cancellation): for the ohmic bath with $J(\omega)\propto\omega$, the integral (17.113) diverges, and the cancellation is necessary to avoid an infinite term in the evolution equation.

The second correlation integral in Eq. (17.110) is

$$\begin{aligned}\int_0^\infty d\tau\,\tau\, G(\tau) &= \frac{2}{\pi}\int_0^\infty d\tau\int_0^\infty d\omega\,\tau\, J(\omega)\sin\omega\tau\\ &= -\frac{2}{\pi}\int_0^\infty d\omega\, J(\omega)\,\partial_\omega\int_0^\infty d\tau\,\cos\omega\tau\\ &= -2\int_0^\infty d\omega\, J(\omega)\,\delta'(\omega)\\ &= J'(0) = M\gamma,\end{aligned} \tag{17.118}$$

where the last expression is specific to the ohmic bath (17.44), where

$$J(\omega) = M\gamma\omega. \tag{17.119}$$

(Note, however, that we have been slippery about the vanishing of a boundary term in the above integration; see Problem 17.5.) We already compute the third correlation integral in Eqs. (17.62):

$$\int_0^\infty d\tau\, G_+(\tau) = 2M\gamma k_{\rm B}T. \tag{17.120}$$

The last correlation integral is

$$\begin{aligned}\int_0^\infty d\tau\,\tau\,G_+(\tau) &= \frac{2\hbar}{\pi}\int_0^\infty d\omega\,J(\omega)\coth\!\left(\frac{\hbar\omega}{2k_{\rm B}T}\right)\int_0^\infty d\tau\,\tau\,\cos\omega\tau \\ &= \frac{2\hbar}{\pi}\int_0^\infty d\omega\,J(\omega)\frac{2k_{\rm B}T}{\hbar\omega}\int_0^\infty d\tau\,\tau\,\cos\omega\tau \\ &= \frac{4M\gamma k_{\rm B}T}{\pi}\int_0^\infty d\omega\int_0^\infty d\tau\,\tau\,\cos\omega\tau \\ &= 4M\gamma k_{\rm B}T\int_0^\infty d\tau\,\tau\,\delta(\tau) \\ &= 0,\end{aligned} \tag{17.121}$$

where again we have assumed an ohmic reservoir, and that we can make the replacement $\coth x \approx 1/x$ in the high-temperature limit.

Collecting Eqs. (17.103), (17.110), (17.117), (17.118), (17.120), and (17.121), we arrive at the following form for the quantum master equation,

$$\dot\rho(t) = -\frac{i}{\hbar}[H_{\rm S},\rho(t)] - \frac{i\gamma}{2\hbar}\big[q,[p,\rho(t)]_+\big] - \frac{M\gamma k_{\rm B}T}{\hbar^2}\big[q,[q,\rho(t)]\big], \tag{17.122}$$

(Caldeira–Leggett master equation)

where to simplify the notation we have dropped the S subscript from the system density operator, $\rho_{\rm S} \longrightarrow \rho$. This is the **Caldeira–Leggett master equation**,[11] and this equation generates the same dynamical evolution in the Schrödinger picture as the quantum Langevin equation (17.47), in the high-temperature limit (Problem 17.6). The $i\gamma$ term represents frictional damping of the particle momentum, while the temperature-dependent term represents momentum diffusion due to the noisy reservoir.

17.2.2.1 Lindblad Form

There is one minor peculiarity of the master equation (17.122). Defining the **Lindblad superoperator** by

$$D[c]\rho = c\rho c^\dagger - \frac{1}{2}[c^\dagger c,\rho]_+, \tag{17.123}$$

(Lindblad superoperator)

one can show that any Markovian quantum master equation must have the form[12]

$$\dot\rho(t) = -\frac{i}{\hbar}\sum_\alpha [H_\alpha,\rho(t)] + \sum_\beta D[c_\beta]\rho(t), \tag{17.124}$$

(Lindblad form of master equation)

where the sums are countable, and the H_α are Hermitian. Such a master equation is said to be in **Lindblad form**. That is, the master equation may have Hamiltonian terms, plus dissipation terms provided that they are of a particular form. If this is not the case, then the evolution may not preserve the positivity of the density operator. What this means intuitively here is that the damping may decrease the momentum variance too quickly compared to the diffusion, which could lead to a violation of the generalized uncertainty relation. (The case where this could happen is for a minimum-uncertainty wave packet with large momentum variance, evolving with large γ and small T.)

The oddity then is that the master equation (17.122) *cannot* be put into Lindblad form, so in principle it is problematic. The T-dependent term is not the problem, because it can be rewritten

$$-\big[q,[q,\rho]\big] = -\big[q,q\rho-\rho q\big]\big] = 2q\rho q - \big[q^2,\rho\big]_+ = 2D[q]\rho. \tag{17.125}$$

[11] A. O. Caldeira and A. J. Leggett, "Path Integral Approach to Quantum Brownian Motion," *Physica A: Statistical Mechanics and its Applications* **121**, 587 (1983) (doi: 10.1016/0378-4371(83)90013-4), Eq. (5.12).

[12] G. Lindblad, "On the generators of quantum dynamical semigroups," *Communications in Mathematical Physics* **48**, 199 (1976) (doi: 10.1007/BF01608499).

However, writing out the damping term,

$$-\frac{i\gamma}{2\hbar}\big[q,[p,\rho(t)]_+\big] = -\frac{i\gamma}{2\hbar}\big[q,p\rho+\rho p\big] = -\frac{i\gamma}{2\hbar}\big[qp\rho+q\rho p-p\rho q-\rho pq\big], \tag{17.126}$$

we can see that because of the mixture of q and p in this expression, the result doesn't match a Lindblad superoperator.

To resolve this, suppose that we try a bit harder to accommodate the damping term by adding an operator c to q in the diffusion term. Writing out the result gives

$$\frac{2M\gamma k_{\text{B}}T}{\hbar^2}D[q+c]\rho = \frac{2M\gamma k_{\text{B}}T}{\hbar^2}\left(D[q]\rho+D[c]\rho+q\rho c^\dagger+c\rho q-\frac{1}{2}(qc+c^\dagger q)\rho-\frac{1}{2}\rho(qc+c^\dagger q)\right). \tag{17.127}$$

Now for the $q\rho c^\dagger$ and $c\rho q$ terms to match up with the similar terms in Eq. (17.126), we could choose

$$c = \frac{i\hbar}{4Mk_{\text{B}}T}\,p. \tag{17.128}$$

Then after a bit of algebra (Problem **??**), the result is

$$\frac{2M\gamma k_{\text{B}}T}{\hbar^2}D[q+c]\rho = \frac{2M\gamma k_{\text{B}}T}{\hbar^2}D[q]\rho+\frac{\gamma}{8Mk_{\text{B}}T}D[p]\rho-\frac{i\gamma}{2\hbar}\big[q,[p,\rho(t)]_+\big]+\frac{i\gamma}{4\hbar}\big[[q,p]_+,\rho\big]. \tag{17.129}$$

This is looking promising, because we have all Lindblad and Hamiltonian-type terms. However, rearranging this, we have

$$-\frac{i\gamma}{2\hbar}\big[q,[p,\rho(t)]_+\big]+\frac{2M\gamma k_{\text{B}}T}{\hbar^2}D[q]\rho = -\frac{i\gamma}{4\hbar}\big[[q,p]_+,\rho\big]+\frac{2M\gamma k_{\text{B}}T}{\hbar^2}D\left[q+\frac{i\hbar}{4Mk_{\text{B}}T}\,p\right]\rho-\frac{\gamma}{8Mk_{\text{B}}T}D[p]\rho. \tag{17.130}$$

On the left-hand side are the dissipation and damping terms from the master equation (17.122). On the right-hand side, the first term has the Hamiltonian form, while the second has the Lindblad form, so these are both acceptable. However, the last term is problematic because of the minus sign, which cannot be absorbed into the c operator in the Lindblad operator (17.123). However, under the assumptions under which the master equation was derived (namely, large temperature), this last term should be negligible anyway compared to the second term. Thus, dropping this problematic term, we may put the master equation (17.122) into Lindblad form as

$$\dot\rho(t) = -\frac{i}{\hbar}[H_{\text{S}},\rho(t)]-\frac{i\gamma}{4\hbar}\big[[q,p]_+,\rho\big]+\frac{2M\gamma k_{\text{B}}T}{\hbar^2}D\left[q+\frac{i\hbar}{4Mk_{\text{B}}T}\,p\right]\rho$$

(Lindblad form of Caldeira–Leggett master equation) (17.131)

though this equation is not otherwise much more enlightening than the previous form. Thus, the conditions under which a violation of rho-positivity should never happen: the high-temperature diffusion should always outcompete the effect of the damping, and the uncertainty principle can't be violated.

17.3 Exercises

Problem 17.1

Derive the integral formulas

$$\int_0^\infty d\tau \cos(\omega\tau) = \pi\delta(\omega), \qquad \int_0^\infty d\tau \sin(\omega\tau) = \mathscr{P}\frac{1}{\omega}, \tag{17.132}$$

which should be interpreted in terms of the regularized forms

$$\lim_{\epsilon\to 0^+}\int_0^\infty d\tau \cos(\omega\tau)\, e^{-\epsilon\tau} = \pi\delta(\omega), \qquad \lim_{\epsilon\to 0^+}\int_0^\infty d\tau \sin(\omega\tau)\, e^{-\epsilon\tau} = \mathscr{P}\frac{1}{\omega}. \tag{17.133}$$

The procedure to derive these formulas is to consider the analogous integral of $e^{-i\omega\tau-\epsilon\tau}$ and apply the identity (13.187)

$$\lim_{\epsilon\to 0^+}\frac{1}{x\pm i\epsilon} = \mathscr{P}\frac{1}{x} \mp i\pi\delta(x), \tag{17.134}$$

taking the real and imaginary parts of the result.

Problem 17.2

Compute the Fourier transform

$$\int_{-\infty}^\infty dt\, e^{i\omega t}\int_{-\infty}^t dt'\, \dot{q}(t')\,\Gamma(t-t') = -\frac{i}{M}J(\omega)\,\tilde{q}(\omega), \tag{17.135}$$

given the damping kernel

$$\Gamma(t) = \frac{1}{2\pi}\int_{-\infty}^\infty d\omega\, \frac{2J(\omega)}{M\omega}e^{-i\omega t}. \tag{17.136}$$

Problem 17.3

Time-dependent perturbation theory gives the Dyson series (13.26)

$$\tilde{U}(t,t_0) = 1 + \sum_{n=1}^\infty \frac{1}{(i\hbar)^n}\int\limits_{t_0\le t_1\le\cdots\le t_n\le t} dt_n\cdots dt_1\,\tilde{V}(t_n)\cdots\tilde{V}(t_1). \tag{17.137}$$

Show that the interaction-picture evolution equation

$$\tilde{\rho}(t) = \tilde{U}(t,t_0)\,\tilde{\rho}(t_0)\,\tilde{U}^\dagger(t,t_0), \tag{17.138}$$

keeping terms in the interaction potential only up to second order, leads to the expression (17.93)

$$\partial_t\tilde{\rho}_{\rm SR}(t) = -\frac{i}{\hbar}[\tilde{H}_{\rm SR}(t),\tilde{\rho}_{\rm SR}(0)] - \frac{1}{\hbar^2}\int_0^t dt'\,[\tilde{H}_{\rm SR}(t),[\tilde{H}_{\rm SR}(t'),\tilde{\rho}_{\rm SR}(t')]]. \tag{17.139}$$

for the total system-reservoir density-operator evolution under a system-reservoir interaction.

Problem 17.4

Show that the reservoir-coupling superoperator (17.104)

$$\mathscr{K}[\rho_{\rm S}(t)] = -\frac{1}{\hbar^2}\int_0^\infty d\tau\,{\rm Tr}_{\rm R}\big[q(0)f(0),\big[q(-\tau)f(-\tau),\rho_{\rm S}(t)\otimes\rho_{\rm R}\big]\big]. \tag{17.140}$$

may be rewritten

$$\mathscr{K}[\rho_{\rm S}(t)] = -\frac{1}{2\hbar^2}\int_0^\infty d\tau\,{\rm Tr}_{\rm R}\big[[f(0),f(-\tau)]\rho_{\rm R}\big]\big[q(0),\big[q(-\tau),\rho_{\rm S}(t)\big]_+\big] \\ -\frac{1}{2\hbar^2}\int_0^\infty d\tau\,{\rm Tr}_{\rm R}\big[[f(0),f(-\tau)]_+\rho_{\rm R}\big]\big[q(0),\big[q(-\tau),\rho_{\rm S}(t)\big]\big]. \tag{17.141}$$

Problem 17.5

Justify the integral formula that occured in Eq. (17.118):

$$\int_0^\infty d\omega\,J(\omega)\,\delta'(\omega) = -\frac{1}{2}J'(0). \tag{17.142}$$

What are the conditions on $J(\omega)$ needed for this result to hold? You should account for the underlying integral representation

$$\delta(\omega) = 2\int_0^\infty d\tau\,\cos\omega\tau \tag{17.143}$$

of the delta function.

Problem 17.6

Derive the equations of motion for the moments $\langle q\rangle$, $\langle p\rangle$, V_q, V_p, and C_{qp} according to the master equation

$$\dot\rho(t) = -\frac{i}{\hbar}[H_{\rm S},\rho(t)] - \frac{i\gamma}{2\hbar}\big[q,[p,\rho(t)]_+\big] - \frac{M\gamma k_{\rm B}T}{\hbar^2}\big[q,[q,\rho(t)]\big], \tag{17.144}$$

using $\langle\dot c\rangle = {\rm Tr}[c\dot\rho]$ for Schrödinger-picture operator c, and verify that they are equivalent to the moment equations generated by the quantum Langevin equation (17.47) in the high-temperature limit.

Chapter 18

Path-Integral Quantization

Now we will develop the path-integral formulation of quantum mechanics,[1] in the case of a single particle in a potential. Although we will derive this formulation based on the results that we have developed so far from standard canonical quantization, the path integral can stand on its own as an independent and alternative framework for quantization.

18.1 Propagator

Recall that we introduced the **propagator** back in Section 1.8.7 as the matrix representation of the evolution operator. Here we will be specifically interested in working with the propagator in the position representation:

$$K(x,t;x_0,t_0) := \langle x|U(t,t_0)|x_0\rangle. \tag{18.1}$$
(propagator)

We will also assume that the evolution is driven by a time-independent Hamiltonian $H(x,p)$:

$$U(t,t_0) = e^{-iH(x,p)(t-t_0)/\hbar}. \tag{18.2}$$

An alternate and common notation for the propagator is

$$K(x,t;x_0,t_0) = \langle x,t|x_0,t_0\rangle, \tag{18.3}$$
(propagator)

where the evolution operator has been ''hidden'' inside the states $|x,t\rangle$ according to the notation

$$|x,t\rangle := e^{iHt/\hbar}|x\rangle. \tag{18.4}$$

This is not the expected time dependence of the time-evolving states $|x(t)\rangle$. Rather, it is best to think of $|x,t\rangle$ as the eigenstate of the Heisenberg-picture operator $x(t)$, as we can see by writing out the eigenvalue equation:

$$x(t)|x,t\rangle = e^{iHt/\hbar}x(0)\,e^{-iHt/\hbar}\,e^{iHt/\hbar}|x\rangle = x\,e^{iHt/\hbar}|x\rangle = x|x,t\rangle. \tag{18.5}$$

Thus, the propagator here is a transition amplitude, from x_0 at time t_0 to x at time t. More precisely, if we recall that

$$|\psi(t)\rangle = U(t,t_0)|\psi(t_0)\rangle, \tag{18.6}$$

and then project into the position basis by applying $\langle x|$ and insert an identity, we find

$$\langle x|\psi(t)\rangle = \langle x|U(t,t_0)|\psi(t_0)\rangle = \int dx_0\,\langle x|U(t,t_0)|x_0\rangle\langle x_0|\psi(t_0)\rangle, \tag{18.7}$$

[1] R. P. Feynman, ''Space-Time Approach to Non-Relativistic Quantum Mechanics,'' *Reviews of Modern Physics* **20**, 367 (1948) (doi: 10.1103/RevModPhys.20.367); Richard P. Feynman and A. R. Hibbs, ''Quantum Mechanics and Path Integrals,'' (McGraw–Hill, 1965).

or

$$\psi(x,t) = \int dx_0\, K(x,t;x_0,t_0)\,\psi(x_0,t_0), \tag{18.8}$$

(evolution via propagator)

so that $K(x,t;x_0,t_0)$ is a convolution kernel corresponding to the evolution. That is, $K(x,t;x_0,t_0)$ is the Green function for the Schrödinger equation (i.e., the retarded Green function if we are considering $t > t_0$, as in Section 13.2.2).

18.1.1 Composition of Evolution

A key technique in the construction of the path integral is the splitting of the propagator at an intermediate time. This is easy to do, we simply insert the identity operator, expanded in the position basis at some intermediate time t', into the propagator inner product,

$$\begin{aligned} K(x,t;x_0,t_0) &= \langle x,t|x_0,t_0\rangle \\ &= \int dx' \langle x,t|x',t'\rangle\langle x',t'|x_0,t_0\rangle, \end{aligned} \tag{18.9}$$

with the result

$$K(x,t;x_0,t_0) = \int dx' K(x,t;x',t')K(x',t';x_0,t_0).$$

(composition property of propagator) (18.10)

This equation says that we can regard the transition from x_0 to x at the corresponding times to be as if the particle ''passed through'' the intermediate x' point, so long as we sum the amplitude over all possible intermediate points x'.

18.2 Derivation of the Path Integral

Now the idea is to split up the time evolution in the same way, but into many small pieces. Specifically, we will divide the time interval from t_0 to t into N equal subintervals of length $\delta t = (t-t_0)/N$, where N is large enough that we can take δt to be infinitesimal. Using the form (18.2) for the evolution operator, we find

$$\begin{aligned} K(x,t;x_0,t_0) &= \langle x|e^{-iH(x,p)(t-t_0)/\hbar}|x_0\rangle \\ &= \langle x_N|e^{-iH(N\delta t)/\hbar}|x_0\rangle \\ &= \langle x_N|e^{-iH\delta t/\hbar}\left[\int dx_{N-1}|x_{N-1}\rangle\langle x_{N-1}|\right]e^{-iH\delta t/\hbar}\cdots e^{-iH\delta t/\hbar}\left[\int dx_1|x_1\rangle\langle x_1|\right]e^{-iH\delta t/\hbar}|x_0\rangle, \end{aligned} \tag{18.11}$$

after inserting $(N-1)$ identity operators in the position representation. At this point we have an $(N-1)$-dimensional integral over a product of N matrix elements,

$$K(x,t;x_0,t_0) = \int\left(\prod_{j=1}^{N-1} dx_j\right)\langle x_N|e^{-iH\delta t/\hbar}|x_{N-1}\rangle\langle x_{N-1}|e^{-iH\delta t/\hbar}|x_{N-2}\rangle\cdots\langle x_1|e^{-iH\delta t/\hbar}|x_0\rangle. \tag{18.12}$$

This is now an infinite-dimensional integral, since we have in mind the limit $N \longrightarrow \infty$. It is crucial to note that we *must* get some simplification in the ''mini-propagators'' over each time interval δt; otherwise, we've just created a huge mess for nothing. Here, what we will gain is that every such mini-propagator will simplify from an operator to a scalar.

18.2.1 Splitting the Evolution Operator

To continue, we will assume a standard particle Hamiltonian of the form

$$H = \frac{p^2}{2m} + V(x) = T(p) + V(x), \tag{18.13}$$

where $p = -i\hbar\partial_x$ as usual, and while we are treating only one dimension, the generalization to multiple dimensions is straightforward. The major simplification that we obtain for infinitesimal time evolution that we may split the evolution operator with this Hamiltonian according to[2]

$$\begin{aligned} e^{-iH\delta t/\hbar} &= 1 - \frac{i\,\delta t}{\hbar}H + O(\delta t^2) \\ &= \left(1 - \frac{i\,\delta t}{\hbar}T(p)\right)\left(1 - \frac{i\,\delta t}{\hbar}V(x)\right) + O(\delta t^2) \\ &= e^{-iT(p)\delta t/\hbar}e^{-iV(x)\delta t/\hbar} + O(\delta t^2). \end{aligned} \tag{18.14}$$

The correction term here is negligible in the following sense: there are N such correction terms that add together, which gives an error $N\delta t^2 = \delta t$, which vanishes as $\delta t \longrightarrow 0$. Then considering any one of the matrix elements in the integrand of (18.12), we have

$$\begin{aligned} \langle x_2|e^{-iH\delta t/\hbar}|x_1\rangle &= \langle x_2|e^{-iT(p)\delta t/\hbar}e^{-iV(x)\delta t/\hbar}|x_1\rangle \\ &= \int dp_1\, \langle x_2|e^{-iT(p)\delta t/\hbar}|p_1\rangle\langle p_1|e^{-iV(x)\delta t/\hbar}|x_1\rangle, \end{aligned} \tag{18.15}$$

where we have inserted a momentum-space identity operator between the operators. Remember that at this point, the position and momentum appearing in the exponentials are operators. Since we have inner products of eigenstates of these operators, we can simply replace them by their eigenvalues,

$$\begin{aligned} \langle x_2|e^{-iH\delta t/\hbar}|x_1\rangle &= \int dp_1\, \langle x_2|p_1\rangle\langle p_1|x_1\rangle e^{-iT(p_1)\delta t/\hbar}e^{-iV(x_1)\delta t/\hbar} \\ &= \frac{1}{2\pi\hbar}\int dp_1\, e^{ip_1(x_2-x_1)/\hbar}e^{-iT(p_1)\delta t/\hbar}e^{-iV(x_1)\delta t/\hbar}, \end{aligned} \tag{18.16}$$

where we have used the usual momentum eigenstate in the position representation:

$$\langle x|p\rangle = \frac{e^{ipx/\hbar}}{\sqrt{2\pi\hbar}}. \tag{18.17}$$

Note that in introducing the momentum integral, we have also introduced a Fourier transform. In fact, by tacking on an extra $|x_2\rangle$ on the front of Eq. (18.15) and then integrating over x_2, we have the recipe for propagating the initial state $|x_2\rangle$ over a small time δt: first propagate using the potential-energy exponential operator, which is diagonal in x, then Fourier transform to momentum space, where we may apply the kinetic operator, and finally transform back to position space to express the result in the x_2 basis.

Since $T(p)$ is quadratic, the momentum integral in the mini-propagator (18.16) is a Gaussian integral. Specifically, we have

$$\langle x_2|e^{-iH\delta t/\hbar}|x_1\rangle = \frac{1}{2\pi\hbar}\,e^{-iV(x_1)\delta t/\hbar}\int dp_1\, e^{ip_1\delta x_1/\hbar}e^{-ip_1^2\delta t/2m\hbar}. \tag{18.18}$$

[2]More formally and generally, this splitting is a truncation of the **Baker–Campbell–Hausdorff expansion**. For details, see R. M. Wilcox, "Exponential Operators and Parameter Differentiation in Quantum Physics," *Journal of Mathematical Physics* **8**, 962 (1967) (doi: 10.1063/1.1705306).

where $\delta x_1 := x_2 - x_1$. This integral has the same form as the Gaussian integral leading to the free-particle propagator (see Problem 2.2); carrying out the integral in the same way, we obtain

$$\begin{aligned}\langle x_2|e^{-iH\delta t/\hbar}|x_1\rangle &= \frac{1}{2\pi\hbar}e^{-iV(x_1)\delta t/\hbar}\sqrt{\frac{2\pi m\hbar}{i\delta t}}e^{im(\delta x_1)^2/2\hbar(\delta t)} \\ &= \sqrt{\frac{m}{i2\pi\hbar\delta t}}\,e^{im\dot{x}_1^2(\delta t)/2\hbar}e^{-iV(x_1)\delta t/\hbar} \\ &= \sqrt{\frac{m}{i2\pi\hbar\delta t}}\,e^{iL(x_1,\dot{x}_1)\delta t/\hbar},\end{aligned} \tag{18.19}$$

where we have taken

$$\dot{x} = \frac{\delta x}{\delta t} \tag{18.20}$$

in view of the $\delta t \longrightarrow 0$ limit, and we have identified

$$L(x,\dot{x}) = \frac{1}{2}m\dot{x}^2 - V(x) \tag{18.21}$$

as the classical Lagrangian. Note that this is one of the interesting aspects of the path-integral approach, which is that the Lagrangian (and, in fact the *classical* Lagrangian) appears here. Also, the exponential factor in Eq. (18.19) contains $L(x_1,\dot{x}_1)\delta t$, which is the classical action over the small time interval δt, something that will feature more prominently below.

18.2.2 Functional Integral

Now collecting all N matrix elements (18.19) and putting them into the propagator (18.12), we have

$$\begin{aligned}K(x,t;x_0,t_0) &= \Big(\frac{m}{i2\pi\hbar\delta t}\Big)^{N/2}\int\left(\prod_{j=1}^{N-1}dx_j\right)e^{iL(x_{N-1},\dot{x}_{N-1})\delta t/\hbar}e^{iL(x_{N-2},\dot{x}_{N-2})\delta t/\hbar}\cdots e^{iL(x_0,\dot{x}_0)\delta t/\hbar} \\ &= \Big(\frac{m}{i2\pi\hbar\delta t}\Big)^{N/2}\int\left(\prod_{j=1}^{N-1}dx_j\right)\left(\prod_{j=0}^{N-1}e^{iL(x_j,\dot{x}_j)\delta t/\hbar}\right).\end{aligned} \tag{18.22}$$

Defining the path-integral volume element

$$Dx := \Big(\frac{m}{i2\pi\hbar\delta t}\Big)^{N/2}\prod_{j=1}^{N-1}dx_j, \tag{18.23}$$

(functional-integral volume element)

we can simplify the notation in Eq. (18.22) and recombine the exponentials to write

$$K(x,t;x_0,t_0) = \int Dx\,\exp\left[\frac{i}{\hbar}\int_{t_0}^{t}dt'\,L(x,\dot{x})\right], \tag{18.24}$$

(Feynman propagator)

where the time integral in the exponential is equivalent to the product in Eq. (18.22) in the limit $N \longrightarrow \infty$. This is a **functional integral** or **path integral**, as we are integrating the **action functional**

$$S[x(t)] = \int_{t_0}^{t}dt'\,L[x(t'),\dot{x}(t')], \tag{18.25}$$

(action functional)

in terms of which the propagator has the even simpler form

$$K(x,t;x_0,t_0) = \int Dx\,\exp\left(\frac{i}{\hbar}S[x]\right), \tag{18.26}$$

(Feynman propagator)

noting that the integration is with respect to the *trajectory* (or function) $x(t)$. Note that the normalization factor in (18.23) is highly divergent, but it is typically hidden inside the differential here since it drops out of calculations on the way to a physical result.

18.2.2.1 Path Integral

We can go a bit further with the interpretation of the paths $x(t)$ that appear in the action functional (18.25) and functional integral (18.26). Remember that from Eqs. (18.19), each mini-propagator involves a kinetic-energy factor of the form

$$e^{im(\delta x_j)^2/2\hbar(\delta t)} = e^{im\dot{x}_j^2(\delta t)/2\hbar}, \tag{18.27}$$

with integrals over x_j and x_{j+1} that involve the previous and following factors, chaining together the successive coordinates x_j. These factors (as well as the accompanying potential factors) are oscillatory, and the integrals are divergent, strictly speaking. However, as in similar oscillatory integrals such as the integral representation (1.154) of the delta function, we can proceed heuristically and forge ahead with calculations and interpretations. Here, the idea is that the integrand should not contribute to the integral in regions where the phase oscillates rapidly, because nearby components of the integrand will cancel. We will return to this idea in discussing the classical limit below, but here we will simply note that we only expect the integrand to be important if the phase angle is of order unity or smaller,

$$\frac{m(\delta x_j)^2}{2\hbar\delta t} \lesssim 1. \tag{18.28}$$

Neglecting constants and being even more informal, we expect typical paths to have

$$\delta x_j \sim \sqrt{\delta t}. \tag{18.29}$$

Since $\delta t \longrightarrow 0$, we can first note that adjacent points x_j and x_{j+1} become arbitrarily close together as $N \longrightarrow \infty$. Further, this scaling of displacement with time is characteristic of *diffusive* paths. In the limit $N \longrightarrow \infty$, the paths $x(t)$ are continuous random walks (see Problem 2.38 for a bit more description). Such paths are (typically) continuous but everywhere nondifferentiable. These statements are more precisely made after transforming to imaginary time, when the kinetic energy measure becomes truly Gaussian (and defines a proper probability measure for diffusive paths), giving a path representation for the solution to the diffusion equation. However, even for the Schrödinger equation we should keep in mind the picture of continuous, diffusing paths from x_0 to x as the typical paths that we sum in the functional integral (18.26).

18.2.3 Phase-Space Path Integral

An alternate form of the path integral, before carrying out the momentum integrals, comes about by rewriting the first line of Eq. (18.18) in terms of $\dot{x}_1 = \delta x_1/\delta t$ and the Hamiltonian $H(x,p)$ as

$$\langle x_2|e^{-iH\delta t/\hbar}|x_1\rangle = \frac{1}{2\pi\hbar}\int dp_1\, e^{ip_1\dot{x}_1\delta t/\hbar}e^{-iH(x_1,p_1)\delta t/\hbar}. \tag{18.30}$$

Then collecting all the matrix elements, we can now write the **phase-space path integral**[3]

$$K(x,t;x_0,t_0) = \int Dx\,Dp\,\exp\left[\frac{i}{\hbar}\int_{t_0}^{t} dt\,\left[p\dot{x} - H(x,p)\right]\right], \tag{18.31}$$

(phase-space propagator)

where the integration measure in phase space is

$$Dx\,Dp := \frac{1}{(2\pi\hbar)^{(N-1)/2}}\left(\prod_{j=1}^{N-1} dx_j\right)\left(\prod_{j=0}^{N-1} dp_j\right). \tag{18.32}$$

(functional-integration measure)

This looks similar to the previous path integral (18.24), except that we now have the phase-space action—the integral of $p\dot{x} - H$—in the propagator instead of the Lagrangian action, and the integration is over both

[3]This general form of the path integral in phase space was given by H. Davies, ''Hamiltonian approach to the method of summation over Feynman histories,'' *Mathematical Proceedings of the Cambridge Philosophical Society* **59**, 147 (1963) (doi: 10.1017/S0305004100002097).

positions and momenta. At this point, in the case of a Hamiltonian quadratic in p, the integral is Gaussian and can be carried out analytically as above. The stationary-phase condition on the p integral gives the classical Hamilton equation

$$\partial_p \left[p\dot{x} - H(x,p)\right] = \dot{x} - \partial_p H(x,p) = 0, \tag{18.33}$$

which can be used to eliminate p in favor of $\dot{x}$ in $p\dot{x} - H(x,p)$ to reproduce the Lagrangian, and thus the Lagrangian form of the propagator (18.24).

Note that while the positions and momenta were introduced in similar ways, there is a fundamental asymmetry between them.[4] In the infinitesimal propagator from x_j to x_{j+1}, we regard the position as moving smoothly between these two coordinates in a time δt. However, the momentum is a *constant* p_j over the same time interval. So in this **time-slicing** construction (the construction with finite N), the path position follows a continuous, polygonal path, while the momentum is discontinuous and piecewise constant.

18.2.4 Example: Free-Particle Propagator

To evaluate the propagator (18.24) for the free particle, $L(x,\dot{x}) = m\dot{x}^2/2$, it is easiest to go back to the discrete form (18.22), which we can write explicitly as

$$\begin{aligned} K(x,t;x_0,t_0) &= \left(\frac{m}{i2\pi\hbar\delta t}\right)^{N/2} \int \left(\prod_{j=1}^{N-1} dx_j\right) \left(\prod_{j=0}^{N-1} e^{im\dot{x}_j^2\delta t/2\hbar}\right) \\ &= \left(\frac{m}{i2\pi\hbar\delta t}\right)^{N/2} \int \left(\prod_{j=1}^{N-1} dx_j\right) \left(\prod_{j=0}^{N-1} e^{im(x_{j+1}-x_j)^2/2\hbar\delta t}\right). \end{aligned} \tag{18.34}$$

Now let

$$x_j = \bar{x}_j + \delta_j, \tag{18.35}$$

where $\bar{x}_j$ is the straight-line path from x_0 to $x = x_N$:

$$\bar{x}_j = x_0 + \left(\frac{x - x_0}{t - t_0}\right)(t_j - t_0) =: x_0 + \bar{v}(t_j - t_0). \tag{18.36}$$

Here, $\bar{v} = (x - x_0)/(t - t_0)$ is the mean velocity of the path, and the δ_j are the "fluctuations" about this average. In particular, note that

$$\delta_0 = \delta_N = 0. \tag{18.37}$$

For the increments in the path integral, we may write

$$x_{j+1} - x_j = (\bar{x}_{j+1} + \delta_{j+1}) - (\bar{x}_j + \delta_j) = (\delta_{j+1} - \delta_j) + \bar{v}\delta t, \tag{18.38}$$

and thus the Gaussian factors in the path integral (18.34) involve squared differences of the form

$$(x_{j+1} - x_j)^2 = (\delta_{j+1} - \delta_j + \bar{v}\delta t)^2 = (\delta_{j+1} - \delta_j)^2 + 2(\delta_{j+1} - \delta_j)\bar{v}\delta t + \bar{v}^2\delta t^2. \tag{18.39}$$

This means that the path integral (18.34) splits into a product of three components, each involving Gaussian functions of each of these terms. For example, the last term leads to the product

$$\prod_{j=0}^{N-1} e^{im\bar{v}^2\delta t/2\hbar} = e^{im\bar{v}^2 N\delta t/2\hbar} = e^{im\bar{v}^2(t-t_0)/2\hbar} = e^{im(x-x_0)^2/2\hbar(t-t_0)}, \tag{18.40}$$

while the second term

$$\prod_{j=0}^{N-1} e^{im(\delta_{j+1}-\delta_j)\bar{v}/\hbar} = e^{im(\delta_N - \delta_0)\bar{v}/\hbar} = 1, \tag{18.41}$$

[4] H. Davies, *op. cit.*; Claude Garrod, "Hamiltonian Path-Integral Methods," *Reviews of Modern Physics* **38**, 483 (1966) (doi: 10.1103/RevModPhys.38.483); M. S. Marinov, "Path integrals in quantum theory: An outlook of basic concepts," *Physics Reports* **60**, 1 (1980) (doi: 10.1016/0370-1573(80)90111-8).

in view of Eq. (18.37). Collecting these with the remaining product leads to the path integral

$$K(x,t;x_0,t_0)=\Big(\frac{m}{i2\pi\hbar\delta t}\Big)^{N/2}e^{im(x-x_0)^2/2\hbar(t-t_0)}\int\left(\prod_{j=1}^{N-1}d\delta_j\right)\left(\prod_{j=0}^{N-1}e^{im(\delta_{j+1}-\delta_j)^2/2\hbar\delta t}\right), \tag{18.42}$$

where we should keep in mind that $\delta_0=\delta_N=0$ in the $j=0$ and $j=N-1$ factors. Also, note that since the coordinate transformation from x_j to δ_j was just a coordinate shift, there is no Jacobian factor to worry about. In making the coordinate transformation here, we have reduced the problem of computing $K(x,t;x_0,t_0)$ to that of a periodic path integral of the form $K(0,t;0,t_0)$.

To finish up the path integral, we can begin by examining the δ_j integral, which involves the terms

$$\begin{aligned}(\delta_2-\delta_1)^2+(\delta_1-\delta_0)^2&=\delta_2^2-2\delta_2\delta_1+2\delta_1^2\\ (\delta_{j+1}-\delta_j)^2+(\delta_j-\delta_{j-1})^2&=\delta_{j+1}^2-2\delta_{j+1}\delta_j+2\delta_j^2-2\delta_j\delta_{j-1}+\delta_{j-1}^2\\ (\delta_N-\delta_{N-1})^2+(\delta_{N-1}-\delta_{N-2})^2&=2\delta_{N-1}^2-2\delta_{N-1}\delta_{N-2}+\delta_{N-2}^2\end{aligned} \tag{18.43}$$

If we add up these contributions, we have an integral of the form

$$K(x,t;x_0,t_0)=\Big(\frac{m}{i2\pi\hbar\delta t}\Big)^{N/2}e^{im(x-x_0)^2/2\hbar(t-t_0)}\int\left(\prod_{j=1}^{N-1}d\delta_j\right)\exp\left[\frac{im}{2\hbar\delta t}\left(\delta_\alpha M_{\alpha\beta}\delta_\beta\right)\right], \tag{18.44}$$

where now $M_{\alpha\beta}$ is a matrix of dimension $(N-1)\times(N-1)$, and has twos along the diagonal, and -1's along the adjacent diagonals:

$$(M_{\alpha\beta})=\begin{bmatrix}2&-1&0&\cdots&0&0\\-1&2&-1&\cdots&0&0\\0&-1&2&\cdots&0&0\\\vdots&\vdots&\vdots&\ddots&\vdots&\vdots\\0&0&0&\cdots&2&-1\\0&0&0&\cdots&-1&2\end{bmatrix}. \tag{18.45}$$

This matrix has determinant

$$\det(M_{\alpha\beta})=N, \tag{18.46}$$

as we will now show. Let $\det_n$ denote the determinant of the $n\times n$ version of the same matrix. Then expanding the determinant in terms of minors along the first row gives the recursion relation

$$\det{}_n=2\det{}_{n-1}-\det{}_{n-2}. \tag{18.47}$$

With the initial values $\det_1=2$ and $\det_2=3$, we can see that the recursion and initial conditions are satisfied by

$$\det{}_n=n+1. \tag{18.48}$$

This establishes the determinant (18.46).

Now to finish up with the path integral, we can use the Gaussian integration formula

$$\int d^Nz\,\exp\left[-z_\alpha S_{\alpha\beta}z_\beta\right]=\frac{\pi^{N/2}}{\sqrt{\det(S_{\alpha\beta})}}, \tag{18.49}$$

for an $N\times N$ matrix $S_{\alpha\beta}$ and adapt it for complex Gaussians as we did in Eq. (18.18). The result is

$$\begin{aligned}K(x,t;x_0,t_0)&=\Big(\frac{m}{i2\pi\hbar\delta t}\Big)^{N/2}e^{im(x-x_0)^2/2\hbar(t-t_0)}\left(\frac{i2\pi\hbar\delta t}{m}\right)^{(N-1)/2}\frac{1}{\sqrt{N}}\\ &=\sqrt{\frac{m}{i2\pi\hbar N\delta t}}\,e^{im(x-x_0)^2/2\hbar(t-t_0)}\end{aligned} \tag{18.50}$$

or finally,

$$K(x,t;x_0,t_0) = \sqrt{\frac{m}{i2\pi\hbar(t-t_0)}}\,\exp\left[\frac{im(x-x_0)^2}{2\hbar(t-t_0)}\right] \qquad (18.51)$$
(free-particle propagator)

Note that this agrees with the free-particle propagator that we derived long ago, Eq. (2.11).

18.3 Classical Limit

One nice feature of the path integral is that it gives a clear path to the classical limit, at least in a heuristic argument.[5] Returning to the propagator (18.26),

$$K(x,t;x_0,t_0) = \int Dx\,\exp\left(\frac{i}{\hbar}S[x]\right), \qquad (18.52)$$

note that as $\hbar \longrightarrow 0$, the exponential becomes highly oscillatory. Except, that is, where the rest of the exponent, $S[x]$, vanishes. Thus, we might expect the oscillatory paths to roughly cancel, and the integral should be dominated by the "stationary" paths, for which slight variations don't change the action. Dropping all but these stationary paths is known as the **stationary-phase approximation**, and amounts to restricting the path integral to *classical* paths satisfying

$$\delta S[x] = 0, \qquad (18.53)$$
(stationary-phase condition)

which is just the variational principle that generates the Euler-Lagrange equation. That is, when $\hbar$ is small compared to the action of the system, the path integral is dominated by the contribution from the classical path. Paths that deviate from the classical path by even a small amount on the classical scale are suppressed because they oscillate wildly and cancel other, slightly deviant paths. When $\hbar$ is larger relative to the action, the paths have more leeway to "explore" around the classical path without suffering the fate of cancellation. Note that the stationary-phase approximation is essentially a variation on the method of steepest descent or saddle-point approximation that we saw before in Section 5.5.2.2.

18.3.1 Semiclassical Propagator

With this picture in mind, we can go on and develop an approximate form for the propagator in the semiclassical regime.[6] Since we expect the classical path x_c to be important, we will consider small deviations δx from it:

$$x(t) = x_c(t) + \delta x(t). \qquad (18.54)$$

Then expanding the action in a functional Taylor series around the classical path, we find

$$S[x] = S[x_c] + \delta S[x_c] + \frac{1}{2}\delta^2 S[x_c] + \cdots \qquad (18.55)$$
(series expansion of the action)

up to second order. Note that by definition, $\delta S[x_c] = 0$, but we leave the first-order term here to illustrate the general pattern.

Let's take a moment to examine the notation here. Given the action functional (18.25),

$$S[x(t)] = \int_{t_0}^{t} dt'\,L[x(t'),\dot{x}(t')], \qquad (18.56)$$

[5] Richard P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw–Hill, 1965), Section 2-3, p. 29.

[6] L. S. Schulman, *Techniques and Applications of Path Integration* (Wiley, 1981), Chapter 13; Hagen Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*, 5th ed. (World Scientific, 2009), Chapter 4.

recall from Section 0.2 that we define the **first variation** $\delta S[x]$ of the functional as

$$\delta S[x;\delta x] := \lim_{\epsilon\to 0} \frac{S[x+\epsilon\,\delta x]-S[x]}{\epsilon} = \partial_\epsilon S[x+\epsilon\,\delta x]\Big|_{\epsilon=0}, \tag{18.57}$$
(first variation)

in analogy to the usual derivative, but the perturbation to the argument is a function $\delta x(t)$. Note that this variation is, roughly speaking, proportional to δx, and hence why we can use it in the series expansion. Then the **second variation** is the variation of the first variation:

$$\begin{aligned}\delta^2 S[x;\delta x;\delta x'] &:= \lim_{\epsilon\to 0} \frac{\delta S[x+\epsilon\,\delta x;\delta x']-\delta S[x;\delta x']}{\epsilon}\\ &= \partial_\epsilon \delta S[x+\epsilon\,\delta x;\delta x']\Big|_{\epsilon=0}\\ &= \partial_\epsilon\partial_{\epsilon'} S[x+\epsilon\,\delta x+\epsilon'\,\delta x']\Big|_{\epsilon=\epsilon'=0}.\end{aligned}$$
(second variation) (18.58)

This pattern of definitions can obviously continue indefinitely for higher-order variations.

The variations can then serve as the definition for functional derivatives. In terms of the first variation, the **first functional derivative** $\delta S/\delta x$ is defined such that the inner product with the perturbation δx gives the first variation:

$$\left\langle \frac{\delta S}{\delta x},\, \delta x \right\rangle := \int_{t_0}^{t} dt'\, \frac{\delta S}{\delta x(t')}\,\delta x(t') := \delta S[x;\delta x]. \tag{18.59}$$
(first functional derivative)

The **second functional derivative** is similarly defined in terms of the second variation as

$$\left\langle \delta x,\, \frac{\delta^2 S}{\delta x^2}\,\delta x' \right\rangle := \int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\,\delta x(t')\,\frac{\delta^2 S}{\delta x(t')\,\delta x(t'')}\,\delta x'(t'') := \delta^2 S[x;\delta x].$$
(second functional derivative) (18.60)

Note that these are all reasonably straightforward generalizations of the same derivatives for a scalar-valued function of a vector $S(x_j)$, where the first derivative is a vector of partial derivatives $\partial S/\partial x_j$, and the second derivative is a matrix of derivatives $\partial^2 S/\partial x_j \partial x_k$.

In terms of the functional derivatives, we can write the series expansion (18.55) for the action as

$$S[x] = S[x_\mathrm{c}] + \int_{t_0}^{t} dt'\, \frac{\delta S}{\delta x(t')}\bigg|_{x=x_\mathrm{c}} \delta x(t') + \frac{1}{2}\int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\, \frac{\delta^2 S}{\delta x(t')\,\delta x(t'')}\bigg|_{x=x_\mathrm{c}} \delta x(t')\,\delta x(t'') + \cdots$$
(series expansion of the action) (18.61)

as an alternative to Eq. (18.55). Again, $\delta S/\delta x$ vanishes when evaluated at x_c, and again this just generalizes the discrete form of the Taylor series.

Inserting this latter expansion into the path integral (18.52), we note again that the first-order term is zero, and we also note that the second-order term gives a Gaussian factor in the fluctuations $\delta x(t)$:

$$K_\mathrm{sc}(x,t;x_0,t_0) = e^{iS[x_\mathrm{c}]/\hbar} \int Dx\, \exp\left(\frac{i}{2\hbar} \int dt' \int dt''\, \delta x(t)\, \frac{\delta^2 S}{\delta x(t')\,\delta x(t'')}\bigg|_{x=x_\mathrm{c}} \delta x(t'') \right). \tag{18.62}$$

We will be careful and go back to the discrete (time-sliced) form for the path integral to evaluate it, as in Eq. (18.22):

$$K_\mathrm{sc}(x,t;x_0,t_0) = \left(\frac{m}{i2\pi\hbar\delta t}\right)^{N/2} e^{iS[x_\mathrm{c}]/\hbar} \int \left(\prod_{j=1}^{N-1} d\delta x_j \right) \exp\left(\frac{i}{2\hbar} \sum_{j=1}^{N-1}\sum_{j'=1}^{N-1} \delta x_j\, \frac{\partial^2 S}{\partial x_j\,\partial x_{j'}}\bigg|_{x=x_\mathrm{c}} \delta x_{j'} \right). \tag{18.63}$$

Note that the sums in the exponential only run from 1 to $N-1$ because we regard the endpoints x_0 and x_N to be fixed. Then using the Gaussian-integral formula (18.49),

$$K_{\rm sc}(x,t;x_0,t_0) = \sqrt{\frac{m}{i2\pi\hbar\delta t}}\left(\frac{m}{\delta t}\right)^{(N-1)/2} \det{}^{-1/2}\left(\frac{\partial^2 S}{\partial x_j\,\partial x_{j'}}\right)\ \exp\left(\frac{i}{\hbar}S[x_{\rm c}]\right), \tag{18.64}$$

where the determinant is over an $(N-1)\times(N-1)$ matrix. In continuous language, we can write this result in terms of a **functional determinant** as

$$K_{\rm sc}(x,t;x_0,t_0) = \sqrt{\frac{m}{i2\pi\hbar\delta t}}\ \det{}^{-1/2}\left[\frac{\delta t}{m}\left(\frac{\delta^2 S}{\delta x^2}\right)\right]\ \exp\left(\frac{i}{\hbar}S[x_{\rm c}]\right), \tag{18.65}$$

(semiclassical propagator)

where we may take the determinant to be defined by the discrete expression (18.64). Note that in deriving this propagator, we have considered lowest-order quantum fluctuations about the classical trajectory, in what amounts to making a Gaussian approximation for the fluctuations. While the exponential gives the quantum phase factor along the classical path, the determinant gives the correction to the amplitude as the size of the Gaussian fluctuations stretches or compresses in phase space.

For the action (18.56), we can write out the first action variation

$$\begin{aligned}\delta S[x;\delta x] &= \int_{t_0}^{t} dt'\ \left(\frac{\partial L}{\partial x}\,\delta x + \frac{\partial L}{\partial \dot x}\,\delta\dot x\right)\\ &= \int_{t_0}^{t} dt'\ \left(\frac{\partial L}{\partial x} - \frac{d}{dt}\frac{\partial L}{\partial \dot x}\right)\delta x\end{aligned} \tag{18.66}$$

and the second variation

$$\begin{aligned}\delta^2 S[x;\delta x] &= \int_{t_0}^{t} dt'\ \left(\frac{\partial^2 L}{\partial x^2}\,\delta x\,\delta x + 2\frac{\partial L}{\partial x\partial\dot x}\,\delta x\,\delta\dot x + \frac{\partial^2 L}{\partial \dot x^2}\,\delta\dot x\,\delta\dot x\right),\\ &= \int_{t_0}^{t} dt' \int_{t_0}^{t} dt''\,\delta(t'-t'')\\ &\quad\times\left(\frac{\partial^2 L}{\partial x(t')\,\partial x(t'')}\,\delta x(t')\,\delta x(t'') + 2\frac{\partial L}{\partial x(t')\,\partial\dot x(t'')}\,\delta x(t')\,\delta\dot x(t'') + \frac{\partial^2 L}{\partial\dot x(t')\,\partial\dot x(t'')}\,\delta\dot x(t')\,\delta\dot x(t'')\right),\end{aligned} \tag{18.67}$$

and thus the functional derivatives

$$\frac{\delta S[x]}{\delta x(t)} = \frac{\partial L}{\partial x} - \frac{d}{dt}\frac{\partial L}{\partial\dot x} \tag{18.68}$$

and

$$\frac{\delta^2 S[x]}{\delta x(t)\,\delta x(t')} = \delta(t-t')\left(\frac{\partial^2 L}{\partial x^2(t)} + 2\frac{\partial L}{\partial x(t)\,\partial\dot x(t)}\frac{d}{dt'}\right) - \frac{d}{dt}\delta(t-t')\frac{\partial^2 L}{\partial\dot x^2(t)}\frac{d}{dt'}. \tag{18.69}$$

In this last expression, note that all derivative operators d/dt operate on everything to the right.

For a particle Lagrangian (18.21),

$$L(x,\dot x) = \frac{1}{2}m\dot x^2 - V(x), \tag{18.70}$$

the first functional derivative is

$$\frac{\delta S[x]}{\delta x(t)} = -V'(x) - m\ddot x, \tag{18.71}$$

while the second derivative becomes

$$\frac{\delta^2 S[x]}{\delta x(t)\,\delta x(t')} = -\delta(t-t')\,V''(x) - m\frac{d}{dt}\delta(t-t')\frac{d}{dt'}, \tag{18.72}$$

in which case the functional determinant in the propagator (18.65) becomes

$$\begin{aligned}\det{}^{-1/2}\left[\frac{\delta t}{m}\left(\frac{\delta^2 S}{\delta x^2}\right)\right] &= \delta t^{-(N-1)/2}\det{}^{-1/2}\left(-\frac{d}{dt}\delta(t-t')\frac{d}{dt'} - \delta(t-t')\,\frac{V''(x_{\rm c})}{m}\right)\\ &= \delta t^{-(N-1)}\det{}^{-1/2}\left(-\partial_t^2 - \frac{V''(x_{\rm c})}{m}\right),\end{aligned} \tag{18.73}$$

where we have used the discrete form of the delta function, which is the identity times δt^{-1}. In fact, we have already evaluated the last determinant here in the case $V(x) = 0$ for the free particle. By noting that the second-order, finite-difference operator for the second derivative can be written

$$\Delta_t^{(2)}\psi(t) := \frac{\psi(t+\delta t) - 2\psi(t) + \psi(t-\delta t)}{\delta t^2}, \tag{18.74}$$

such that

$$\partial_t^2\psi(t) = \Delta_t^{(2)}\psi(t) + O(\delta t^3), \tag{18.75}$$

the matrix $\mathbf{M}$ in Eq. (18.45) is the discrete representation for the operator $-\delta t^2\partial_t^2$. Recalling from Eq. (18.46) that $\det\mathbf{M} = N$, then

$$\det\left(-\partial_t^2\right) = \delta t^{-2(N-1)}N, \tag{18.76}$$

and this means, for example, that we can write the propagator (18.65) in continuous notation in terms of a ''renormalized'' determinant:

$$K_{\rm sc}(x,t;x_0,t_0) = \sqrt{\frac{m}{i2\pi\hbar(t-t_0)}}\,\sqrt{\frac{\det(-\partial_t^2)}{\det[-\partial_t^2 - V''(x_{\rm c})/m]}}\,\exp\left(\frac{i}{\hbar}S[x_{\rm c}]\right), \tag{18.77}$$

(semiclassical propagator)

where we used $t - t_0 = N\delta t$.

18.3.1.1 Gel'fand–Yaglom Method

To evaluate the functional determinant further here, we can extend the recursion method that we used in Section 18.2.4 for the free-particle determinant. In place of the matrix (18.45) for the operator $-\delta t\partial_t^2$, we can compute the determinant we need in terms of a similar $(N-1)\times(N-1)$ matrix:

$$\frac{\det\left[-\partial_t^2 - V''(x_{\rm c})/m\right]}{\det(-\partial_t^2)} = \frac{1}{N}\det\begin{bmatrix} 2-\delta t^2\omega_{N-1}^2 & -1 & 0 & \cdots & 0 & 0\\ -1 & 2-\delta t^2\omega_{N-2}^2 & -1 & \cdots & 0 & 0\\ 0 & -1 & 2-\delta t^2\omega_{N-3}^2 & \cdots & 0 & 0\\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots\\ 0 & 0 & 0 & \cdots & 2-\delta t^2\omega_2^2 & -1\\ 0 & 0 & 0 & \cdots & -1 & 2-\delta t^2\omega_1^2 \end{bmatrix}, \tag{18.78}$$

where

$$\omega_j^2 := \frac{V''(x_{{\rm c},j})}{m} = \frac{V''[x_{\rm c}(t_j)]}{m} \tag{18.79}$$

defines an effective, time-dependent, harmonic-oscillator frequency based on the curvature of the potential along the classical path. As in the free-particle case, the $n\times n$ version of the determinant satisfies the recursion relation

$$\det_n = \left[2-\delta t^2\omega_n^2\right]\det_{n-1} - \det_{n-2}, \tag{18.80}$$

with initial values

$$\begin{aligned}\det_1 &= 2-\delta t^2\omega_1^2\\ \det_2 &= (2-\delta t^2\omega_2^2)(2-\delta t^2\omega_1^2) - 1.\end{aligned} \tag{18.81}$$

To cast this recursion into continuous form, note that we can rewrite Eq. (18.80) as

$$\frac{\det_n - 2\det_{n-1} + \det_{n-2}}{\delta t^2} + \omega_n^2 \det_{n-1} = 0. \tag{18.82}$$

Defining

$$D_n := \delta t \det_n, \tag{18.83}$$

the recursion is the same,

$$\frac{D_n - 2D_{n-1} + D_{n-2}}{\delta t^2} - \omega_n^2 D_{n-1} = 0. \tag{18.84}$$

but we can recast the initial conditions as

$$\begin{aligned} D_1 &= \delta t(2 - \delta t^2 \omega_1^2) \\ \frac{D_2 - D_1}{\delta t} &= (2 - \delta t^2 \omega_2^2)(2 - \delta t^2 \omega_1^2) - 3 + \delta t^2 \omega_1^2. \end{aligned} \tag{18.85}$$

In the continuum limit $\delta t \longrightarrow 0$, $D(t)$ then satisfies the differential equation

$$\begin{aligned} \left[\partial_t^2 + \omega^2(t)\right] D(t) &= 0 \\ D(0) &= 0 \\ \dot{D}(0) &= 1. \end{aligned}$$

(continuous representation of the determinant) (18.86)

The determinant then is simply $D(t)/\delta t$, where t here is the final time of the propagator. This recasting of the functional determinant into the solution of an ordinary differential equation is specific to determinants of Schrödinger-type operators $-\partial_x^2 + V(x)$ in one dimension, and this is the **Gel'fand–Yaglom method** for computing functional determinants.[7]

18.3.1.2 Van Vleck–Morette Determinant

Now we will use the Gel'fand–Yaglom method to establish a simple form for the semiclassical functional determinant.[8] Using the classical equation of motion $m\ddot{x}_c = -V'(x_c)$ and differentiating with respect to time leads to

$$\left[\partial_t^2 + \frac{V''(x_c)}{m}\right] \dot{x}_c = 0. \tag{18.87}$$

This in turn implies that $\dot{x}_c(t)$ is a solution to the differential equation (18.86). To emphasize this, we will write the solution

$$D_1(t) = \dot{x}_c(t). \tag{18.88}$$

Since we have a second-order differential equation, there are two independent solutions D_1 and D_2, and the Wronskian determinant

$$W := \det \begin{bmatrix} D_1 & D_2 \\ \dot{D}_1 & \dot{D}_2 \end{bmatrix} = D_1 \dot{D}_2 - D_2 \dot{D}_1 \tag{18.89}$$

is constant, because the coefficient of ∂_t^2 is constant and the coefficient of ∂_t vanishes. Dividing through by D_1^2,

$$\frac{\dot{D}_2}{D_1} - \frac{D_2}{D_1^2} \dot{D}_1 = \frac{W}{D_1^2}, \tag{18.90}$$

[7] I. M. Gel'fand and A. M. Yaglom, "Integration in Functional Spaces and its Applications in Quantum Physics," *Journal Mathematical Physics* **1**, 48 (1960) (doi: 10.1063/1.1703636); Hagen Kleinert, *op. cit.*, Section 2.4; M. Chaichian and A. Demichev, *Path Integrals in Physics, Volume I: Stochastic Processes in Quantum Mechanics* (Institute of Physics, 2001), p. 168.

[8] Here we are mainly following M. Chaichian and A. Demichev, *op. cit.*, Section 2.2.3; see also Hagen Kleinert, *op. cit.*, Sections 2.4.5 and 4.3.

and noting that the left-hand side is the derivative of D_2/D_1, we can integrate both sides to obtain

$$\frac{D_2(t)}{D_1(t)} - \frac{D_2(t_0)}{D_1(t_0)} = \int_{t_0}^{t} dt' \, \frac{W}{D_1^2(t')}, \tag{18.91}$$

or to simplify,

$$D_2(t) = \frac{D_2(t_0)}{D_1(t_0)} D_1(t) + W D_1(t) \int_{t_0}^{t} \frac{dt'}{D_1^2(t')}. \tag{18.92}$$

The general solution $D(t)$ can be written as a superposition $c_1 D_1 + c_2 D_2$, or

$$D(t) = c_1 \dot{x}_{\rm c}(t) + c_2 \dot{x}_{\rm c}(t) \int_{t_0}^{t} \frac{dt'}{\dot{x}_{\rm c}^2(t')}, \tag{18.93}$$

where we have absorbed some of the t_0-dependent constants in the coefficients. The initial conditions from (18.86) give $c_1 = 0$ from $D(t_0) = 0$, and $c_2 = \dot{x}_{\rm c}(t_0)$ from $\dot{D}(t_0) = 1$. Thus, we have the solution

$$D(t) = \dot{x}_{\rm c}(t) \, \dot{x}_{\rm c}(t_0) \int_{t_0}^{t} \frac{dt'}{\dot{x}_{\rm c}^2(t')} \tag{18.94}$$

to represent the functional derivative.

We will continue by transforming this into a simpler form. First, recall that a classical particle in one dimension, by virtue of the conserved energy

$$E = \frac{1}{2} m \dot{x}_{\rm c}^2 + V(x_{\rm c}) = \frac{p_{\rm c}^2}{2m} + V(x_{\rm c}), \tag{18.95}$$

can always be solved in the sense of obtaining an integral for $t(x)$:

$$t - t_0 = \int_{x_0}^{x} dx' \frac{m}{\sqrt{2m[E - V(x')]}} = \int_{x_0}^{x} dx' \frac{m}{p(x')}. \tag{18.96}$$

Differentiating this gives

$$\frac{\partial t}{\partial E} = -\int_{x_0}^{x} dx' \frac{m^2}{\big(2m[E - V(x')]\big)^{3/2}} = -\int_{x_0}^{x} dx' \frac{m^2}{p^3(x')}. \tag{18.97}$$

Then we can use this result to simplify the integral

$$\begin{aligned} \int_{t_0}^{t} \frac{dt'}{\dot{x}_{\rm c}^2(t')} &= m^2 \int_{t_0}^{t} \frac{dt'}{p_{\rm c}^2(t')} \\ &= m^3 \int_{t_0}^{t} \frac{\dot{x}_{\rm c} \, dt'}{p_{\rm c}^3(t')} \\ &= m^3 \int_{x_0}^{x} \frac{dx_{\rm c}}{p_{\rm c}^3(x_{\rm c})} \\ &= -m \frac{\partial t}{\partial E}. \end{aligned} \tag{18.98}$$

Now to calculate $\partial E \partial t$. Starting with the phase-space action, we have

$$\begin{aligned} S[x_{\rm c}] &= \int_{t_0}^{t} dt' \, \Big[p_{\rm c}(t') \, \dot{x}_{\rm c}(t') - H(x_{\rm c}, p_{\rm c}) \Big] \\ &= \int_{x_0}^{x} dx_{\rm c} \, p_{\rm c}(x_{\rm c}) - (t - t_0) E. \end{aligned} \tag{18.99}$$

Differentiating with respect to the endpoint x,

$$\begin{aligned}\frac{\partial S[x_{\rm c}]}{\partial x} &= p_{\rm c}(x) + \int_{x_0}^{x} dx_{\rm c}\,\frac{\partial p_{\rm c}}{\partial x} - (t-t_0)\frac{\partial E}{\partial x} \\ &= p_{\rm c}(x) + \left[\int_{x_0}^{x} dx_{\rm c}\,\frac{\partial p_{\rm c}}{\partial E} - (t-t_0)\right]\frac{\partial E}{\partial x},\end{aligned} \tag{18.100}$$

where we pulled $\partial E/\partial x$ out of the integral, since we regard E as only depending on boundary conditions (e.g., on x_0 and $\dot{x}_0$, or x_0 and x). Then

$$\frac{\partial p_{\rm c}}{\partial E} = \left(\frac{\partial E}{\partial p_{\rm c}}\right)^{-1} = \left(\frac{\partial p_{\rm c}}{m}\right)^{-1} = \frac{1}{\dot{x}_{\rm c}}, \tag{18.101}$$

and so the second term in Eq. (18.100) vanishes, so that

$$\frac{\partial S[x_{\rm c}]}{\partial x} = p_{\rm c}(x). \tag{18.102}$$

Differentiating with respect to the initial coordinate,

$$\frac{\partial^2 S[x_{\rm c}]}{\partial x_0 \partial x} = \frac{\partial p_{\rm c}(x)}{\partial x_0} = \frac{\partial}{\partial x_0}\sqrt{2m[E-V(x)]} = \frac{m}{p_{\rm c}(x)}\frac{\partial E}{\partial x_0}. \tag{18.103}$$

To find $\partial E/\partial x_0$, we can differentiate Eq. (18.99) with respect to x_0 to obtain

$$\frac{\partial S[x_{\rm c}]}{\partial x_0} = -p_{\rm c}(x_0) - (t-t_0)\frac{\partial E}{\partial x_0}, \tag{18.104}$$

and then differentiate with respect to t to obtain

$$\frac{\partial E}{\partial x_0} = -\frac{\partial^2 S[x_{\rm c}]}{\partial t \partial x_0}. \tag{18.105}$$

From Eq. (18.99), we can differentiate with respect to x_0

$$\begin{aligned}\frac{\partial S[x_{\rm c}]}{\partial x_0} &= -p_{\rm c}(x_0) + \int_{x_0}^{x} dx_{\rm c}\,\frac{\partial p_{\rm c}}{\partial x_0} - (t-t_0)\frac{\partial E}{\partial x_0} \\ &= -p_{\rm c}(x_0) + \left[\int_{x_0}^{x} dx_{\rm c}\,\frac{\partial p_{\rm c}}{\partial E} - (t-t_0)\right]\frac{\partial E}{\partial x_0} \\ &= -p_{\rm c}(x_0),\end{aligned} \tag{18.106}$$

in analogy to Eq. (18.102). Thus, Eq. (18.105) becomes

$$\frac{\partial E}{\partial x_0} = \frac{\partial p_{\rm c}(x_0)}{\partial t} = \frac{\partial p_{\rm c}(x_0)}{\partial E}\frac{\partial E}{\partial t} = \frac{m}{p_{\rm c}(x_0)}\frac{\partial E}{\partial t}, \tag{18.107}$$

and putting this in Eq. (18.103) we have

$$\frac{\partial^2 S[x_{\rm c}]}{\partial x_0 \partial x} = \frac{m^2}{p_{\rm c}(x_0)p_{\rm c}(x)}\frac{\partial E}{\partial t}. \tag{18.108}$$

Solving for $\partial E/\partial t$,

$$\frac{\partial E}{\partial t} = \dot{x}_{\rm c}(x_0)\dot{x}_{\rm c}(x)\frac{\partial^2 S[x_{\rm c}]}{\partial x_0 \partial x}. \tag{18.109}$$

Putting this into Eq. (18.98),

$$\int_{t_0}^{t} \frac{dt'}{\dot{x}_c^2(t')} = -m \left(\dot{x}_c(x_0) \dot{x}_c(x) \frac{\partial^2 S[x_c]}{\partial x_0 \partial x} \right)^{-1}, \tag{18.110}$$

so the determinant solution $D(t)$ in Eq. (18.94) finally becomes

$$D(t) = -m \left(\frac{\partial^2 S[x_c]}{\partial x_0 \partial x} \right)^{-1} \tag{18.111}$$

The original determinant that we needed in Eq. (18.78) becomes

$$\frac{\det\left[-\partial_t^2 - V''(x_c)/m\right]}{\det(-\partial_t^2)} = \frac{1}{N\delta t} D(t) = \frac{m}{(t-t_0)} \left(-\frac{\partial^2 S[x_c]}{\partial x_0 \partial x} \right)^{-1} \tag{18.112}$$

At long last, the semiclassical propagator (18.77) simplifies to

$$K_{sc}(x,t;x_0,t_0) = \frac{1}{\sqrt{2\pi i\hbar}} \sqrt{-\frac{\partial^2 S[x_c]}{\partial x_0 \partial x}} \exp\left(\frac{i}{\hbar} S[x_c] \right), \tag{18.113}$$

(semiclassical propagator)

so that the determinant reduces to a derivative of the classical action at the propagator endpoints.

More generally, in multiple dimensions, this result generalizes to

$$K_{sc}(\mathbf{x},t;\mathbf{x}_0,t_0) = \frac{1}{\sqrt{2\pi i\hbar}} \det{}^{1/2}\left[-\frac{\partial^2 S[\mathbf{x}_c]}{\partial \mathbf{x}_0 \partial \mathbf{x}} \right] \exp\left(\frac{i}{\hbar} S[\mathbf{x}_c] \right). \tag{18.114}$$

(semiclassical propagator)

The determinant here,

$$\det\left[-\frac{\partial^2 S[\mathbf{x}_c]}{\partial \mathbf{x}_0 \partial \mathbf{x}} \right] = \det\left[-\frac{\partial \mathbf{p}_0}{\partial \mathbf{x}} \right] = \det\left[-\frac{\partial \mathbf{p}}{\partial \mathbf{x}_0} \right], \tag{18.115}$$

(Van Vleck–Morette determinant)

is called the **Van Vleck–Morette determinant**.[9] This determinant has an interpretation as follows. In the variational spirit of the path integral, the classical trajectory $\mathbf{x}_c$ is specified in terms of its endpoints $\mathbf{x}_0$ and $\mathbf{x}$. Alternately, it can be specified in terms of the initial conditions $(\mathbf{x}_0, \mathbf{p}_0)$ or the end conditions $(\mathbf{x}, \mathbf{p})$. The Van Vleck–Morette determinant is the determinant of the coordinate transformation between the variational and initial/end specifications. Since the phase-space area of a small bundle of paths around the classical path is invariant along the path (classically, at least), roughly speaking the determinant maps this area into position space, to represent the effect of local convergence or divergence of classical trajectories on the amplitude. (In optics terminology, this is akin to using Gaussian beams instead of rays for tracing optical systems, and the spreading or converging of the beam waist influences the intensity at the beam center.)

We are also glossing over what happens if the functional determinant in Eq. (18.65) vanishes, such that the Van Vleck–Morette determinant diverges. This corresponds to the formation of **caustics** in the classical trajectories, and requires more careful treatment.[10]

18.3.2 Example: Semiclassical Propagator for the Harmonic Oscillator

As an example of the semiclassical propagator, we will evaluate this explicitly for a harmonic oscillator of frequency ω. Note that for this case, the semiclassical propagator (18.65) is *exact*, because it was based on

[9] The determinant was introduced in the semiclassical context by J. H. Van Vleck, *Proceedings of the National Academy of Sciences* **14**, 178 (1928) (doi: 10.1073/pnas.14.2.178); and introduced in the context of path integration by C. DeWitt-Morette, *Physical Review* **81**, 848 (1951) (doi: 10.1103/PhysRev.81.848). See also, for example, Bryce DeWitt, *The Global Approach to Quantum Field Theory*, vol. 1 (Oxford, 2003), Chapter 14.

[10] M. V. Berry and K. E. Mount, "Semiclassical approximations in wave mechanics," *Reports on Progress in Physics* **35**, 315 (1972) (doi: 10.1088/0034-4885/35/1/306).

a truncation at the second derivative, and higher derivatives will vanish anyway for the harmonic oscillator, which has a quadratic Lagrangian.

18.3.2.1 Classical Action

Thus, starting with the classical action,

$$S[x_{\mathrm{c}}] = \int_{t_0}^{t} dt' \left(\frac{m\dot{x}^2}{2} - \frac{m\omega^2 x^2}{2} \right), \tag{18.116}$$

we will integrate by parts on the first term to obtain

$$S[x_{\mathrm{c}}] = \frac{mx\dot{x}}{2}\bigg|_{t_0}^{t} - \frac{m}{2}\int_{t_0}^{t} dt'\, x\big(\ddot{x} + \omega^2 x\big). \tag{18.117}$$

The second factor in the integrand vanishes under the classical equations of motion, so we only have the boundary term

$$S[x_{\mathrm{c}}] = \frac{m}{2} x\dot{x}\big|_{t_0}^{t}. \tag{18.118}$$

We will then use the classical trajectory

$$x_{\mathrm{c}}(t) = x_0 \cos\omega(t - t_0) + \frac{\dot{x}_0}{\omega}\sin\omega(t - t_0) \tag{18.119}$$

to evaluate the action integral, with the result

$$\begin{aligned} S[x_{\mathrm{c}}] &= \frac{m}{2}\left[x_0\dot{x}_0\Big(\cos^2\omega(t-t_0) - \sin^2\omega(t-t_0)\Big) + \left(\frac{\dot{x}_0^2}{\omega} - \omega x_0^2\right)\cos\omega(t-t_0)\sin\omega(t-t_0)\right] - \frac{m}{2}x_0\dot{x}_0 \\ &= \frac{m}{2}\left[\left(\frac{\dot{x}_0^2}{\omega} - \omega x_0^2\right)\cos\omega(t-t_0)\sin\omega(t-t_0) - 2x_0\dot{x}_0\sin^2\omega(t-t_0)\right]. \end{aligned} \tag{18.120}$$

Now rearranging the general solution (18.116) to obtain $\dot{x}_0$ at the final spacetime coordinates (x, t),

$$\dot{x}_0 = \frac{\omega(x - x_0\cos\omega t)}{\sin\omega t} \tag{18.121}$$

we can eliminate the initial derivative. After a bit of algebra we find

$$S[x_{\mathrm{c}}] = \frac{m\omega}{2\sin\omega(t-t_0)}\Big[\big(x_0^2 + x^2\big)\cos\omega(t-t_0) - 2x_0x\Big]$$

(harmonic-oscillator action) (18.122)

for the classical action in terms of only the time interval and the end coordinates $x_0 = x_{\mathrm{c}}(t_0)$ and $x = x_{\mathrm{c}}(t)$.

18.3.2.2 Determinant

Then to obtain the Van Vleck–Morette determinant for the harmonic oscillator, we simply differentiate the action:

$$\frac{\partial^2 S[x_{\mathrm{c}}]}{\partial x_0 \partial x} = -\frac{m\omega}{\sin\omega(t-t_0)}.$$

(Van Vleck–Morette determinant, harmonic-oscillator) (18.123)

Then assembling the parts of the semiclassical propagator (18.113), we have

$$K(x,t;x_0,t_0) = \sqrt{\frac{m\omega}{2\pi i\hbar\sin\omega(t-t_0)}}\ \exp\left(\frac{im\omega}{2\hbar\sin\omega(t-t_0)}\Big[\big(x_0^2+x^2\big)\cos\omega(t-t_0) - 2x_0x\Big]\right).$$

(propagator, harmonic oscillator) (18.124)

Again, though we derived this expression via the semiclassical propagator, this is identical to the fully quantum propagator. Any higher-order corrections to the path integral go as higher powers of $\hbar^{-1}$, and as functional derivatives of the action beyond second order. It is also easy to check that this expression reduces correctly to the free-particle propagator (2.11) in the limit $\omega \longrightarrow 0$. In deriving that result, we also used the classical (straight-line) path to simplify the calculation.

18.4 Optical Path Integral

An interesting variation on the quantum-mechanical path integral is to handling *optical* waves. The electromagnetic wave equation in an inhomogeneous dielectric medium is

$$\left[\nabla^2 - \frac{n^2(\mathbf{r})}{c^2}\partial_t^2\right]\mathscr{E}(\mathbf{r},t) = 0, \tag{18.125}$$

where $n(\mathbf{r})$ is the medium's refractive-index profile, and to make the problem tractable we will treat the electric field in the scalar-field approximation. The goal here is to show how to adapt the path-integral formulation to derive a propagator for ''scalar optics.''[11]

A major obstacle to applying the path-integral method here is that the propagator represents an evolution operator $e^{-iHt/\hbar}$. This is specific to the Schrödinger equation, which is first order in time. However, the wave equation (18.125) is *second* order in time, so the path-integral method doesn't obviously carry over. Fortunately, there is a trick to handle this, which dates back to Feynman.[12] We will handle the derivation by leveraging some of the resolvent-operator formalism that we've developed, but first it's useful to look at how the trick works schematically.

18.4.1 Monochromatic Field

Before we start, let's go ahead and eliminate the time dependence by considering a monochromatic field of frequency ω,

$$\mathscr{E}(\mathbf{r},t) = \mathscr{E}(\mathbf{r})\, e^{-i\omega t}, \tag{18.126}$$

in which case the wave equation becomes

$$\left[\nabla^2 + n^2(\mathbf{r})k^2\right]\mathscr{E}(\mathbf{r}) = 0, \tag{18.127}$$

where $k = \omega/c$. Now this will look like a time-independent Schrödinger equation if we rearrange it to read

$$\Big[-\nabla^2 + V(\mathbf{r})\Big]\mathscr{E} = k^2\mathscr{E}, \tag{18.128}$$

where the effective potential is

$$V(\mathbf{r}) := -\big[n^2(\mathbf{r}) - 1\big]k^2. \tag{18.129}$$

Here, $\hbar = 1$ and the ''energy'' is k^2.

18.4.2 An Extra Dimension

Now for the trick. Normally, we could Fourier-transform a time-independent Schrödinger equation to obtain a time-dependent form, but the energy in Eq. (18.128) is fixed at k^2. So let's replace it for the moment by a fictitious energy parameter E, so that

$$\Big[-\nabla^2 + V(\mathbf{r})\Big]\mathscr{E} = E\mathscr{E}, \tag{18.130}$$

[11] L. S. Schulman, *Techniques and Applications of Path Integration* (Wiley, 1981), Chapter 20.

[12] The wave equation here has the same form as that of the relativistic (Klein–Gordon) particle, where the effective potential represents a space-dependent mass. The trick to put the relativistic equation in first-order form for path-integration purposes is due to R. P. Feynman, ''Mathematical Formulation of the Quantum Theory of Electromagnetic Interaction,'' *Physical Review* **80**, 440 (1950) (doi: 10.1103/PhysRev.80.440).

where we recover the original equation for $E = k^2$.

Then defining the time-dependent wave function by introducing a fictitious "time" T,

$$\varphi(\mathbf{r}, T) := \mathscr{E}(\mathbf{r})\, e^{-iET}, \tag{18.131}$$

the wave equation is equivalent to

$$i\partial_T \varphi = \left[-\nabla^2 + V(\mathbf{r})\right]\varphi. \tag{18.132}$$

This has the form of a Schrödinger equation with time parameter T and a potential determined by the refractive index. (The T parameter is sometimes called a "proper time" because this trick also works if we don't eliminate t in favor of ω, in which case T parameterizes the "world line" in the $\mathbf{r}$–t space-time).

A solution to Eq. (18.132) will in general correspond to a superposition of different values of E, which we can write schematically as

$$\varphi(\mathbf{r}, T) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\, \tilde{\varphi}(\mathbf{r}, E)\, e^{-iET}, \tag{18.133}$$

where $\tilde{\varphi}(\mathbf{r}, E)$ is the amplitude at (fictitious) energy E. However, we only want the $E = k^2$ component of this solution, which will yield the desired solution $\mathscr{E}(\mathbf{r})$ of the optical wave equation (18.127). We can do this using a simple Fourier projection of this component:

$$\mathscr{E}(\mathbf{r}) = \int_{-\infty}^{\infty} dT\, \varphi(\mathbf{r}, T)\, e^{ik^2 T}. \tag{18.134}$$

We can verify that this is indeed the solution to the wave equation (18.127) by writing

$$\mathscr{E}(\mathbf{r}) = \int_{-\infty}^{\infty} dT\, \frac{1}{2\pi}\int_{-\infty}^{\infty} dE\, \tilde{\varphi}(\mathbf{r}, E)\, e^{-iET}\, e^{ik^2 T} = \int_{-\infty}^{\infty} dE\, \tilde{\varphi}(\mathbf{r}, E)\, \delta(E - k^2) = \tilde{\varphi}(\mathbf{r}, k^2), \tag{18.135}$$

after using the usual integral representation

$$\delta(E) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dT\, e^{-iET} \tag{18.136}$$

of the delta function. This is the correct component of the extended solution that corresponds to the original wave equation.

Recalling that the Feynman propagator (18.24) is

$$K(x, t; x_0, t_0) = \int Dx\, \exp\left[\frac{i}{\hbar}\int_{t_0}^{t} dt' \left(\frac{1}{2}m\dot{x}^2 - V(x)\right)\right], \tag{18.137}$$

we can adapt this result to the extended optical wave equation by setting $m = 1/2$, $\hbar = 1$, $t = T$, and $t_0 = 0$ to obtain

$$K(\mathbf{x}, T; \mathbf{x}_0, 0) = \int D\mathbf{x}\, \exp\left[i\int_0^T d\tau \left(\frac{\dot{x}^2}{4} - V(\mathbf{x})\right)\right], \tag{18.138}$$

after changing notation to multiple spatial dimensions.

18.4.3 Optical Green Function

Finally, we just need to perform the integration in Eq. (18.134) to project out the physical part of the propagator. But let's do this carefully to make sure we know what we're calculating. Remember that the retarded Green operator is identical to the evolution operator for $\tau > 0$ [Eq. (13.38)]

$$G^+(\tau) = U(\tau, 0)\, \Theta(\tau), \tag{18.139}$$

and so in the position representation, this is just the (retarded) propagator (i.e., the propagator for $\tau > 0$):

$$G^+(\mathbf{r}, \mathbf{r}'; \tau) := \langle \mathbf{r}|G^+(\tau)|\mathbf{r}'\rangle = K(\mathbf{r}, \tau; \mathbf{r}', 0)\, \Theta(\tau) =: K^+(\mathbf{r}, \tau; \mathbf{r}', 0). \tag{18.140}$$

Then the energy-space Green function is given by the Fourier-transform relation [Eq. (13.39)]

$$G^+(\mathbf{r},\mathbf{r}';E) = \frac{1}{i\hbar}\int_0^\infty d\tau\, e^{i(E+i0^+)\tau/\hbar}\, G^+(\mathbf{r},\mathbf{r}';\tau). \tag{18.141}$$

Note that the time integration here does the same thing as the integral projection in Eq. (18.134). Adapting the transformation (18.141) to the propagator (18.138) by setting $\hbar = 1$, we have

$$G^+(\mathbf{r},\mathbf{r}';E) = -i\int_0^\infty d\tau\, e^{i(E+i0^+)\tau/\hbar}\, G^+(\mathbf{r},\mathbf{r}';\tau). \tag{18.142}$$

Putting in the propagator gives

$$G^+(\mathbf{r},\mathbf{r}';E) = -i\int_0^\infty dT\, e^{i(E+i0^+)T}\int D\mathbf{x}\,\exp\left[i\int_0^T d\tau\left(\frac{\dot{x}^2}{4}-V(\mathbf{x})\right)\right]. \tag{18.143}$$

Changing variables from E to $k=\sqrt{E}$ gives

$$G^+(\mathbf{r},\mathbf{r}';k) = -i\int_0^\infty dT\, e^{ik^2T}\int D\mathbf{x}\,\exp\left[i\int_0^T d\tau\left(\frac{\dot{x}^2}{4}-V(\mathbf{x})\right)\right], \tag{18.144}$$

and now the convergence helper $i0^+$ is understood to be present when necessary.

Remember that this Green function has the interpretation as the solution to the (monochromatic) optical wave equation at position $\mathbf{r}$, given a "point source" field $-i\delta(\mathbf{r}-\mathbf{r}')$, with an implied time-dependent factor $e^{-i\omega t}$. [The $-i$ comes from: the source is normally $i\hbar\delta(\tau)\,\delta^3(\mathbf{r}-\mathbf{r}')$ for the Schrödinger equation (in the position representation), and also here with $\hbar=1$ and a minus sign in going back from the Schödingerized wave equation (18.128) to the optical wave equation (18.127).] Since there is a common factor of $-i$ on both the Green function and the source, it makes sense to just drop them, and define the Green function to be

$$G^+(\mathbf{r},\mathbf{r}';k) = \int_0^\infty dT\, e^{ik^2T}\int D\mathbf{x}\,\exp\left[i\int_0^T d\tau\left(\frac{\dot{x}^2}{4}-V(\mathbf{x})\right)\right], \tag{18.145}$$

(optical Green function)

corresponding to a source field $\delta^3(\mathbf{r}-\mathbf{r}')$.

This could, for example, be integrated over the field profile at an aperture to yield the diffracted field solution $\mathscr{E}(\mathbf{r},t)$ away from the aperture. Explicitly, this is

$$\mathscr{E}(\mathbf{r},t) = \int_A d\mathbf{r}'\, G^+(\mathbf{r},\mathbf{r}';k)\,\mathscr{E}_A(\mathbf{r}')\,e^{-i\omega t} \tag{18.146}$$

(Green-function solution for wave propagation)

where $\mathscr{E}_A(\mathbf{r}')$ is the field amplitude of the aperture.

18.4.4 Geometric-Optics Limit

Now let's end with an amusing connection between wave optics and geometric optics. The action functional in the path integral (18.145) is clearly

$$S[\mathbf{x}] = \int_0^T d\tau\left(\frac{\dot{x}^2}{4}-V(\mathbf{x})\right), \tag{18.147}$$

but because of the extra T integration, we should really consider the entire argument of the exponential

$$S_T[\mathbf{x},T] = k^2T + \int_0^T d\tau\left(\frac{\dot{x}^2}{4}-V(\mathbf{x})\right) \tag{18.148}$$

as an extended action. In the classical (large k^2) limit, the dominant contribution will come from classical paths, ones where the extended action $S_T[\mathbf{x}, T]$ is stationary, with respect to variations in both $\mathbf{x}$ and T. The stationary condition when we vary T is a little tricky,

$$\frac{\partial S_T}{\partial T} = k^2 + \frac{\partial S}{\partial T} = k^2 - H = 0, \tag{18.149}$$

where $\partial_t S = -H$ is the Hamilton–Jacobi equation (0.88); note that naïve time-differentiation of the integral in $S[\mathbf{x}]$ would appear to give the Lagrangian instead of the Hamiltonian, but the (classical) path also changes as T varies. The variation with respect to the path is straightforwardly an application of the Euler–Lagrange equation,

$$\frac{\delta S_T}{\delta \mathbf{x}} = -\nabla V(\mathbf{x}) - \frac{\ddot{\mathbf{x}}}{2} = 0, \tag{18.150}$$

which gives the trajectories of the paths more directly. However it is important to implement constraint equation (18.149), which we can rewrite as

$$H = \frac{\dot{x}^2(T)}{4} + V(\mathbf{x}) = k^2. \tag{18.151}$$

Because the Hamiltonian is constrained to a constant value, Maupertuis' action principle (0.31) applies, so that we can alternately require stationarity of the reduced action

$$S_{\text{reduced}}[\mathbf{p}] = \int_{t_1}^{t_2} \dot{\mathbf{q}} \cdot \mathbf{p}\, dt. \tag{18.152}$$

In the notation of the wave-equation path integral, $\mathbf{q} = \mathbf{x}$ and $\mathbf{p} = \dot{\mathbf{x}}/2$, so the reduced action is

$$S_{\text{reduced}}[\mathbf{x}] = \frac{1}{2}\int_0^T \dot{x}^2\, d\tau. \tag{18.153}$$

To put this in a more illuminating form, note that the arc length functional is independent of the unphysical proper time T,

$$s[\mathbf{x}] = \int_0^T \sqrt{\frac{dx_\alpha}{d\tau}\frac{dx_\alpha}{d\tau}}\, d\tau = \int_0^T \sqrt{\dot{x}^2}\, d\tau \tag{18.154}$$

and so we can change variables from T to s to obtain a physical parameterization of the action:

$$S_{\text{reduced}}[\mathbf{x}] = \frac{1}{2}\int_0^s \sqrt{\dot{x}^2}\, ds'. \tag{18.155}$$

Next, using the constraint (18.151),

$$S_{\text{reduced}}[\mathbf{x}] = \int_0^s \sqrt{k^2 - V(\mathbf{x})}\, ds'. \tag{18.156}$$

Using the definition (18.129) of the effective potential, the effective action becomes

$$S_{\text{reduced}}[\mathbf{x}] = k\int_0^s n(\mathbf{x})\, ds'. \tag{18.157}$$

(path-integral action for optical wave equation)

Stationarity of this reduced action is equivalent to Fermat's principle of geometric optics, which says that a light ray makes the optical-path-length functional

$$\ell[\mathbf{r}] = \int_0^d n(\mathbf{r})\, ds \tag{18.158}$$

(Fermat's principle)

stationary, $\delta\ell = 0$. Thus, the path integral for the wave equation directly produces geometric optics.

18.5 Exercises

Problem 18.1

We derived the Feynman propagator (18.24),

$$K(x,t;x_0,t_0) = \int_{x_0}^{x} Dx\, \exp\left[\frac{i}{\hbar}\int_{t_0}^{t} dt' \left(\frac{1}{2}m\dot{x}^2 - V(x)\right)\right], \tag{18.159}$$

from the evolution operator and thus from the Schrödinger equation. To complete the proof that the path-integral approach is equivalent to the Schrödinger equation, we should really derive the Schrödinger equation from the propagator (18.159).

To do this, we can first start by propagating a wave function over a small time interval δt:

$$\psi(x,\delta t) = \int dx_0\, K(x,\delta t;x_0,0)\, \psi(x_0,0). \tag{18.160}$$

In terms of the propagator, this becomes

$$\psi(x,\delta t) = \int dx_0\, \psi(x_0,0) \int_{x_0}^{x} Dx\, \exp\left[\frac{i}{\hbar}\,\delta t \left(\frac{1}{2}m\dot{x}^2 - V(x)\right)\right], \tag{18.161}$$

after approximating the time integral by a constant integrand. Since the time interval is short, we can take the Feynman Dx differential (18.23) to correspond to only $N = 1$ time slice,

$$\int Dx = \sqrt{\frac{m}{i2\pi\hbar\,\delta t}}, \tag{18.162}$$

so that the path integration is trivial (in the sense of requiring only a single ‘‘normal’’ integral):

$$\psi(x,\delta t) = \sqrt{\frac{m}{i2\pi\hbar\delta t}} \int dx_0\, \psi(x_0,0)\, \exp\!\left(\frac{im\,\delta x^2}{2\hbar\,\delta t}\right)\left(1 - \frac{i\,\delta t}{\hbar}\,V\right). \tag{18.163}$$

Here, we have also written $\delta x = x - x_0$ and $\dot{x} = \delta x/\delta t$. We have also expanded the exponential, noting that $\delta x^2/\delta t$ is of order unity, so the expansion of that term is not justified. Note that $V(x)$ and $V(x_0)$ differ only by a negligible amount of order δt, since we are working overall only to order δt; to emphasize this negligible difference, we are omitting the functional dependence of V for the moment. Because of this, this proof will also carry through for time-dependent potentials $V(x,t)$, generalizing the path integral a bit.

Now complete the derivation by expanding $\psi(x_0,0)$ around $x_0 = x$ to second order in δx, and carry out the resulting (Gaussian) integrals. Keeping only terms up to order δt in the resuling equation should yield the Schrödinger equation.

Chapter 19

Constrained Quantization

Back when discussing the axioms of quantum mechanics in Chapter 1, we went over the Dirac's quantization prescription, which is to promote pairs of canonically conjugate variables to operators in the Hamiltonian. The operator character of the conjugate pairs is defined by promoting their Poisson bracket to a commutator, with a factor of $i\hbar$. However, this assumes that there are no hitches along the way in defining the classical Hamiltonian, but this is not always the case. If there are constraints to deal with, these must be handled with care. The theory of handling constraints in classical mechanics, especially within the Hamiltonian formalism, forms the groundwork of the more careful quantization procedure that we will work through here. Hence, while we will summarize the main points of handling constraints in classical mechanics, the material here will rely heavily on the material in Chapter 0, in particular starting with Section 0.5 and continuing to the end of the chapter.

19.1 Overview of Constraints in Classical Mechanics and Quantization

Dirac quantization recipe mainly works with constraints in classical mechanics, but gives a prescription for quantizing constrained classical systems. The constraints have the form $\phi(\mathbf{q}, \mathbf{p}) = 0$, and may be imposed on the system, or often they crop up when transforming the Lagrangian to a Hamiltonian (for example, if the Lagrangian is independent of $\dot{q}$, then the conjugate momentum to q vanishes, $p = 0$, which is a constraint). There are two important classifications of constraints:

- A **second-class constraint** arises because the constraint function ϕ has a nonvanishing Poisson bracket with another constraint function or the Hamiltonian. These constraints modify the dynamical evolution, which differs from the unconstrained version. (An example is a particle in two dimensions, constrained to a circle.) These constraints occur in pairs, indicating degrees of freedom that decouple from the constraint manifold.
- A **first-class constraint** has a vanishing Poisson bracket with the Hamiltonian and every other constraint function. These indicate **gauge freedoms**, or a redundancy in the sense that different points in phase space correspond to the same physical state.

In either case, any constraint can be added to the Hamiltonian by tacking on a term of the form $\lambda\phi$, where λ is a Lagrange multiplier. This doesn't change the Hamiltonian on the constraint manifold, where $\phi = 0$. In the case of second-class constraints, the Lagrange multiplier can be fixed entirely in terms of other phase-space coordinates. These constraints are eliminated by replacing the Poisson bracket (which determines the unconstrained evolution) by the **Dirac bracket**, which is essentially a modified Poisson bracket that respects the second-class constraints. The Lagrange multipliers for first-class constraints parameterize the gauge freedom, or redundance in the phase-space coordinates.

In the simpler case of no constraints, quantization occurs by promoting canonical pairs to operators:

the operator character of the canonical variables is defined by changing the Poisson bracket to a commutator (tacking on a factor of $1/i\hbar$ to obtain the commutator).

19.2 Relativistic Particle

As a first prototype of quantizing a constrained system, we will return to the classical relativistic particle of Section 0.5.3. Since we have handled the constraints there, we have done most of the hard work, and we will make heavy use of the results from there.

19.2.1 Quantization of the Extended Hamiltonian

First, let's consider the extended Hamiltonian (0.240) for the relativistic particle,

$$\tilde{H} = e(\tau)\left(\frac{p^2}{2m} - \frac{p_t^2}{2mc^2} + \frac{1}{2}mc^2\right), \tag{19.1}$$

where recall that the einbein (Lagrange multiplier) $e(\tau)$ represents the gauge freedom of reparameterization invariance. The entire form of this Hamiltonian is the mass-shell constraint function with the Lagrange multiplier; it thus came from the original Hamiltonian $H = 0$, which is still satisfied by the extended Hamiltonian $\tilde{H} \approx 0$ on the constraint surface.

Since the constraint here is first class, the Poisson and Dirac brackets are identical. The nonvanishing Poisson brackets have the standard form

$$[r^\alpha, p_\beta]_{\text{P}} = \delta^\alpha{}_\beta, \qquad [t, p_t]_{\text{P}} = 1, \tag{19.2}$$

and so the canonical variables get promoted to operators by changing the Poisson brackets to commutators in the usual way:

$$[r_\alpha, p_\beta] = i\hbar\delta_{\alpha\beta}, \qquad [t, p_t] = i\hbar. \tag{19.3}$$

These quantum brackets then imply standard forms for the momentum operators in the ''position'' representation,

$$\mathbf{p} = \frac{\hbar}{i}\nabla, \qquad p_t = \frac{\hbar}{i}\partial_t, \tag{19.4}$$

after making a suitable gauge choice of the wave-function phase (see Section 1.7.4).

In the position representation, the Schrödinger equation becomes

$$i\hbar\partial_\tau\psi(\mathbf{r}, t; \tau) = \tilde{H}\psi = e(\tau)\left(\frac{\hbar^2}{2mc^2}\partial_t^2 - \frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}mc^2\right)\psi \tag{19.5}$$

in terms of the extended Hamiltonian (19.1), and in terms of the proper-time parameter τ. Because of the constraint $\tilde{H} \approx 0$, it is conventional to apply the constraint explicitly, in which case the proper time and gauge freedom drop out, leaving the wave equation

$$\left(\frac{\hbar^2}{2mc^2}\partial_t^2 - \frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}mc^2\right)\psi(\mathbf{r}, t) = 0. \tag{19.6}$$

In more conventional form, this wave equation is expressed

$$\left(\frac{1}{c^2}\partial_t^2 - \nabla^2 + \frac{m^2c^2}{\hbar^2}\right)\psi(\mathbf{r}, t) = 0, \tag{19.7}$$

(Klein–Gordon equation)

which is the **Klein–Gordon equation**.[1] The combination of constants $\hbar/mc$ is an important constant with units of length. In terms of the electron mass m_e, this is the **reduced Compton wavelength** $\lambda\!\!\!^{-}_C = \hbar/m_e c \approx 3.86 \times 10^{-13}$ m (the "normal" Compton wavelength is $\lambda_C = h/m_e c$).

19.2.2 Quantization of the Gauge-Fixed Hamiltonian

Another version of the relativistic-particle Hamiltonian has the gauge freedom fixed as $\tau = t$ (Section 0.5.3.2). The mass-shell constraint and the time constraint are both second class in this version of the problem. The analysis of Dirac brackets shows that the canonical pair t and p_t loses its canonical character. The interpretation of the vanishing Hamiltonian is that it can be transferred to a smaller phase space $(\mathbf{r}, \mathbf{p})$, with reduced Hamiltonian (0.235) given by p_t:

$$H(\mathbf{r}, \mathbf{p}; t) = \sqrt{p^2c^2 + m^2c^4}. \tag{19.8}$$

That is, in this version of the problem the proper time is already eliminated at the classical stage. In this case the Schrödinger equation becomes

$$i\hbar\partial_t \psi(\mathbf{r}, t) = H\psi = \sqrt{-\hbar^2c^2\nabla^2 + m^2c^4}\ \psi \tag{19.9}$$

in the position representation, making the standard identification for the momentum operator. This version of the wave equation doesn't have a lot of fans, because the square root involves derivative operators at all orders, and it is thus a nonlocal operator (Problem 19.2). However, this equation amounts to the operator identification

$$i\hbar\partial_t = H = \sqrt{-\hbar^2c^2\nabla^2 + m^2c^4}, \tag{19.10}$$

which we can iterate to obtain the alternate identification

$$-\hbar^2\partial_t^2 = H^2 = -\hbar^2c^2\nabla^2 + m^2c^4. \tag{19.11}$$

Applying this operator identity to a wave function leads again to the Klein–Gordon equation (19.7), via a slightly different route.

19.2.3 Discussion

The Klein–Gordon equation (19.7), being the quantization of a Lorentz-invariant action, is a manifestly Lorentz-invariant wave equation. However, it was rejected for quite some time as a reasonable wave equation for a relativistic quantum particle. To see the problem, in working with the squared Hamiltonian as in Eq. (19.11), the wave equation admits eigenvalues of H^2 rather than just H. This means that any positive energy is accompanied by its negative counterpart. That is, free-particle solutions of the form

$$\psi(\mathbf{r}, t) = \psi_0\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}. \tag{19.12}$$

This is an eigenstate of the Hamiltonian (19.10), with eigenvalue

$$E = \sqrt{\hbar^2c^2k^2 + m^2c^4} = \hbar\omega, \tag{19.13}$$

but the Klein–Gordon equation admits eigenvectors of H^2, so the permissible free-particle energies are

$$E_\pm = \pm\sqrt{\hbar^2c^2k^2 + m^2c^4} = \pm\hbar\omega, \tag{19.14}$$

[1] After Oskar Klein, "Quantentheorie und fünfdimensionale Relativitätstheorie, *Zeitschrift für Physik* **37**, 895 (1926) (doi: 10.1007/BF01397481); W. Gordon, "Der Comptoneffekt nach der Schrödingerschen Theorie," *Zeitschrift für Physik* **40** 117 (1926) (doi: 10.1007/BF01390840). This was derived at around the same time by V. Fock, "Zur Schrödingerschen Wellenmechanik," *Zeitschrift für Physik* **38**, 242 (1926) (doi: 10.1007/BF01399113); V. Fock, "Über die invariante Form der Wellen- und der Bewegungsgleichungen für einen geladenen Massenpunkt," *Zeitschrift für Physik* **39**, 226 (1926) (doi: 10.1007/BF01321989).

both positive and negative.

The existence of negative energies is not directly a problem, but it leads to a complication. Suppose that we define a density by

$$\rho := \frac{i\hbar}{2mc^2}\left(\psi^*\partial_t\psi - \psi\partial_t\psi^*\right), \tag{19.15}$$

and a current by

$$\mathbf{j} := \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right). \tag{19.16}$$

Then it follows from the Klein–Gordon equation that these quantities obey the usual continuity relation (Problem 19.1):

$$\partial_t\rho = -\nabla\cdot\mathbf{j}. \tag{19.17}$$

For the eigenstate (19.12), we can make the identification $i\hbar\partial_t \longrightarrow E_\pm$, in which case we obtain the density

$$\rho = \frac{\hbar}{mc^2}\,\mathrm{Im}[\psi\partial_t\psi^*] = \frac{E_\pm}{mc^2}|\psi|^2. \tag{19.18}$$

This means that the density (19.15) can't be interpreted as a probability density, because it may be negative. Furthermore it isn't sufficient to postulate that only positive-energy states are physical: if interactions are allowed with other particles, positive-energy states can scatter into negative-energy states, and in this sense the density (19.15) isn't even conserved if interactions are allowed. The situation is analogous to what happens in the optical wave equation. In a homogeneous dielectric medium, an light wave can propagate as a plane wave, but in the presence of refractive-index gradients or interfaces, optical waves can reflect, reversing direction, as a consequence of the second time derivative in the wave equation.

The modern view of the negative-energy states is due to Feynman.[2] In this interpretation, the negative-energy state is a solution traveling backwards in time; this corresponds to an antiparticle. Thus interactions can scatter particle states into antiparticle states, or more precisely, particle states can appear to merge (in a linear progression of time) with an antiparticle state, giving rise to a pair-annihilation process. This interpretation is handled more naturally in a second-quantized form of the Klein–Gordon equation (i.e., treat the Klein–Gordon equation as a classical wave equation, and quantize it). The Klein–Gordon equation can be transformed to more explicitly decouple the particle and antiparticle solutions into components that obey an equation that is first-order in time. This form is called the **Feshbach–Villars representation**.[3]

19.2.4 Dirac Equation

To continue the story of relativistic wave equations just a bit further, let's return to the precursor (19.9) to the Klein–Gordon equation in representation-free notation, with $\mathbf{p} = -i\hbar\nabla$ as usual:

$$i\hbar\partial_t|\psi\rangle = \sqrt{p^2c^2 + m^2c^4}\,|\psi\rangle. \tag{19.19}$$

Again, the differential operator here involves derivatives at all orders and turns out to be a nonlocal operator, and thus seemingly problematic as part of a wave equation. However, a major advance in physics came from Dirac's inspired effort[4] to make sense of the square-root operator. The idea is to write

$$p^2c^2 + m^2c^4 = \left(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\right)^2, \tag{19.20}$$

where the expression on the right-hand side works out to be equivalent to the one on the left provided we interpret α_j and β as matrices, specifically 4×4 matrices. In terms of the Pauli matrices (Section 9.2) σ_j and the 2×2 identity matrix $\mathcal{I}_2$, these matrices may be written

$$\alpha_j = \begin{bmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{bmatrix}, \qquad \beta = \begin{bmatrix} \mathcal{I}_2 & 0 \\ 0 & -\mathcal{I}_2 \end{bmatrix}, \tag{19.21}$$

[2] R. P. Feynman, "The Theory of Positrons," *Physical Review* **76**, 749 (1949) (doi: 10.1103/PhysRev.76.749).

[3] Herman Feshbach and Felix Villars, "Elementary Relativistic Wave Mechanics of Spin 0 and Spin 1/2 Particles," *Reviews of Modern Physics* **30**, 24 (1958) (doi: 10.1103/RevModPhys.30.24); A. S. Davydov, *Quantum Mechanics*, 2nd ed, translated by D. ter Haar (Pergamon, 1976), Chapter 8, Section 56, p. 219 (ISBN: 0080204384).

[4] P. A. M. Dirac, "The Quantum Theory of the Electron," *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **117**, 610 (1928) (doi: 10.1098/rspa.1928.0023) (JSTOR: 94981).

where the zero entries here are 2×2 null matrices. That Eq. (19.20) works out follows from the fact that the squares of all of these matrices gives the identity,

$$\alpha_j^2 = \begin{bmatrix} \sigma_j^2 & 0 \\ 0 & \sigma_j^2 \end{bmatrix} = \begin{bmatrix} \mathcal{I}_2 & 0 \\ 0 & \mathcal{I}_2 \end{bmatrix}, \qquad \beta^2 = \begin{bmatrix} \mathcal{I}_2 & 0 \\ 0 & \mathcal{I}_2 \end{bmatrix}, \tag{19.22}$$

while any anticommutator of two different matrices vanishes,

$$[\alpha_j, \alpha_k]_+ = \begin{bmatrix} [\sigma_j, \sigma_k]_+ & 0 \\ 0 & [\sigma_j, \sigma_k]_+ \end{bmatrix} = 0 \qquad (j \neq k), \qquad [\alpha_j, \beta]_+ = \begin{bmatrix} 0 & -[\sigma_j, \mathcal{I}_2] \\ [\sigma_j, \mathcal{I}_2] & 0 \end{bmatrix} = 0, \tag{19.23}$$

owing to the anticommutator $[\sigma_\alpha, \sigma_\beta]_+ = 2\delta_{\alpha\beta}\mathcal{I}_2$. Thus, all cross-terms vanish, and the remaining terms give the left-hand side of Eq. (19.20), with an implied 4×4 identity matrix. Note that the Dirac matrices are often written in a "relativistic notation" as the **gamma matrices**: $\gamma^0 \equiv \beta$, $\gamma^1 \equiv \alpha_1$, $\gamma^2 \equiv \alpha_2$, $\gamma^3 \equiv \alpha_3$.

Now putting together Eqs. (19.19) and (19.20), we find

$$i\hbar\partial_t|\psi\rangle = \big(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\big)|\psi\rangle, \tag{19.24}$$

(Dirac equation)

which acts as an alternative to the Klein–Gordon equation (19.7). But what remains is to interpret the matrix structure of this wave equation, which was not present in the Klein–Gordon equation.

19.2.4.1 Free-Particle Eigenstates

Since the Dirac equation is represented in terms of 4×4 matrices, the solutions must be interpreted as appropriate four-vectors; for example, in the position representation, we have

$$\langle x|\psi\rangle = \begin{bmatrix} \psi_1(x) \\ \psi_2(x) \\ \psi_3(x) \\ \psi_4(x) \end{bmatrix}. \tag{19.25}$$

It is somewhat more convenient to group the components as

$$\langle x|\psi\rangle = \begin{bmatrix} \chi(x) \\ \phi(x) \end{bmatrix}, \tag{19.26}$$

where χ and ϕ are two-vectors (i.e., spinors, as suggested by the presence of Pauli matrices). Now in considering free-particle eigenstates, we should work in the momentum representation, and so we will assume a solution of the form

$$\langle p|\psi\rangle = \begin{bmatrix} \chi(p) \\ \phi(p) \end{bmatrix} e^{-iEt/\hbar}. \tag{19.27}$$

In this case the Dirac equation becomes

$$E\begin{bmatrix} \chi \\ \phi \end{bmatrix} = \big(c\boldsymbol{\alpha}\cdot\mathbf{p} + \beta mc^2\big)\begin{bmatrix} \chi \\ \phi \end{bmatrix}, \tag{19.28}$$

or written in terms of Pauli matrices,

$$\begin{bmatrix} E - mc^2 & -c\boldsymbol{\sigma}\cdot\mathbf{p} \\ -c\boldsymbol{\sigma}\cdot\mathbf{p} & E + mc^2 \end{bmatrix}\begin{bmatrix} \chi \\ \phi \end{bmatrix} = 0. \tag{19.29}$$

Writing this out as the coupled pair of equations,

$$\chi = -\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E - mc^2}\,\phi, \qquad \phi = -\frac{c\boldsymbol{\sigma}\cdot\mathbf{p}}{E + mc^2}\,\chi, \tag{19.30}$$

these decouple to give, for example,

$$\chi = \frac{c^2(\boldsymbol{\sigma}\cdot\mathbf{p})^2}{E^2 - m^2c^4}\chi. \tag{19.31}$$

Since the coefficients of χ must match on either side, this implies that the energy eigenvalues satisfy $E^2 = p^2c^2 + m^2c^4$, which leads to possible eigenenergies

$$E_\pm = \pm\sqrt{p^2c^2 + m^2c^4}, \tag{19.32}$$

after using $(\boldsymbol{\sigma}\cdot\mathbf{p})^2 = p^2$. In fact, rewriting Eq. (19.29) as the matrix eigenvalue equation

$$\begin{bmatrix} mc^2 & c\boldsymbol{\sigma}\cdot\mathbf{p} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} & -mc^2 \end{bmatrix}\begin{bmatrix} \chi \\ \phi \end{bmatrix} = E\begin{bmatrix} \chi \\ \phi \end{bmatrix}, \tag{19.33}$$

we can diagonalize this equation in essentially the same way as a 2×2 Hamiltonian (see Problem 1.23 or Section 3.5.1); The resulting eigenvectors are

$$\begin{aligned} \psi_+ &= \phi\sin\theta + \chi\cos\theta \\ \psi_- &= \phi\cos\theta - \chi\sin\theta, \end{aligned} \tag{19.34}$$

where

$$\tan 2\theta = \frac{|p|}{mc} \qquad \left(0 \le \theta < \frac{\pi}{2}\right). \tag{19.35}$$

In this case, the transformed Hamiltonian is written in terms of the eigenvalues (19.32) as

$$H' = \beta\sqrt{p^2c^2 + m^2c^4}, \tag{19.36}$$

(diagonalized Dirac Hamiltonian)

which is just what we started out with, Eq. (19.19). The difference now is that both positive- and negative-energy solutions are allowed, with energies $E > mc^2$ and $E < -mc^2$ surrounding a ''gap'' of width $2mc^2$ allowed. The four-component structure is still present. The unitary transformation diagonalizing the Dirac Hamiltonian here is called a **Foldy–Wouthuysen transformation**[5] This transformation explicitly decouples positive- and negative-energy solutions, which are both still spinors. The interpretation is that the Dirac equation naturally yields spin-1/2 fermions, with both the regular particles (with positive energy) and antiparticles (with negative energy). Thus, this is the natural wave equation to properly handle an electron with intrinsic spin.

19.2.4.2 Interpretation

Returning to the problem of negative-energy solutions of Section 19.2.3, another problem comes with the coupling of electrons to the electromagnetic field. We know (Section 15.2) that coupling to the vacuum electromagnetic field induces spontaneous decay to lower levels, and that the transition rate scales as the cube of the transition energy. The unfortunate side effect is that positive-energy solutions will undergo quick spontaneous decay to negative energy solutions, emitting high-frequency photons in the process. Furthermore, if we interpret negative-energy solutions as representing positrons (electron antiparticles, with charge $+e$), then such a transition would violate charge conservation. To explain why this doesn't happen, Dirac postulated[6] that the natural state of the universe is for all the negative energy states to be filled by electrons. This natural state of filled, negative-energy solutions is called the **Dirac sea** of filled states. In this case, since we are dealing with fermions, Pauli exclusion (Section 10.4) prevents electrons from falling into negative energy states. In the case where an electron is promoted from the sea to a positive-energy state (say by

[5] Leslie L. Foldy and Siegfried A. Wouthuysen, ''On the Dirac Theory of Spin 1/2 Particles and its Non-Relativistic Limit,'' *Physical Review* **78**, 29 (1950) (doi: 10.1103/PhysRev.78.29).

[6] P. A. M. Dirac, ''A Theory of Electrons and Protons,'' *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **126**, 360 (1930) (doi: 10.1098/rspa.1930.0013) (JSTOR: 95359). Note that in this paper Dirac interpreted the negative-energy states as representing protons rather than positrons.

absorption of a gamma ray), it leaves a **hole** in the sea. The hole (the absence of one electron) acts as an effective particle, moving in the opposite way as a normal electron (i.e., with the opposite charge), and can be interpreted as a positron. This electron excitation out of the sea can thus be interpreted as the creation of an electron–positron pair, and the transition energy accounts for the $2m_e c^2$ rest energy of the pair as well as any kinetic energy of the pair beyond the rest-energy gap. The pair is of course also annihilated if the electron decays down to fill the hole.

Of course, the interpretation of Section 19.2.3 of antiparticles being particles traveling backwards in time still applies here. In the case of the diagonalized Hamiltonian (19.36), the momentum eigenstates are also eigenstates of this Hamiltonian, in which case the four components of the energy eigenstates all have the form

$$\psi(\mathbf{r}, t) = \psi_0 \, e^{i(\mathbf{p}\cdot\mathbf{r} \mp |E|t)/\hbar}, \tag{19.37}$$

with energies E given by Eq. (19.32). In this case, the negative energy has the same effect as reversing the sign of t.

Another important manifestation of the negative energy states is that they are necessary in a superposition to obtain a localized wave packet. The contribution of these states becomes significant, for example, when the wave packet of an electron is localized on a scale comparable to the Compton wavelength. Since the superposition involves interference of states spanning the energy gap of $2m_e c^2$, there is a rapid oscillation in the motion of the wave packet (with a minimum frequency of $2m_e c^2/h = 2.5 \times 10^{20}\,\text{Hz}$). This motion is called **zitterbewegung** (''trembling motion'').[7] An interesting consequence of zitterbewegung is that it can be viewed as a circulation about the electron spin axis with a radius of the reduced Compton wavelength, and that the electron spin magnetic moment is thus a kind of zitterbewegung-induced orbital angular momentum on a small length scale.[8]

19.3 Electromagnetic Field

Another important example of quantization of a constrained system is the quantization of the electromagnetic field, or **Maxwell field**. Again, we have handled the Hamiltonian constraints within the Dirac formalism before in Section 0.5.5, and we will just summarize the results here. The Lagrangian (0.263) for the field is

$$L(\mathscr{A}, \phi, \mathscr{A}_t, \phi_t) = \frac{\epsilon_0}{2} \int d^3r \left[(\nabla\phi + \mathscr{A}_t)^2 - c^2 (\nabla \times \mathscr{A})^2 - \rho\phi + \mathbf{j}\cdot\mathscr{A} \right], \tag{19.38}$$

and this Lagrangian is obviously invariant under the gauge transformation $\phi \longrightarrow \phi + \chi_t$, $\mathscr{A} \longrightarrow \mathscr{A} - \nabla\chi$, in the case of the source terms after integration by parts. (Recall that subscripts indicate derivatives, $\chi_t \equiv \partial_t \chi$.) The fields are defined in terms of the potentials as

$$\begin{aligned} \mathscr{E} &:= -\nabla\phi - \mathscr{A}_t \\ \mathscr{B} &:= \nabla \times \mathscr{A}, \end{aligned} \tag{19.39}$$

and these quantities are obviously gauge-invariant (left unchanged by the gauge transformation). The canonical momenta (0.265) are defined by differentiating the Lagrangian,

$$\mathbf{\Pi}(\mathbf{r}, t) = \frac{\delta}{\delta \mathscr{A}_t} L = \epsilon_0 (\nabla\phi + \mathscr{A}_t) = -\epsilon_0 \mathscr{E}, \qquad \pi(\mathbf{r}, t) = \frac{\delta}{\delta \phi_t} L = 0, \tag{19.40}$$

while the extended Hamiltonian turns out to be [from Eq. (0.288), after attaching two constraints with Lagrange multiplers, making a canonical transformation to clean up the constraints, and fixing the gauge freedom of the arbitrary scalar momentum π]

$$\tilde{H} = \int d^3r \left[\frac{1}{2\epsilon_0} \Pi^2 + \frac{1}{2} \epsilon_0 c^2 (\nabla \times \mathscr{A})^2 + \phi\rho - \mathbf{j}\cdot\mathscr{A} + \pi\chi_t - \mathbf{\Pi}\nabla\chi \right], \tag{19.41}$$

[7] Erwin Schrodinger, ''Über die kräftefreie Bewegung in der relativistischen Quantenmechanik,'' *Sitzungsberichte der Preussischen Akademie der Wissenschaften, Physikalisch-Mathematische Klasse* **24**, 418 (1930); James D. Bjorken and Sidney D. Drell, *Relativistic Quantum Mechanics* (McGraw–Hill, 1964) (ISBN: 070054932), p. 38.

[8] Kerson Huang, ''On the Zitterbewegung of the Dirac Electron,'' *American Journal of Physics* **20**, 479 (1952) (doi: 10.1119/1.1933296).

where χ represents the explicit gauge freedom that is an implicit part of the Lagrangian (19.38).

The canonical Poisson bracket (0.276) is

$$[\mathscr{A}^\alpha(\mathbf{r},t),\Pi_\beta(\mathbf{r}',t)]_{\text{P}} = \delta^\alpha{}_\beta\,\delta^3(\mathbf{r}-\mathbf{r}'), \tag{19.42}$$

in which case Dirac's prescription is to promote it to the commutator

$$[\mathscr{A}_\alpha(\mathbf{r},t),\Pi_\beta(\mathbf{r}',t)] = i\hbar\delta_{\alpha\beta}\,\delta^3(\mathbf{r}-\mathbf{r}'). \tag{19.43}$$
(canonical commutator)

With this commutator the canonical fields becomes operators, and the extended Hamiltonian (19.41) likewise becomes an operator. The Hamilton equations (0.282) and (0.285) for the vector degree of freedom in this extended Hamiltonian then become the Heisenberg equations

$$\begin{aligned}\mathscr{A}_t &= \frac{1}{\epsilon_0}\mathbf{\Pi} - \nabla\phi\\ \mathbf{\Pi}_t &= -\epsilon_0 c^2\nabla\times\nabla\times\mathscr{A} + \mathbf{j}.\end{aligned} \tag{19.44}$$

Again, only the second equation is really dynamical; the first is the definition of the electric field in terms of the potentials. Of course, these are gauge-invariant equations, and the usual gauge freedom $\phi \longrightarrow \phi + \chi_t$, $\mathscr{A} \longrightarrow \mathscr{A} - \nabla\chi$ is preserved.

19.3.1 Coulomb Gauge

While the above quantization of the electromagnetic field is general in preserving the intrinsic gauge freedom, it also obscures some of the physics: there are really only two independent photon polarizations to be quantized, but this is not clear from the commutator (19.44). Thus it is illuminating to re-quantize the electromagnetic field after fixing Coulomb gauge ($\nabla\cdot\mathscr{A} = 0$), as in Section 0.5.5.3. To recap the classical situation, the Coulomb-gauge condition acts as an additional constraint, which implies the additional constraint (0.298) on the scalar potential

$$\phi(\mathbf{r},t) = \frac{1}{4\pi\epsilon_0}\int d^3r'\,\frac{\rho(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}. \tag{19.45}$$

As a consequence of these two extra constraints, all constraints become second class: All Lagrange multipliers are consequently eliminated from the extended Hamiltonian, and no gauge freedom remains. The canonical (Dirac) bracket (0.309) turned out to be

$$[\mathscr{A}^\alpha(\mathbf{r},t),\Pi_\beta(\mathbf{r}',t)]_{\text{D}} = \delta^\perp_{\alpha\beta}(\mathbf{r}-\mathbf{r}'), \tag{19.46}$$

in terms of the transverse delta function (0.308):

$$\delta^\perp_{\alpha\beta}(\mathbf{r}) := \left(\delta_{\alpha\beta} - \frac{\partial_\alpha\partial_\beta}{\nabla^2}\right)\delta^3(\mathbf{r}). \tag{19.47}$$

Upon canonical quantization, then, the bracket (19.46) is promoted to the commutator

$$[\mathscr{A}^\alpha(\mathbf{r},t),\Pi_\beta(\mathbf{r}',t)] = i\hbar\delta^\perp_{\alpha\beta}(\mathbf{r}-\mathbf{r}'). \tag{19.48}$$
(canonical commutator)

This result is significant because it differs from the free-gauge commutator (19.43), in particular because the transverse delta function (19.47) is nonlocal in space. Thus the elimination of the longitudinal field from the quantization procedure (and the reduction to quantizing only two propagating polarizations) has a significant effect on the canonical structure of the electromagnetic field. Incidentally, this elimination of the longitudinal field has a relatively simple interpretation. The gauge transformation transferred any

content of the longitudinal part of the vector potential to the scalar potential. But Eq. (19.45) says that the scalar potential is associated with the instantaneous Coulomb field due to the source charge distribution. If the electromagnetic field interacts with an ensemble of atoms (i.e., interacts with their electrons), then this instantaneous field is just the interatomic binding potential seen by the electrons. When studying the hydrogen atom in Section 8.4, we took this binding potential to be a (classical) background potential.

The classical equations of motion (0.316) generated by the Dirac bracket,

$$\begin{aligned} \mathscr{A}_t &= \frac{1}{\epsilon_0}\mathbf{\Pi}^\perp \\ \mathbf{\Pi}_t &= -\epsilon_0 c^2 \nabla\times\nabla\times\mathscr{A} + \mathbf{j}^\perp = \epsilon_0 c^2 \nabla^2 \mathscr{A}^\perp + \mathbf{j}^\perp, \end{aligned} \tag{19.49}$$

then also carry over to the quantized field as Heisenberg equations. These are of course essentially the same equations of motion as in the gauge-free case (19.44), although any mention of longitudinal components has here been explicitly omitted.

19.3.1.1 Comparison to Normal-Mode Quantization

Before in Section 15.2.1, we quantized the electromagnetic field by decomposing the electromgnetic field into a set of normal modes (decoupled modes). For each mode we found a pair of effective canonical variables, in terms of which the mode took the form of a harmonic oscillator. Promoting the resulting canonical variables to operators led to the quantized expression (15.32)

$$\mathscr{E}_{\mathbf{k},\zeta}(\mathbf{r},t) = -\hat{\varepsilon}_{\mathbf{k},\zeta}\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0\mathscr{V}}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k},\zeta}(t) + \text{H.c.} \tag{19.50}$$

for the electric field mode of wave vector $\mathbf{k}$ and polarization $\zeta \in \{1,2\}$. Note that we are now explicitly labeling the photon annihilation operator $a_{\mathbf{k},\zeta}$, the unit polarization vector $\hat{\varepsilon}_\zeta$, and the mode frequency $\omega_{\mathbf{k}}$ with the model labels as appropriate. The total electric-field operators is given by summing over all modes,

$$\mathscr{E}(\mathbf{r},t) = -\sum_{\mathbf{k},\zeta}\hat{\varepsilon}_{\mathbf{k},\zeta}\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{2\epsilon_0\mathscr{V}}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k},\zeta}(t) + \text{H.c.}, \tag{19.51}$$

where the possible $\mathbf{k}$ exist on a cubic lattice [Eq. (15.18)]

$$\mathbf{k}(\mathbf{n}) = \frac{2\pi n_x}{L}\hat{x} + \frac{2\pi n_y}{L}\hat{y} + \frac{2\pi n_z}{L}\hat{z}, \tag{19.52}$$

due to the quantization in volume $\mathscr{V} = L^3$. To facilitate comparison to the quantized fields in Eq. (19.48), it is useful to take the limit $\mathscr{V} \longrightarrow \infty$ right away (rather than waiting for it to cancel sometime before the end of a specific calculation, as in the treatment of spontaneous emission in Section 15.2.4). The guiding principle is that the total energy of a mode is a quadratic integral of the fields. For the free-space modes in particular that we are working with, the energy associated with the electric field is identical to that of the magnetic field, so it suffices to consider the integral of the squared electric field. The idea is to choose the same normalization as for the free-space momentum eigenstates [see Eq.(1.157) and Problem 1.42]. This amounts to making the replacement

$$\frac{1}{\sqrt{\mathscr{V}}}\, e^{i\mathbf{k}\cdot\mathbf{r}} \longrightarrow \frac{1}{\sqrt{(2\pi)^3}}\, e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{19.53}$$

so that the inner product of two such mode functions yields $\delta^3(\mathbf{k}-\mathbf{k}')$, as appropriate for normalization in a continuum of modes. Making this replacement in Eq. (19.50) leads to

$$\mathscr{E}_{\mathbf{k},\zeta}(\mathbf{r},t) = -\hat{\varepsilon}_{\mathbf{k},\zeta}\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{16\pi^3\epsilon_0}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k},\zeta}(t) + \text{H.c.}, \tag{19.54}$$

in which case the total field is given by summing over all modes:

$$\boldsymbol{\mathscr{E}}(\mathbf{r},t) = -\sum_{\zeta}\int d^3k\left[\hat{\varepsilon}_{\mathbf{k},\zeta}\sqrt{\frac{\hbar\omega_{\mathbf{k}}}{16\pi^3\epsilon_0}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,a_{\mathbf{k},\zeta}(t) + \text{H.c.}\right].$$

(quantized electric-field mode, large-volume limit) (19.55)

Also, in Coulomb gauge, the field is related to the potential by $\boldsymbol{\mathscr{E}} = -\partial_t\boldsymbol{\mathscr{A}}$, so that

$$\boldsymbol{\mathscr{A}}(\mathbf{r},t) = \sum_{\zeta}\int d^3k\left[i\hat{\varepsilon}_{\mathbf{k},\zeta}\sqrt{\frac{\hbar}{16\pi^3\epsilon_0\omega_{\mathbf{k}}}}\,e^{i\mathbf{k}\cdot\mathbf{r}}\,a_{\mathbf{k},\zeta}(t) + \text{H.c.}\right].$$

(quantized vector-potential mode, large-volume limit) (19.56)

Also, for the mode operators, we have the commutator

$$[a_{\mathbf{k},\zeta}, a^\dagger_{\mathbf{k}',\zeta'}] = \frac{\delta^3(\mathbf{k}-\mathbf{k}')\,\delta_{\zeta\zeta'}}{(2\pi)^3}, \qquad (19.57)$$

(mode-operator commutator)

because the modes were quantized as independent harmonic oscillators. In passing over to the continuum limit, the orthogonality of the harmonic oscillators also appears as a delta function in the wave vectors, in view of the replacement $\delta^3_{\mathbf{k}\mathbf{k}'} \longrightarrow \delta^3(\mathbf{k}-\mathbf{k}')/(2\pi)^3$, in analogy to Eq. (19.53).

Now using Eqs. (19.55), (19.56), and (19.57), we can proceed to compute the canonical commutator of the electromagnetic field. Starting with the commutator of two components, the mode commutator (19.57) produces a delta function, which removes one of the wave-vector integrals as well as one polarization sum:

$$[\mathscr{A}_\alpha(\mathbf{r},t), \mathscr{E}_\beta(\mathbf{r}',t)] = -\frac{\hbar}{16\pi^3\epsilon_0}\sum_{\zeta}\int d^3k\left[i(\hat{\varepsilon}_{\mathbf{k},\zeta}\cdot\hat{r}_\alpha)(\hat{\varepsilon}^*_{\mathbf{k},\zeta}\cdot\hat{r}_\beta)\,e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} - \text{H.c.}\right]. \qquad (19.58)$$

What remains is to carry out the remaining polarization sum. To do this, consider two orthonormal sets of basis vectors $(\hat{r}_1,\hat{r}_2,\hat{r}_3)$ and $(\hat{k}_1,\hat{k}_2,\hat{k}_3)$. Here orthonormality means that $\hat{r}_\alpha\cdot\hat{r}_\beta = \delta_{\alpha\beta}$. On the other hand, we can write out the same dot product expressed in the $\hat{k}_\gamma$ basis as

$$\hat{r}_\alpha\cdot\hat{r}_\beta = \sum_\gamma(\hat{r}_\alpha\cdot\hat{k}_\gamma)(\hat{k}_\gamma\cdot\hat{r}_\beta) = \delta_{\alpha\beta}. \qquad (19.59)$$

Rearranging this expression to separate out two terms of the sum, we have

$$(\hat{r}_\alpha\cdot\hat{k}_1)(\hat{k}_1\cdot\hat{r}_\beta) + (\hat{r}_\alpha\cdot\hat{k}_2)(\hat{k}_2\cdot\hat{r}_\beta) = \delta_{\alpha\beta} - (\hat{r}_\alpha\cdot\hat{k}_3)(\hat{k}_3\cdot\hat{r}_\beta). \qquad (19.60)$$

Now since the two polarization vectors $\hat{\varepsilon}_{\mathbf{k},\zeta}$ form an orthonormal basis with $\hat{k}$ (in the sense $\hat{\varepsilon}_{\mathbf{k},1}\cdot\hat{\varepsilon}^*_{\mathbf{k},2} = 1$ in the case of complex polarization vectors, as is the case for helicity states), we can set $\hat{k}_1 = \hat{\varepsilon}_{\mathbf{k},1}$, $\hat{k}_2 = \hat{\varepsilon}^*_{\mathbf{k},2}$, and $\hat{k}_3 = \mathbf{k}/k$ to obtain the polarization sum

$$\sum_\zeta(\hat{\varepsilon}_{\mathbf{k},\zeta}\cdot\hat{r}_\alpha)(\hat{\varepsilon}^*_{\mathbf{k},\zeta}\cdot\hat{r}_\beta) = \delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}. \qquad (19.61)$$

Thus Eq. (19.58) becomes

$$[\mathscr{A}_\alpha(\mathbf{r},t), \mathscr{E}_\beta(\mathbf{r}',t)] = -\frac{i\hbar}{(2\pi)^3\epsilon_0}\int d^3k\left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}. \qquad (19.62)$$

To recognize the integral here, we can return to the transverse delta function (19.47):

$$\delta^\perp_{\alpha\beta}(\mathbf{r}) = \left(\delta_{\alpha\beta} - \frac{\partial_\alpha\partial_\beta}{\nabla^2}\right)\delta^3(\mathbf{r}). \qquad (19.63)$$

Using the integral representation of the delta function, we have

$$\delta^{\perp}_{\alpha\beta}(\mathbf{r}) = \left(\delta_{\alpha\beta} - \frac{\partial_\alpha \partial_\beta}{\nabla^2}\right) \frac{1}{(2\pi)^3} \int d^3k\, e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{19.64}$$

and then passing the derivatives through the integral sign, we can write

$$\delta^{\perp}_{\alpha\beta}(\mathbf{r}) = \frac{1}{(2\pi)^3} \int d^3k \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) e^{i\mathbf{k}\cdot\mathbf{r}}.$$

(transverse delta function, k-representation) (19.65)

This is the k-space representation of the transverse delta function, which involves the characteristic sum (19.61) over the two independent polarizations. Thus Eq. (19.58) becomes

$$[\mathscr{A}_\alpha(\mathbf{r},t), \mathscr{E}_\beta(\mathbf{r}',t)] = -\frac{i\hbar}{\epsilon_0}\delta^{\perp}_{\alpha\beta}(\mathbf{r}-\mathbf{r}'). \tag{19.66}$$

Since the canonical momentum field is $\mathbf{\Pi} = -\epsilon_0 \mathscr{E}$, this commutator is identical to the canonical commutator (19.48) that we derived from the Dirac bracket.

Again, the canonical commutator (19.66) is nonlocal in space; here we see more clearly that the nonlocality is a manifestation of the removal of the longitudinal parts of the fields. It is of course also possible to compute other commutators for various electromagnetic-field combinations, in essentially the same way. These are called the **Jordan–Pauli commutators** [9] These field–field commutators are local in the sense of vanishing except for $\mathbf{r} = \mathbf{r}'$. At unequal times, the commutator vanishes unless the spacetime coordinates for the two fields lie on the same light cone.

19.3.2 Creation and Annihilation of Photons

The electromagnetic fields (19.55) and (19.56) derived from the individual quantization of the normal modes involve expressions of the fields in terms of photon creation and annihilation operator. This is a useful extra bit of information that didn't come out of the constrained quantization of the field. Thus it is useful to briefly discuss a general decomposition of the field into its creation and annihilation components.[10] The key observation is that the mode annihilation operators have monochromatic time dependence of the form

$$a_{\mathbf{k},\zeta}(t) = a_{\mathbf{k},\zeta}(0)\, e^{-i\omega_{\mathbf{k}} t}, \tag{19.67}$$

which we call "positive-frequency" oscillation (since $e^{-i\omega t}$ is the conventional time dependence in physics, being the time dependence of a right-moving plane wave). The creation operator has the time dependence

$$a^\dagger_{\mathbf{k},\zeta}(t) = a^\dagger_{\mathbf{k},\zeta}(0)\, e^{i\omega_{\mathbf{k}} t}, \tag{19.68}$$

which is oscillation at a negative frequency (thinking of the time dependence $e^{i\omega_{\mathbf{k}} t} = e^{-(-i\omega_{\mathbf{k}} t)}$ in standard form).

The annihilation part of the electromagnetic field (19.55) then comes from summing over only the positive-frequency components. For an arbitrary function $f(t)$, if we write out the Fourier transform

$$\tilde{f}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} f(t), \tag{19.69}$$

and thus we can define the positive-frequency part by

$$\tilde{f}^{(+)}(\omega) := \Theta(\omega)\, \tilde{f}(\omega). \tag{19.70}$$

[9] After P. Jordan and W. Pauli, Jr., "Zur Quantenelektrodynamik ladungsfreier Felder," *Zeitschrift für Physik* **47**, 151 (1928) (doi: 10.1007/BF02055793) (doi: 10.1007/BF02055793). For explicit expressions, as well as general expressions for field commutators for arbitrary sets of mode functions, see Daniel A. Steck, *Quantum and Atom Optics*, available online at `https://steck.us/teaching` (2007).

[10] Roy J. Glauber, "The Quantum Theory of Optical Coherence," *Physical Review 130*, 2529 (1963) (doi: 10.1103/PhysRev.130.2529).

In the time domain, this reads

$$f^{(+)}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t}\,\Theta(\omega)\,\tilde{f}(\omega) = \frac{1}{2\pi}\int_{0}^{\infty} d\omega\, e^{-i\omega t}\tilde{f}(\omega). \tag{19.71}$$

For this integral to converge at the $\omega \longrightarrow \infty$ limit, the time variable should be interpreted in the sense $t \longrightarrow t - i0^+$ in order to obtain a decaying exponential in ω. Doing this and eliminating $\tilde{f}(\omega)$ leads to

$$f^{(+)}(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt' \int_{0}^{\infty} d\omega\, e^{-i\omega(t-t'-i0^+)} f(t'), \tag{19.72}$$

and carrying out the ω integral gives

$$f^{(+)}(t) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} dt'\, \frac{f(t')}{t - t' - i0^+}. \tag{19.73}$$

Changing the integraiion variable to $\tau = t - t'$ finally gives

$$f^{(+)}(t) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\tau\, \frac{f(t-\tau)}{\tau - i0^+}. \tag{19.74}$$

The analogous negative-frequency expression follows from defining

$$\tilde{f}^{(-)}(\omega) := \Theta(-\omega)\,\tilde{f}(\omega), \tag{19.75}$$

which leads to

$$f^{(-)}(t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\tau\, \frac{f(t-\tau)}{\tau + i0^+}. \tag{19.76}$$

Note that these expressions are closely analogous to the retarded and advanced Green-functions in Section 13.2, which excluded either positive or negative *times* in the evolution operator.

Thus we can define the annihilation part of the electric field in a general way via

$$\boldsymbol{\mathscr{E}}^{(+)}(\mathbf{r},t) = \frac{1}{2\pi i}\int_{-\infty}^{\infty} d\tau\, \frac{\boldsymbol{\mathscr{E}}(\mathbf{r},t-\tau)}{\tau - i0^+},$$

(electric field operator, annihilation part) (19.77)

while the creation part of the field is

$$\boldsymbol{\mathscr{E}}^{(-)}(\mathbf{r},t) = -\frac{1}{2\pi i}\int_{-\infty}^{\infty} d\tau\, \frac{\boldsymbol{\mathscr{E}}(\mathbf{r},t-\tau)}{\tau + i0^+}.$$

(electric field operator, annihilation part) (19.78)

Since these parts each correspond to half the frequency spectrum their sum is the entire fields,

$$\boldsymbol{\mathscr{E}}(\mathbf{r},t) = \boldsymbol{\mathscr{E}}^{(+)}(\mathbf{r},t) + \boldsymbol{\mathscr{E}}^{(-)}(\mathbf{r},t) = \boldsymbol{\mathscr{E}}^{(+)}(\mathbf{r},t) + \text{H.c.} \tag{19.79}$$

The annihilation part of the field is more generally defined by the property

$$\boldsymbol{\mathscr{E}}^{(+)}(\mathbf{r},t)|0\rangle = 0, \tag{19.80}$$

where $|0\rangle$ represents the vacuum state of the electromagnetic field (where every field mode is in the vacuum state).

19.3.3 Photon Wave Function

Clearly, $a^\dagger_{\mathbf{k},\zeta}$ is a creation operator for the mode with wave number $\mathbf{k}$ and polarization ζ. It is then tempting to interpret $\boldsymbol{\mathscr{E}}^{(-)}(\mathbf{r},t)$, being something like a Fourier transform of $a^\dagger_{\mathbf{k},\zeta}$, as a creation operator for a photon

at point $\mathbf{r}$. This is indeed the case for some quantized fields, but the situation is a bit trickier for the electromagnetic field, as already suggested by the nonlocal canonical commutator (19.66).

Because of its association with the creation operator $a^\dagger_{\mathbf{k},\zeta}$, we can interpret $\hat{\varepsilon}_{\mathbf{k},\zeta}\, e^{i\mathbf{k}\cdot\mathbf{r}}/(2\pi)^{3/2}$ as a wave function for a photon with well-defined momentum and polarization. In fact, it is useful to recall the classical result that the momentum density of the electromagnetic field in vacuum is $\epsilon_0 \mathscr{E} \times \mathscr{B}$, from which it follows that the the time-averaged momentum of a plane wave is

$$\bar{p} = \frac{\bar{U}}{c}\hat{k}, \tag{19.81}$$

where $\bar{U}$ is the time-averaged energy of the electromagnetic field. With $\bar{U} = \hbar\omega_{\mathbf{k}}$ for one photon and $\omega_{\mathbf{k}} = ck$, the photon momentum is thus the familiar

$$\bar{p} = \hbar\mathbf{k} \tag{19.82}$$

in the case of a plane wave.

19.3.3.1 Mode-Summed Annihilation Operator

Now to attempt to construct a creation operator for the electromagnetic field at a particular point in space. Consider the operator

$$\mathbf{A}(\mathbf{r}) := \frac{1}{(2\pi)^{3/2}} \sum_\zeta \int d^3k\, \hat{\varepsilon}_{\mathbf{k},\zeta}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k},\zeta}, \tag{19.83}$$

which sums over modes with all possible wave vectors and polarizations. In the absence of polarizations (and the annihilation operators), the spatial profile would have the form $\delta^3(\mathbf{r})$, in view of the integral representation of the delta function. However, due to the sum over the two independent polarizations for each mode, it is not at all clear that $\mathbf{A}(\mathbf{r})$ should be localized in the same sense. In fact it is not, which we will now demonstrate. First, note that this operator is not, as stated, well defined, because there is some arbitrariness in the choice of the two polarization vectors, as they only need to be chosen mode-wise to be orthogonal to $\mathbf{k}$. Rather than attempt to fix a choice and carry out an explicit mode summation, we will take a shortcut that both fixes the polarization choice and goes directly to the final result. The key observation is that $\mathbf{A}(\mathbf{r})$ is a transverse field in the sense $\nabla \cdot \mathbf{A}(\mathbf{r}) = 0$, because it is the sum over transverse modes. Replacing the polarization sum by a sum over basis vectors $\hat{\varepsilon}_x$, $\hat{\varepsilon}_y$, and $\hat{\varepsilon}_z$ is not correct because it will count the $\hat{k}$ direction for every mode, which violates the transverse-field constraint. However, because this sum is easy, let's go with it and fix the result afterwards. Thus, for example,

$$\hat{\varepsilon}_z \frac{1}{(2\pi)^3} \int d^3k\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k}} =: \hat{\varepsilon}_z\, a(\mathbf{r}), \tag{19.84}$$

and then summing over the three basis vectors gives a sum of the form $(\hat{\varepsilon}_x + \hat{\varepsilon}_y + \hat{\varepsilon}_z)\, a(\mathbf{r})$. Again, this isn't correct because it overcounts a third, unphysical polarization. However, we can correct this by projecting out the physical part via the transverse delta function (19.47). Thus, for example, the α component of the corrected mode sum is

$$\begin{aligned}
\sum_\beta \int d^3\mathbf{r}'\, \delta^\perp_{\alpha\beta}(\mathbf{r}-\mathbf{r}')\big[\hat{\varepsilon}_z\, a(\mathbf{r}')\big]_\beta &= \int d^3\mathbf{r}' \left(\delta_{\alpha z} - \frac{\partial_\alpha \partial_z}{\nabla^2}\right) \delta^3(\mathbf{r}-\mathbf{r}')\, a(\mathbf{r}') \\
&= \left(\delta_{\alpha z} - \frac{\partial_\alpha \partial_z}{\nabla^2}\right) a(\mathbf{r}) \\
&= \frac{1}{(2\pi)^3} \int d^3k \left(\delta_{\alpha z} - \frac{k_\alpha k_z}{k^2}\right) e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k}},
\end{aligned} \tag{19.85}$$

ignoring the polarization of the annihilation operator for the moment. Summing over the three basis vectors then gives

$$A_\alpha(\mathbf{r}) = \frac{1}{(2\pi)^3} \sum_\beta \int d^3k \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2}\right) e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k},\beta}. \tag{19.86}$$

Since the $\hat{\varepsilon}_\beta$ direction is not generally a physical polarization, the operator $a_{\mathbf{k},\beta}$ should be interpreted as referring to the polarization corresponding to the projection of $\hat{\varepsilon}_\beta$ onto the $\hat{k}$ plane ($\hat{\varepsilon}_\beta$ was effectively a linear combination of physical and unphysical annihilation operators, the unphysical part having been removed by the transverse delta function). Note the arbitrariness of this expression comes from the choice of particular basis vectors in a particular coordinate system; any set of mutually orthonormal basis vectors could have determined an analogous expression. In any case, the form here has the spatial profile of the transverse delta function, which as we have noted before is nonlocal in space.

19.3.3.2 Frequency Dependence of the Electric-Field Operator and the Photon Wave Function

While the field in Eq. (19.86) is nonlocal, it is not the same as the electric field. Recall that Eq. (19.55) gives $\boldsymbol{\mathscr{E}}(\mathbf{r},t)$ as a linear combination of the momentum wave functions and creation operators, *but* with the weighting factor $\sqrt{k} \propto \omega_{\mathbf{k}}$:

$$\boldsymbol{\mathscr{E}}(\mathbf{r},t) = -\sum_\zeta \int d^3k \left[\hat{\varepsilon}_{\mathbf{k},\zeta} \sqrt{\frac{\hbar\omega_{\mathbf{k}}}{16\pi^3\epsilon_0}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, a_{\mathbf{k},\zeta}(t) + \text{H.c.} \right]. \tag{19.87}$$

This frequency-dependent weighting is the essential difference from the superposition in Eq. (19.55). Suppose that we define the generalization of the Laplacian operator by

$$-\sqrt[4]{-\nabla^2}\, f(\mathbf{r}) := \frac{1}{(2\pi)^{3/2}} \int d^3k\, \sqrt{k}\, \tilde{f}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{19.88}$$

Note that the root is defined in terms of $-\nabla^2$ because it is a positive-definite operator. This operator is a fractional generalization of ∇^2, in the sense that a four-fold application to a function $f(\mathbf{r})$ is equivalent to an application of ∇^2. This operator is nonlocal in the sense of being a convolution with respect to a function with power-law tails (i.e., the convolution kernel is the Fourier transform of $\sqrt{k}$; see Problem 19.2).[11]

According to the argument above, the electric-field operator is inherently nonlocal: A photon can't be localized on a scale smaller than the wavelength of light. This observation has led to a long-standing controversy over the existence of the ''photon wave function'' in the position representation. As early as 1927, Dirac[12] understood that a wave function for a photon differs from the wave function for a massive particle, because the photon wave function is real, and it corresponds to an energy density rather than a probability density. However, due to the nonlocal character of the field operator, a famous textbook[13] discussed the ''impossibility of introducing a photon wave function in the coordinate representation.'' However, more recent treatments have defended the concept of a photon wave function in terms of other operators.[14]

[11] Mateusz Kwaśnicki, ''Ten Equivalent Definitions of the Fractional Laplace Operator,'' *Fractional Calculus and Applied Analysis* **20**, 7 (2017) (doi: 10.1515/fca-2017-0002).

[12] P. A. M. Dirac, ''The Quantum Theory of the Emission and Absorption of Radiation,'' *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **114**, 243 (1927) (doi: 10.1098/rspa.1927.0039).

[13] A. I. Akhiezer and V. B. Berestetskii, *Quantum Electrodynamics*, English translation by G. M. Volkoff (Wiley Interscience, 1965) (ISBN: 0470018488), Section 2.2.

[14] Iwo Bialynicki-Birula, ''Photon Wave Function,'' in *Progress in Optics XXXVI*, E. Wolf, Ed. (Elsevier, 1996) (arXiv: quant-ph/0508202v1), p. 245; Brian J. Smith and M. G. Raymer, ''Photon wave functions, wave-packet quantization of light, and coherence theory,'' *New Journal of Physics* **9**, 414 (2007) (doi: 10.1088/1367-2630/9/11/414).

19.4 Exercises

Problem 19.1

Defining the density

$$\rho := \frac{i\hbar}{2mc^2}\left(\psi^*\partial_t\psi - \psi\partial_t\psi^*\right), \tag{19.89}$$

and the current

$$\mathbf{j} := \frac{\hbar}{2mi}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right), \tag{19.90}$$

show that the Klein–Gordon equation implies the continuity equation for these quantities. (Try multiplying the Klein–Gordon equation by ψ^* and subtract the complex conjugate of the equation.)

Problem 19.2

The Laplacian operator $\triangle \equiv \nabla^2$ is diagonal in the momentum representation, owing to the expression

$$\triangle\, e^{i\mathbf{k}\cdot\mathbf{r}} = -k^2\, e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{19.91}$$

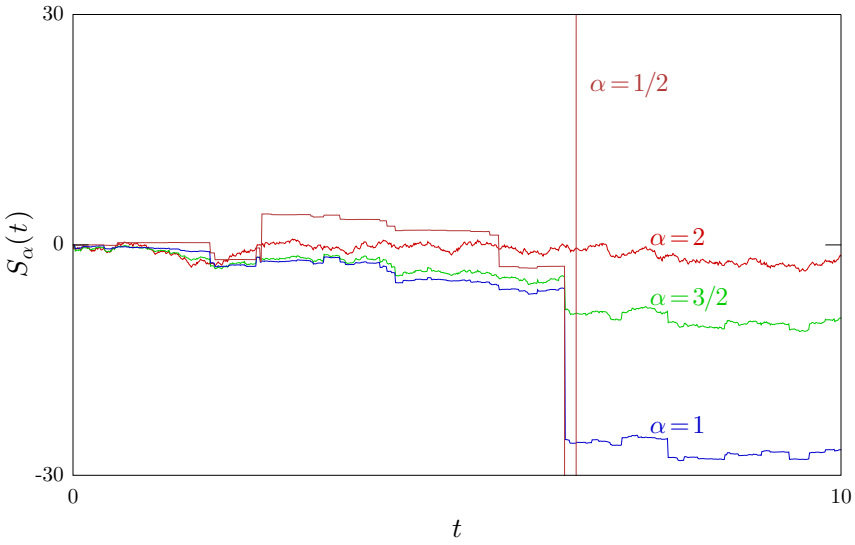
where $k = p/\hbar$. Then it is useful to define a fraction $\alpha/2$ of the Laplacian by

$$-(-\triangle)^{\alpha/2}\, e^{i\mathbf{k}\cdot\mathbf{r}} := \left(-|k|^\alpha\right) e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{19.92}$$

for $\alpha \in (0, 2]$. Note that this operator is defined in terms of a power of $-\triangle$ because it is positive definite, and a fractional power of a nonpositive operator could lead to (undesired) complex eigenvalues. In one dimension, this Laplacian is commonly written as the fractional derivative $\partial^\alpha/\partial|x|^\alpha \equiv -(-\triangle)^{\alpha/2}$, which in this form is often called the **Riesz–Feller derivative**). The case $\alpha = 2$ recovers the standard Laplacian, and fractional derivatives outside this range can be defined by the recursion $-(-\triangle)^{(\alpha+2)/2} = -(-\triangle)^{\alpha/2}\triangle$.

So what good is it? Well, one can generalize quantum mechanics to ''fractional quantum mechanics''[15] by changing ∇^2 to $-D_\alpha(-\triangle)^{\alpha/2}$ in the Schrödinger equation in the position representation (D_α is just a coefficient introduced to make the units work out). Unfortunately, it isn't clear if this generalization is at very useful. (Note, however, that the Hamiltonian for a relativistic particle may be written $\sqrt{p^2c^2 - m^2c^4}$, which in the massless limit has the form of the $\alpha = 1$ derivative.) The analogous replacement in the diffusion equation (recall Problem 2.38) is an important generalization to model **anomalous diffusion**. Recalling that the position variance of a solution to the diffusion equation grows linearly with time, the solution to the fractional diffusion equation with the same initial condition but with $\alpha \in (0, 2)$ would grow *more quickly* than t (in fact the *slope* of $V_\mathbf{r}(t)$ grows without bound). In modeling the aggregate behavior of an ensemble of random walkers, roughly speaking, anomalous diffusion allows for the possibility of large steps, called **Lévy flights** or **extreme events**, with a power-law tail in the frequency distribution. Some example paths illustrating Lévy flights for different α are shown below (notice the jumps in the $\alpha < 2$ cases).

[15] Nikolai Laskin, ''Fractional quantum mechanics and Lévy path integrals,'' *Physics Letters A* **268**, 298 (2000) (doi: 10.1016/S0375-9601(00)00201-2); Nick Laskin, ''Fractional Schrödinger equation,'' *Physical Review E* **66**, 056108 (2002) (doi: 10.1103/physreve.66.056108).



Anomalous diffusion models a wide range of phenomena from the dynamics of laser-cooled atoms to stock-market prices on short time scales to the foraging behavior of albatrosses. This fractional derivative also arises in "fractional electromagnetism" in cuprate semiconductors.[16]

The goal of this problem is to use what you know about Fourier analysis to develop an expression for the fractional derivative—which turns out to be an integral! First, let's set up some Fourier basics. Suppose we assume a Fourier-transform convention

$$\tilde{f}(\mathbf{k}) = \frac{1}{(2\pi)^{d/2}} \int d^d r\, f(\mathbf{r})\, e^{-i\mathbf{k}\cdot\mathbf{r}}, \qquad f(\mathbf{r}) = \frac{1}{(2\pi)^{d/2}} \int d^d k\, \tilde{f}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{19.93}$$

This is the usual convention in quantum mechanics, but setting $\hbar = 1$, and generalized to d spatial dimensions. By this point you should already have proven the convolution theorem (Problem 2.5), which in this convention reads

$$g(\mathbf{r}) := (f * K)(\mathbf{r}) := \int d^d r'\, K(\mathbf{r}-\mathbf{r}')\, f(\mathbf{r}') \qquad \Longleftrightarrow \qquad \tilde{g}(\mathbf{k}) = (2\pi)^{d/2} \tilde{K}(\mathbf{k})\, \tilde{f}(\mathbf{k}) \tag{19.94}$$

for some kernel $K(\mathbf{r})$.

Now the action of the fractional derivative on a general function $f(\mathbf{r})$ is given by completing the Fourier transform implicit in Eq. (19.92):

$$-(-\triangle)^{\alpha/2}\, f(\mathbf{r}) := -\frac{1}{(2\pi)^{d/2}} \int d^d k\, \tilde{f}(\mathbf{k})\, (-\triangle)^{\alpha/2}\, e^{i\mathbf{k}\cdot\mathbf{r}} = \frac{1}{(2\pi)^{d/2}} \int d^d k\, \left(-|k|^\alpha\right) \tilde{f}(\mathbf{k})\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{19.95}$$

The aim is now to employ the convolution theorem to invert the Fourier integral on the right-hand side.

(a) To proceed, we will need to find the Fourier counterpart to $|k|^\alpha$. However, directly approaching the inverse transform in d dimensions is not so easy, because $|k|^\alpha$ doesn't factorize into different dimensions (unless $\alpha = 2$), and the integration in spherical coordinates is cumbersome beyond $d = 3$. Happily, there is a nice trick to do this; we will use the trick to work out the *forward* transform of $r^{-\gamma}$. First, let's start with the integral representation of the gamma function:

$$\Gamma(z) = \int_0^\infty ds\, s^{z-1}\, e^{-s}. \tag{19.96}$$

[16] Gabriele La Nave, Kridsanaphong Limtragool, and Philip W. Phillips "*Colloquium*: Fractional electromagnetism in quantum matter and high-energy physics," *Reviews of Modern Physics* **91**, 021003 (2019) (doi: 10.1103/RevModPhys.91.021003).

Change the integration variable to $s = r^2\lambda^2$, and then set $z = \gamma/2$ to obtain the integral formula

$$\frac{1}{r^\gamma} = \frac{2}{\Gamma(\gamma/2)} \int_0^\infty d\lambda\, \lambda^{\gamma-1}\, e^{-\lambda^2 r^2}. \tag{19.97}$$

(b) The point of the transformation is that the dependence on $\mathbf{r}$ is Gaussian on the right-hand side, and is thus a separable function in d dimensions. Compute the Fourier transform of this formula to show that the Fourier transform of $r^{-\gamma}$ may be written

$$\frac{1}{(2\pi)^{d/2}} \int d^d r\, \frac{e^{-i\mathbf{k}\cdot\mathbf{r}}}{r^\gamma} = \frac{2^{d/2-\gamma}\Gamma[(d-\gamma)/2]}{\Gamma(\gamma/2)}\, k^{\gamma-d}. \tag{19.98}$$

Then invert the transform and change variables in the exponents to show that the inverse transform of k^α is given by

$$\frac{2^{d/2+\alpha}\Gamma[(\alpha+d)/2]}{\Gamma(-\alpha/2)} \frac{1}{r^{\alpha+d}} = \frac{1}{(2\pi)^{d/2}} \int d^d k\; k^\alpha\, e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{19.99}$$

What is the range of α for which this derivation is valid?

(c) Finally, apply the convolution theorem (19.94) to Eq. (19.95) to obtain the integral expression

$$-(-\triangle)^{\alpha/2}\, f(\mathbf{r}) = \frac{2^\alpha \Gamma[(\alpha+d)/2]}{\pi^{d/2}|\Gamma(-\alpha/2)|} \int d^d r'\, \frac{f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^{\alpha+d}} \tag{19.100}$$

for the fractional Laplacian. [Note the modulus on $\Gamma(-\alpha/2)$, since $\Gamma(-\alpha/2) < 0$ for $\alpha \in (0,2)$.]

The integral here is divergent for the parameters of interest, $\alpha \in (0,2)$ and $d \geq 1$. The integral is commonly regularized as

$$-(-\triangle)^{\alpha/2}\, f(\mathbf{r}) = \frac{2^\alpha \Gamma[(\alpha+d)/2]}{\pi^{d/2}|\Gamma(-\alpha/2)|} \int d^d r'\, \frac{f(\mathbf{r}') - f(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|^{\alpha+d}}, \tag{19.101}$$

which is the **Hadamard finite part** of the original integral (basically, the divergent part has been subtracted away).

Equation (19.101) is the main result: The thing to notice here is that the fractional Laplacian is a *nonlocal* operator (convolution with a power-law-tailed function)—unless α is an even integer, in which case it's quite local, in the sense that $\nabla^2 f(\mathbf{r})$ only depends on f at points arbitrarily close to $\mathbf{r}$. This makes the fractional Laplacian tricky to handle, and a number of erroneous results have appeared in the literature, especially regarding how the fractional Laplacian works with Dirichlet boundary conditions (i.e., the infinite square well in fractional quantum mechanics).

Chapter 20

Second Quantization

20.1 Motivation

In the way we have been doing things, we start off with the Schrödinger equation

$$i\hbar|\dot{\psi}\rangle = \hat{H}|\psi\rangle. \tag{20.1}$$

If this is to represent the evolution of the state of N particles all subject to the same external potential, then the Hamiltonian should be

$$\hat{H} = \sum_{j=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_j^2 + V(\hat{\mathbf{r}}_j, t)\right) = \sum_{j=1}^{N}\left(\frac{\hat{p}_j^2}{2m} + V(\hat{\mathbf{r}}_j, t)\right), \tag{20.2}$$

and the wave function in the position representation is

$$\langle \mathbf{r}_1, \ldots, \mathbf{r}_N|\psi(t)\rangle = \psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t). \tag{20.3}$$

In the case of *distinguishable* particles, this is fine, and we can associate each canonical pair of coordinates $(\mathbf{r}_j, \mathbf{p}_j)$ with one of the particles. In the case of *indistinguishable* particles (Section 10.4), there is an extra requirement of (anti)symmetrization, and the labeling of a particular particle may be problematic. This formalism thus has some awkward details when it comes to handling multiple particles. Furthermore, the Hilbert space is fixed by the number of particles, and it is not so natural to consider cases where the number of particles may change dynamically. For these reasons we will consider an alternative formalism to handling many particles in quantum mechanics.[1]

Note that throughout this chapter, we will ignore the possibility of a spin degree of freedom for the quantum particles. So while we will talk about bosons and fermions, we will do so as if they are scalar particles, in order to keep the discussion reasonably simple. Note also that, breaking tradition with all the previous chapters, operators on the abstract Hilbert space will now be donning hats (except for operators like ∇ where there can't be any confusion). There will be many comparisons between operators and ordinary functions, and here the clarity from the explicit distinction will be worth the extra clutter.

20.1.1 Second Quantization

The alternative approach begins with a return to the Schrödinger equation for a *single* particle, expressed in the position representation:

$$i\hbar\dot{\psi}(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\nabla^2\psi + V(\mathbf{r}, t)\,\psi. \tag{20.4}$$

[1] For excellent sources of related reading, see Paul Roman, *Advanced Quantum Theory: An Outline of the Fundamental Ideas* (Addison–Wesley, 1965) (ISBN: 0201064952); and Henk T.C. Stoof, Koos B. Gubbels, Dennis B. M. Dickerscheid, *Ultracold Quantum Fields* (Springer, 2009) (ISBN: 9781402087639).

This is, of course, the basis for quantum mechanics, but the idea is to now reinterpret this as some equation of motion for a complex scalar field ψ, a **matter field** representing some kind of stuff. In this interpretation, this is now a *classical* field equation, in the same sense as Maxwell's equations for the electromagnetic field. In fact, in this interpretation, the matter field need not even be unit-normalized (in fact, we really don't want to be in general). Then the idea will be to quantize this classical field equation, just as we did for the Maxwell field (Section 19.3). This is not obviously a good idea. In the case of the Maxwell field, the classical field equations had a clear physical interpretation. But the significance of the ordinary Schrödinger equation as a classical field theory is less clear. In any case, **first quantization** occurred when we wrote down the Schrödinger equation (20.4) via canonical quantization of a classical particle. The procedure now for quantizing the Schrödinger equation ''again'' is accordingly called **second quantization**.[2] To anticipate results to come, the distinction between first and second quantization is the (first) quantization of a *single* particle, and then the (second) quantization of many particles from the single-particle wave equation.

20.2 Canonical Quantization: Bosons

To quantize the Schrödinger equation, we will proceed by the canonical method (Section 1.6.1), identifying canonical coordinates and the associated Hamiltonian, and then promoting Poisson brackets to commutators. There are some minor technical complications along the way, and technically the methods for handling constrained systems in Chapter 19 are needed, but we will sidestep those here. Some of these technical details are left as an exercise (Problem 0.9). We will also be making use of variational calculus (Section 0.2) in the following treatment, although we will try to keep these mathematical details somewhat self-contained.

20.2.1 Lagrangian and Hamiltonian

To begin, the Lagrangian that reproduces the Schrödinger equation (20.4) is

$$L = \int d^3r \left(i\hbar\psi^* \dot{\psi} - \frac{\hbar^2}{2m} \nabla\psi^* \cdot \nabla\psi - \psi^* V(\mathbf{r},t)\psi \right). \tag{20.5}$$
(matter-field Lagrangian)

Again, we have the complex field ψ involved, along with the conjugate field ψ^*. As complex fields, it is convenient to take ψ and ψ^* as independent generalized coordinates. Taking the real and imaginary parts of ψ is another possibility that leads to equivalent results. Thus, for example the field $\psi(\mathbf{r},t)$ is analogous to the classical (vector) generalized coordinate $q^\alpha(t)$, with the discrete index α being replaced by the continuous ''index'' $\mathbf{r}$ (thus, the dot-product sum $\sum_\alpha$ carries over to the integral $\int d^3r$). A great deal of the functional calculus here can be thought of quite intuitively in terms of this analogy.

Now we will consider the action integral

$$S = \int dt\, L(\psi, \psi^*, \dot{\psi}, \nabla\psi, \nabla\psi^*; t), \tag{20.6}$$

where the time integral is between definite limits t_1 and t_2, suppressed here to reduce clutter. The linear variation of the action in response to a variation $\delta\psi^*$ in ψ^* (holding ψ fixed) is

$$\delta S = \int dt \int d^3r \left(\frac{\delta L}{\delta\psi^*} \delta\psi^* + \frac{\delta L}{\delta(\nabla\psi^*)} \cdot \delta(\nabla\psi^*) \right). \tag{20.7}$$

[2] Quantization along these lines was first done for the electromagnetic field by P. A. M. Dirac, ''The Quantum Theory of the Emission and Absorption of Radiation,'' *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **114**, 243 (1927) (doi: 10.1098/rspa.1927.0039). Canonical quantization of the matter field, leading to bosons, was then carried out by P. Jordan and O. Klein, ''Zum Mehrkörperproblem der Quantentheorie,'' *Zeitschrift für Physik* **45**, 751 (1927) (doi: 10.1007/BF01329553), who referred to quantization of de Broglie waves. The fermion version of the problem was first worked out by P. Jordan and E. Wigner, ''Ober das Paulische Äquivalenzverbot,'' *Zeitschrift für Physik* **47**, 651 (1928). The term ''second quantization'' appears, for example, in the title V. Fock, ''Konfigurationsraum und zweite Quantelung,'' *Zeitschrift für Physik* **75**, 622 (1932) (doi: 10.1007/bf01344458).

What we have written is essentially a functional chain rule. The variation $\delta\psi^*(\mathbf{r})$ is indexed by $\mathbf{r}$ (and t, in fact), and the functional derivative $\delta L/\delta\psi^*(\mathbf{r})$ is a function of $\mathbf{r}$ in the same sense that the partial derivative $\partial L/\partial q^\alpha$ is a function of the discrete index α. In the discrete case, the chain rule would then involve the inner product $(\partial L/\partial q^\alpha)\,\delta q^\alpha$, which here goes over to the integral with $\delta\psi^*(\mathbf{r})$. Now, integrating by parts via the identity $\nabla(\phi\mathbf{A}) = (\nabla\phi)\cdot\mathbf{A} + \phi\nabla\cdot\mathbf{A}$, discarding the surface term, we obtain

$$\delta S = \int dt \int d^3r \left(\frac{\delta L}{\delta\psi^*} - \nabla\cdot\frac{\delta L}{\delta(\nabla\psi^*)}\right)\delta\psi^*. \tag{20.8}$$

Then we can identify the parenthetic quantity as the functional derivative (appearing as in inner product with the perturbation $\delta\psi^*$ to produce the total variation) as

$$\frac{\delta S}{\delta\psi^*} = \frac{\delta L}{\delta\psi^*} - \nabla\cdot\frac{\delta L}{\delta(\nabla\psi^*)}. \tag{20.9}$$

Carrying out these derivatives (which amount to partial derivatives, discarding the integration, again in analogy to the partial derivative $\partial/\partial q^\alpha$), we find

$$\frac{\delta S}{\delta\psi^*} = i\hbar\dot{\psi} + \frac{\hbar^2}{2m}\nabla^2\psi - V\psi. \tag{20.10}$$

Then the variational principle, which is that the action should be first-order stationary with respect to variation of ψ^*,

$$\frac{\delta S}{\delta\psi^*} = 0, \tag{20.11}$$

clearly yields the Schrödinger equation (20.4). Similarly, it is not hard to verify that the conjugate action principle

$$\frac{\delta S}{\delta\psi} = 0 \tag{20.12}$$

yields

$$-i\hbar\dot{\psi}^*(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi^* + \psi^*\,V(\mathbf{r},t), \tag{20.13}$$

the conjugated Schrödinger equation.

Now we can work out the conjugate momentum field to ψ as

$$\pi = \frac{\delta L}{\delta\dot{\psi}} = i\hbar\psi^*, \tag{20.14}$$

(conjugate momentum field)

while the conjugate momentum field to ψ^* is

$$\tilde{\pi} = \frac{\delta L}{\delta\dot{\psi}^*} = 0. \tag{20.15}$$

The latter result seems a little odd, and appears as a constraint. The defining relation for π also appears as a constraint (instead of a dynamical equation, as for example in particle mechanics it would be related to the velocity and thus a time derivative would appear). The interpretation is that ψ and ψ^* are not *really* independent variables, and basically now the conjugate momentum π will track the conjugate field. Technically, these constraints require some care, but here they are simple enough that we will just make use of these constraint equations as needed.

Now the Hamiltonian is given as usual in terms of the Lagrangian by

$$H = \int d^3r \left(\pi\dot{\psi} + \tilde{\pi}\dot{\psi}^*\right) - L. \tag{20.16}$$

Putting in the two equations for the conjugate momenta, we have

$$H = i\hbar \int d^3r\, \psi^* \dot{\psi} - \int d^3r \left(i\hbar \psi^* \dot{\psi} - \frac{\hbar^2}{2m} \nabla\psi^* \cdot \nabla\psi - \psi^* V \psi \right). \tag{20.17}$$

Now we see that the time-derivative terms cancel; simplifying and rewriting in terms of only the canonical pair (ψ, π), we obtain the canonical Hamiltonian

$$H = \int d^3r \left(-\frac{i\hbar}{2m} \nabla\pi \cdot \nabla\psi - \frac{i}{\hbar} \pi V(\mathbf{r}, t) \psi \right) \tag{20.18}$$

(matter-field Hamiltonian)

for the matter field. Incidentally, we can work out Hamilton's equations, which read

$$\begin{aligned} \dot{\pi} &= -\frac{\delta H}{\delta \psi} = -\frac{i\hbar}{2m} \nabla^2 \pi + \frac{i}{\hbar} \pi V \\ \dot{\psi} &= \frac{\delta H}{\delta \pi} = \frac{i\hbar}{2m} \nabla^2 \psi - \frac{i}{\hbar} V \psi. \end{aligned} \tag{20.19}$$

The latter equation is just the Schrödinger equation for ψ, and the former equation is the conjugate Schrödinger equation for π (and thus ψ^*).

20.2.2 Brackets and Commutators

To proceed, we need the classical Poisson bracket, which we defined before [Eq. (0.35)] via

$$[f, g]_{\text{P}} := \frac{\partial f}{\partial q^\alpha} \frac{\partial g}{\partial p_\alpha} - \frac{\partial f}{\partial p_\alpha} \frac{\partial g}{\partial q^\alpha}. \tag{20.20}$$

The appropriate generalization to fields is

$$\big[f(\mathbf{r}), g(\mathbf{r}') \big]_{\text{P}} := \int d^3r'' \left[\frac{\delta f(\mathbf{r})}{\delta \psi(\mathbf{r}'')} \frac{\delta g(\mathbf{r}')}{\delta \pi(\mathbf{r}'')} - \frac{\delta f(\mathbf{r})}{\delta \pi(\mathbf{r}'')} \frac{\delta g(\mathbf{r}')}{\delta \psi(\mathbf{r}'')} \right]. \tag{20.21}$$

The functional derivatives that we need to compute are simple generalizations of the derivative rule $\partial x_i / \partial x_j = \delta_{ij}$, which becomes $\delta x(t)/\delta x(t') = \delta(t - t')$ in the functional language. Thus, the canonical bracket is

$$\big[\psi(\mathbf{r}), \pi(\mathbf{r}') \big]_{\text{P}} = \int d^3r''\, \delta^3(\mathbf{r} - \mathbf{r}'')\, \delta^3(\mathbf{r}' - \mathbf{r}'') = \delta^3(\mathbf{r} - \mathbf{r}'). \tag{20.22}$$

In quantizing this system, we thus promote ψ and π to operators $\hat{\psi}$ and $\hat{\pi}$, satisfying the commutation relations

$$\begin{aligned} \big[\hat{\psi}(\mathbf{r}), \hat{\pi}(\mathbf{r}') \big] &= i\hbar \delta^3(\mathbf{r} - \mathbf{r}') \\ \big[\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}') \big] &= 0 \\ \big[\hat{\pi}(\mathbf{r}), \hat{\pi}(\mathbf{r}') \big] &= 0 \end{aligned} \tag{20.23}$$

(bosonic matter-field commutators)

where the latter two follow from the analogous trivial Poisson brackets. Note in particular that the canonical bracket may be rewritten in the useful form

$$\big[\hat{\psi}(\mathbf{r}), \hat{\psi}^\dagger(\mathbf{r}') \big] = \delta^3(\mathbf{r} - \mathbf{r}'), \tag{20.24}$$

in terms of only the coordinate field and conjugate.

The Hamilton equations (20.19) are still valid after quantization. Now, however, we should interpret them as Heisenberg equations of motion for the canonical field operators. (But see the discussion below in Section 20.3.2 on symmetrization of the Hamiltonian, which affects the form of these Heisenberg equations.)

20.3 Expansion into Normal Modes

Going back to the single-particle Hamiltonian

$$\hat{H}^{(1)} := -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) \tag{20.25}$$

corresponding to the first-quantized Schrödinger equation (20.4), we will make use of its energy eigenfunctions $\phi_j(\mathbf{r})$, satisfying

$$\hat{H}^{(1)}\phi_j(\mathbf{r}) = E_j\phi_j(\mathbf{r}), \tag{20.26}$$

and forming a complete, orthonormal set (assuming a discrete spectrum). A general function of space and time can be represented as a time-dependent superposition of these mode functions. The matter-field operator can be similarly written as a superposition of the mode functions, but we must regard the superposition coefficients $\hat{a}_j(t)$ as operators:

$$\hat{\psi}(\mathbf{r},t) = \sum_j \hat{a}_j(t)\,\phi_j(\mathbf{r}). \tag{20.27}$$

In order to satisfy the Schrödinger equation (20.4), the time dependence of the operators must be of the form $\hat{a}_j(t) = \hat{a}_j(0)\,e^{-iE_jt/\hbar} =: \hat{a}_j(0)\,e^{-i\omega_j t}$.

Now to work out the properties of the mode operators $\hat{a}_j$, we can take the mode expansion of the field commutator (with the field operators at zero time)

$$\left[\hat{\psi}(\mathbf{r}),\hat{\psi}(\mathbf{r}')\right] = 0 = \sum_{jj'}\left[\hat{a}_j,\hat{a}_{j'}\right]\phi_j(\mathbf{r})\,\phi_{j'}(\mathbf{r}'), \tag{20.28}$$

multiply by $\phi_k^*(\mathbf{r})\,\phi_{k'}^*(\mathbf{r}')$, and then integrate over $\mathbf{r}$ and $\mathbf{r}'$, using the orthonormality of the mode functions. The result is the mode commutator

$$\left[\hat{a}_k,\hat{a}_{k'}\right] = 0. \tag{20.29}$$

Similarly, with the canonical-pair commutator

$$\left[\hat{\psi}(\mathbf{r}),\hat{\psi}^\dagger(\mathbf{r}')\right] = \delta^3(\mathbf{r}-\mathbf{r}') = \sum_{jj'}\left[\hat{a}_j,\hat{a}_{j'}^\dagger\right]\phi_j(\mathbf{r})\,\phi_{j'}^*(\mathbf{r}'), \tag{20.30}$$

we can again multiply by $\phi_k^*(\mathbf{r})\,\phi_{k'}(\mathbf{r}')$ and integrate to find

$$\left[\hat{a}_k,\hat{a}_{k'}^\dagger\right] = \delta_{kk'}. \tag{20.31}$$

Finally, the remaining commutator

$$\left[\hat{\pi}(\mathbf{r}),\hat{\pi}(\mathbf{r}')\right] = 0 \tag{20.32}$$

with the same procedure yields

$$\left[\hat{a}_k^\dagger,\hat{a}_{k'}^\dagger\right] = 0. \tag{20.33}$$

Summarizing these commutation relations for the mode operators, we have

$$\begin{aligned}\left[\hat{a}_k,\hat{a}_{k'}^\dagger\right] &= \delta_{kk'}\\ \left[\hat{a}_k,\hat{a}_{k'}\right] &= 0\\ \left[\hat{a}_k^\dagger,\hat{a}_{k'}^\dagger\right] &= 0.\end{aligned} \tag{20.34}$$
(bosonic mode commutators)

It will turn out that these commutators are appropriate for describing bosons, and thus we will refer to these relations as **bosonic commutation relations** for the mode operators. The commutators (20.23) are similarly bosonic.

What we have found in Eqs. (20.34) is that the $\hat{a}_k$ are the annihilation operators for *independent* harmonic oscillators, just as in the case of the electromagnetic field. Thus, all of the formalism we developed for the harmonic oscillator applies here to the individual modes. In particular,

$$\hat{n}_k := \hat{a}_k^\dagger \hat{a}_k \tag{20.35}$$
(number operator, kth mode)

is the number operator for the kth mode, which we can interpret as representing the number of particles in mode k. The sum of these,

$$\hat{N} := \sum_k \hat{a}_k^\dagger \hat{a}_k, \tag{20.36}$$
(total number operator)

is the total-particle-number operator for the matter field.

20.3.1 Normal-Mode Hamiltonian

Returning to the Hamiltonian (20.18), which is now an operator after second quantization, we can eliminate the momentum operator to write

$$\hat{H} = \int d^3r \left(\frac{\hbar^2}{2m} \nabla\hat{\psi}^\dagger \cdot \nabla\hat{\psi} + \hat{\psi}^\dagger V(\mathbf{r},t)\,\hat{\psi} \right). \tag{20.37}$$

Integration by parts, we can put this Hamiltonian into the standard form

$$\hat{H}(t) = \int d^3r\, \hat{\psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) \right) \hat{\psi}(\mathbf{r}) = \int d^3r\, \hat{\psi}^\dagger H^{(1)} \hat{\psi},$$
(matter-field Hamiltonian) (20.38)

in terms of the single-particle Hamiltonian operator (which is now *not* an operator on the Hilbert space, because for example $\mathbf{r}$ is now just a dummy integration variable). Then putting in the mode expansion (20.27), we obtain

$$\hat{H}(t) = \sum_{jj'} \hat{a}_j^\dagger\, \hat{a}_{j'} \int d^3r\, \phi_j^* H^{(1)} \phi_{j'}. \tag{20.39}$$

Since we are dealing with eigenmodes of $H^{(1)}$, the integral s has the value $E_{j'}\delta_{jj'} =: \hbar\omega_j \delta_{jj'}$, and thus the Hamiltonian becomes

$$\hat{H} = \sum_j \hbar\omega_j \hat{a}_j^\dagger \hat{a}_j. \tag{20.40}$$
(normal-mode Hamiltonian)

This is indeed the Hamiltonian for a collection of decoupled harmonic oscillators of frequencies ω_j. The operator $\hat{a}_j^\dagger$ raises the total energy by the mode energy E_j, and thus we can interpret this as creating a particle in the jth mode with this associated (single-particle) energy. Similarly, $\hat{a}_j$ annihilates a particle in that mode.

20.3.2 Fixing the Zero-Point Energy

However, the zero-point energy $\hbar\omega_j/2$ for each of the oscillators is missing in the Hamiltonian (20.40). What happened? The problem is that we took classical coefficients $a_j(t)$ and $a_j^*(t)$, and we quantized them by imposing commutation relations. The classical Hamiltonian involved the product $a_j^* a_j$, which went over to the quantum-mechanical $\hat{n}_j = \hat{a}_j^\dagger \hat{a}_j$. However, these operators don't commute, and thus there is an ordering ambiguity that we did not address.

From our earlier discussion of classical–quantum correspondence (Section 6.1.3), the appropriate operator combination to match $a_j^* a_j$ is the symmetrized form $[\hat{a}_j^\dagger, \hat{a}_j]_+/2$ which is of course the same as $\hat{a}_j^\dagger \hat{a}_j + 1/2$. Making this adjustment in the Hamiltonian (20.40), we obtain

$$\hat{H} = \sum_j \hbar\omega_j \left(\hat{a}_j^\dagger \hat{a}_j + \frac{1}{2} \right), \tag{20.41}$$
(bosonic Hamiltonian in normal modes)

as expected.

This ordering ambiguity traces back to the ordering of the canonical variables in the Hamiltonian (20.18), since it is bilinear in $\hat{\psi}$ and $\hat{\phi}$. This is also the case in the form (20.38) which is bilinear in $\hat{\psi}^\dagger$ and $\hat{\psi}$. As quantum Hamiltonians, these should both also be symmetrized in the same way. In both forms, this guarantees the Hermiticity of the canonical Hamiltonian, which is of course a good thing [though note that in the form (20.38), there is no problem with Hermiticity]. It may seem that ignoring this ordering issue only misses an arbitrary energy offset (and a divergent one, at that). However, in certain problems, this offset is physically important (as in the Casimir effect, which is sensitive to variations in the $\hbar\omega_j$'s). We will also see that it is possible to account for this energy offset in an alternate way, when we discuss the chemical potential in Section 20.6.2.

20.4 Comparison to First Quantization

When we dealt before with (first-quantized) states of multiple particles (Section 10.4.1), we wrote two-particle states as

$$|\psi\rangle = |(\psi_1)_A\,(\psi_2)_B\rangle \tag{20.42}$$

in the case of distinguishable particles. In the indistinguishable case the particle labels A and B are unphysical, and the state (or representation) must be explicitly symmetrized or antisymmetrized. Now we will look at analogous states in second quantization to see how they compare to these former states.

20.4.1 Fock States

Since we have the field as a collection of harmonic oscillators, we can define the **vacuum state** $|0\rangle$ such that

$$\hat{a}_k|0\rangle = 0, \qquad \forall_k. \tag{20.43}$$

That is, $|0\rangle$ is the ground state for *every* field mode. As a matter of notation, we can write the creation of a single particle in the kth mode as

$$\hat{a}_k^\dagger|0\rangle = |1_k\rangle. \tag{20.44}$$

That is, we only label the occupied mode, and the unlabeled modes are still in their ground states. In the case of creating n particles in the kth mode,

$$\left(\hat{a}_k^\dagger\right)^n|0\rangle = \sqrt{n!}|n_k\rangle, \tag{20.45}$$

there is also a factor of $\sqrt{n!}$ involved, owing to the action $a^\dagger|n-1\rangle = \sqrt{n}|n\rangle$ of the creation operator. Now in the general case of particles occupying many modes, we would write the normalized state as.

$$\frac{1}{\sqrt{n_1!n_2!\cdots n_k!\cdots}}\left(\hat{a}_1^\dagger\right)^{n_1}\left(\hat{a}_2^\dagger\right)^{n_2}\cdots\left(\hat{a}_k^\dagger\right)^{n_k}\cdots|0\rangle = |n_1, n_2, \ldots, n_k, \ldots\rangle. \tag{20.46}$$

This state has a definite number of particles n_k in the kth mode. Thus, the state is an eigenstate of each mode-number operator $\hat{n}_k = \hat{a}_k^\dagger\hat{a}_k$:

$$\hat{n}_k|n_1, n_2, \ldots, n_k, \ldots\rangle = n_k|n_1, n_2, \ldots, n_k, \ldots\rangle. \tag{20.47}$$

Then the total number of particles is the sum of the occupation numbers in each mode:

$$\hat{N}|n_1, n_2, \ldots, n_k, \ldots\rangle = N|n_1, n_2, \ldots, n_k, \ldots\rangle., \qquad \hat{N} = \sum_k \hat{n}_k., \qquad N = \sum_k n_k. \tag{20.48}$$

Now in a definite N-particle state of finite N, this sum must converge, implying an upper bound $k \leq N$ of occupied modes. Thus, we could write an N-particle state as

$$|n_1, \ldots, n_k\rangle = \frac{1}{\sqrt{n_1!\cdots n_k!}}\left(\hat{a}_1^\dagger\right)^{n_1}\cdots\left(\hat{a}_k^\dagger\right)^{n_k}|0\rangle, \tag{20.49}$$

(bosonic N-particle state)

dropping the labels for unoccupied modes. But owing to the last of the commutators (20.34), which we can write as

$$\hat{a}_k^\dagger \hat{a}_{k'}^\dagger = \hat{a}_{k'}^\dagger \hat{a}_k^\dagger, \tag{20.50}$$

the order of particle creation is irrelevant. Thus we can freely permute the creation operators, and explicitly averaging over all $N!$ possible permutations, we could write instead

$$|n_1, \ldots, n_k\rangle = \frac{1}{\sqrt{n_1! \cdots n_k!}} \frac{1}{N!} \sum_{\boldsymbol{\sigma} \in P(N)} \hat{a}_{\sigma_1}^\dagger \cdots \hat{a}_{\sigma_N}^\dagger |0\rangle. \tag{20.51}$$

(bosonic N-particle state)

Here, we are using the notation of permutations $\boldsymbol{\sigma}$ of $\{1, \ldots, N\}$ (where each permutation component is a different value $\sigma_k \in \{1, \ldots, N\}$).

The bosonic states (20.49) and (20.51) are completely equivalent, and thus we see that exchange symmetry is built in to these particle-number states, enforced by creation-operator commutation. This is why we described the commutators (20.34) as the *bosonic* mode commutators. Note that we can explicitly avoid the unphysical particle labels with this built-in symmetrization. Such labels would come about by tagging the first created particle as particle A, the second created particle as particle B, and so on. But since the creation order is arbitrary, there is no need for such labels—we simple keep track of how many particles ended up in each mode.

These states of definite particle number are commonly called **Fock states**[3] The states we have considered so far are also eigenstates of each mode-number operator $\hat{n}_k$, and are thus energy eigenstates with total energy

$$E = \sum_{j=1}^{k} n_j E_j. \tag{20.52}$$

It is also possible to have Fock states that have a definite total particle number but *not* well-defined numbers of particles in each mode. A simple way to see this is to consider superpositions of different Fock states of the same total particle number. The mode-occupation-number states we have considered are handy as basis Fock states—they define the **occupation-number representation**—but other useful representations are possible.

One more note about the Fock state (20.51) is in order. We have explicitly omitted the time dependence of the creation operators $\hat{a}_j^\dagger$, and they should be interpreted as their initial values $\hat{a}_j^\dagger(0)$. This is because, in quantizing the matter field into a dynamical operator, we are implicitly working in the Heisenberg picture. The creation operators here are associated with defining an initial state (static in the Heisenberg picture), which is the reason for omitting their time dependence. In transforming to the Schrödinger picture, we would simply use $\hat{\psi}(\mathbf{r}, t = 0)$ for the field operator and introduce the time dependence $\hat{a}_j(t) = \hat{a}_j(0)\, e^{-i\omega t}$ in the Fock-state expression (20.51), which gives the states in the mode-number representation their natural time dependence.

20.4.2 Localized Fock States

Returning to the mode expansion (20.27), suppose that we project out the jth creation operator via

$$\hat{a}_j^\dagger(t) = \int d^3r\, \hat{\psi}^\dagger(\mathbf{r}, t)\, \phi_j(\mathbf{r}). \tag{20.53}$$

Putting this expression at $t = 0$ repeatedly into Fock state (20.51), we can write the mode-number Fock state as

$$|n_1, \ldots, n_k\rangle = \frac{1}{\sqrt{n_1! \cdots n_k!}} \frac{1}{N!} \int d^3r_1 \cdots d^3r_N\, \hat{\psi}^\dagger(\mathbf{r}_1) \cdots \hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle \sum_{\boldsymbol{\sigma} \in P(N)} \phi_{\sigma_1}(\mathbf{r}_1) \cdots \phi_{\sigma_N}(\mathbf{r}_N). \tag{20.54}$$

[3]Named after V. Fock, "Konfigurationsraum und zweite Quantelung," *Zeitschrift für Physik* **75**, 622 (1932) (doi: 10.1007/bf01344458).

Note that this is a weighted superposition of states of the form

$$|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle := \frac{1}{\sqrt{N!}}\hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle,$$

(localized bosonic Fock state) (20.55)

which we will now identify as a *localized*, bosonic Fock state. Its nature as a Fock state comes from seeing that it is an eigenstate of the total-number operator $\hat{N}$, with eigenvalue N (Problem 20.1):

$$\hat{N}|\Psi\rangle = N|\Psi\rangle. \tag{20.56}$$

Furthermore, it is possible to show that it is normalized in the sense (Problem 20.2)

$$\langle\Psi(\mathbf{r}'_1,\ldots,\mathbf{r}'_N)|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle = \frac{1}{N!}\sum_{\boldsymbol{\sigma}\in P(N)}\delta^3(\mathbf{r}_1-\mathbf{r}'_{\sigma_1})\cdots\delta^3(\mathbf{r}_N-\mathbf{r}'_{\sigma_N}). \tag{20.57}$$

That is, the normalization is of the form of a product of delta functions $\delta^3(\mathbf{r}_k-\mathbf{r}'_k)$, which is expected in a continuous coordinate space, just as for ordinary position eigenstates $|\mathbf{r}\rangle$ in first quantization. However, there is again an average over all permutations of one of the sets of coordinates (here, the primed coordinates, but either set will do). Again, this is the natural exchange symmetrization appropriate for bosons, built right in to the state's normalization. The exchange-symmetrization property follows directly from the (bosonic) field commutators (20.23). The properties (20.55) and (20.57) of the localized Fock state also cement the notion of $\psi^\dagger(\mathbf{r})$ as the creation operator for a single boson at location $\mathbf{r}$.

Now what remains is the amplitude of the localized Fock state in the mode-number state (20.54). We can project this out using the orthonormality relation (20.57) to obtain

$$\langle\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)|n_1,\ldots,n_k\rangle = \frac{1}{\sqrt{n_1!\cdots n_k!N!}}\sum_{\boldsymbol{\sigma}\in P(N)}\phi_{\sigma_1}(\mathbf{r}_1)\cdots\phi_{\sigma_N}(\mathbf{r}_N). \tag{20.58}$$

Note that the exchange symmetrization here came from both the permutation sum in Eq. (20.55) as well as the (redundant) permutation average in the orthonormality relation (20.57). In any case, for the Fock state $|n_1,\ldots,n_k\rangle$, this expression gives the probability amplitude for a joint position measurement to find a particle at each of $\mathbf{r}_1,\ldots,\mathbf{r}_N$. Squaring this amplitude gives rise to the generalization of the exchange interaction in the joint position density of two bosons that we considered before [Eq. (10.98)].

The amplitude (20.58) also corresponds directly to an N-body wave function in first quantization. In particular it is an eigenfunction of the combination of N one-body Hamiltonians

$$\hat{H} = \sum_{j=1}^{N}\hat{H}^{(1)}(\mathbf{r}_j). \tag{20.59}$$

in terms of the one-body Hamiltonian $\hat{H}^{(1)}(\mathbf{r})$ defined in Eq. (20.25). The corresponding energy eigenvalue is $\sum_{j=1}^{k} n_j E_j$, as expected. Thus, the second-quantized formalism can fully reproduce the results from first quantization.

20.5 Fermions

So far, we have seen that canonical quantization of the matter field ψ, satisfying the one-particle Schrödinger equation, leads naturally to a formalism for handling many identical bosons. But what happened to fermions? Remember that even exchange symmetry of bosons follows from the commutation relations (20.23) and (20.34), in particular in the forms

$$\hat{\psi}^\dagger(\mathbf{r})\,\hat{\psi}^\dagger(\mathbf{r}') = \hat{\psi}^\dagger(\mathbf{r}')\,\hat{\psi}^\dagger(\mathbf{r}), \qquad \hat{a}_k^\dagger\hat{a}_{k'}^\dagger = \hat{a}_{k'}^\dagger\hat{a}_k^\dagger, \tag{20.60}$$

so that the order of creation of a pair of particles is irrelevant. That is, in second quantization, swapping the order of creation of two particles is the counterpart of swapping particle labels in first quantization. Then for fermions, what we would expect is that swapping particles should be accompanied by a minus sign:

$$\hat{\psi}^\dagger(\mathbf{r})\,\hat{\psi}^\dagger(\mathbf{r}') = -\hat{\psi}^\dagger(\mathbf{r}')\,\hat{\psi}^\dagger(\mathbf{r}), \qquad \hat{a}_k^\dagger \hat{a}_{k'}^\dagger = -\hat{a}_{k'}^\dagger \hat{a}_k^\dagger. \tag{20.61}$$

This suggests that there should be *anti*commutation relations for fermions that replace the bosonic commutation relations. Thus, for field operators we will take the anticommutation relations

$$\begin{aligned} \big[\hat{\psi}(\mathbf{r}), \hat{\pi}(\mathbf{r}')\big]_+ &= i\hbar\delta^3(\mathbf{r}-\mathbf{r}') \\ \big[\hat{\psi}(\mathbf{r}), \hat{\psi}(\mathbf{r}')\big]_+ &= 0 \\ \big[\hat{\pi}(\mathbf{r}), \hat{\pi}(\mathbf{r}')\big]_+ &= 0 \end{aligned} \tag{20.62}$$
(fermionic matter-field commutators)

to replace the bosonic commutators (20.23), and in terms of mode operators, we will take the anticommutation relations

$$\begin{aligned} \big[\hat{a}_k, \hat{a}_{k'}^\dagger\big]_+ &= \delta_{kk'} \\ \big[\hat{a}_k, \hat{a}_{k'}\big]_+ &= 0 \\ \big[\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger\big]_+ &= 0. \end{aligned} \tag{20.63}$$
(fermionic mode commutators)

to replace the bosonic commutators (20.63). The same normal-mode decomposition (20.27),

$$\hat{\psi}(\mathbf{r},t) = \sum_j \hat{a}_j(t)\,\phi_j(\mathbf{r}), \tag{20.64}$$

still applies here, and is consistent with both of the above sets of anticommutations. Note that these anticommutators are *extra* axioms that we take as a *replacement* for canonical quantization—fermions have no natural counterpart in classical mechanics (i.e., the exclusion principle is a purely quantum effect).

The anticommutators (20.61) can be written for the same position or mode as

$$\big[\hat{\psi}^\dagger(\mathbf{r})\big]^2 = 0, \qquad \big(\hat{a}_k^\dagger\big)^2 = 0. \tag{20.65}$$

These identities embody Pauli exclusion: in the latter case, two fermions cannot be created in the same mode. In the former case, two fermions cannot be created at the same position—something we saw earlier in the exchange interaction, where two fermions could not be detected at the same position [Eq. (10.100)]. It furthermore follows that the square of the number operator $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ for the kth mode is

$$\begin{aligned} \hat{n}_k^2 = \big(\hat{a}_k^\dagger \hat{a}_k\big)^2 &= \hat{a}_k^\dagger \hat{a}_k \hat{a}_k^\dagger \hat{a}_k \\ &= \hat{a}_k^\dagger \big(1 - \hat{a}_k^\dagger \hat{a}_k\big)\hat{a}_k \\ &= \hat{a}_k^\dagger \hat{a}_k = \hat{n}_k, \end{aligned} \tag{20.66}$$

and thus the fermionic mode-number operator is a projector. Its eigenvalues then satisfy $\lambda^2 = \lambda$, and so its eigenvalues are 0 and 1. That is, any mode can contain either 0 or 1 fermions (or a superposition of these), but no more.

20.5.1 Fermionic Fock States

As in the bosonic case, we can have fermionic Fock states of well defined particle number. The counter part of the mode-number Fock state (20.49) for bosons is

$$|1_1, \ldots, 1_N\rangle = \hat{a}_1^\dagger \cdots \hat{a}_N^\dagger |0\rangle \tag{20.67}$$
(fermionic N-particle state)

for N total fermions There can be no powers of creation operators beyond the first, so there are no factorial factors. Also any occupied modes can be labeled with a single fermion, while the unlabeled modes are still unoccupied. At this point, the order of the creation operators *does* matter, as the exchange of two neighboring operators includes a sign change. In fact, this leaves a sign ambiguity in the state (20.49), which we can fix by assuming that the occupied modes are labeled in a fixed, increasing order, and defining the state as written to have the positive sign. As in the bosonic case, we can still consider an average over all permutations, but now we must track the sign associated with each one. The counterpart to (20.51) is then

$$|1_1,\ldots,1_N\rangle = \frac{1}{N!}\sum_{\boldsymbol{\sigma}\in P(N)} \epsilon_{\boldsymbol{\sigma}}\, \hat{a}^\dagger_{\sigma_1}\cdots\hat{a}^\dagger_{\sigma_N}|0\rangle, \qquad \begin{matrix}(20.68)\\ \text{(fermionic } N\text{-particle state)}\end{matrix}$$

where $\epsilon_{\boldsymbol{\sigma}}$ is a permutation symbol (generalized Levi–Civita symbol), which is $+1$ if $\boldsymbol{\sigma}$ is an even permutation of $\{1,\ldots,N\}$, and -1 if it is an odd permutation. The exchange-antisymmetric nature of this state is then made explicit.

Analogous results to the bosonic case also hold for localized fermionic Fock states. Using again the projected form of the mode operator (20.53), we can rewrite the Fock state (20.68) as

$$|1_1,\ldots,1_N\rangle = \frac{1}{N!}\int d^3r_1\cdots d^3r_N\, \hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle \sum_{\boldsymbol{\sigma}\in P(N)} \epsilon_{\boldsymbol{\sigma}}\, \phi_{\sigma_1}(\mathbf{r}_1)\cdots\phi_{\sigma_N}(\mathbf{r}_N), \tag{20.69}$$

giving the counterpart to Eq. (20.54). Here we can then identify the localized, fermionic Fock state

$$|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle := \frac{1}{\sqrt{N!}}\hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle, \qquad \begin{matrix}\\ \text{(localized fermionic Fock state)}\end{matrix}\quad (20.70)$$

which is the counterpart of the bosonic form (20.55), having exactly the same form except the rules by which the creation operators play. This is still a state of N total particles (Problem 20.1), and it has the analogous delta-function normalization (Problem 20.2)

$$\langle\Psi(\mathbf{r}'_1,\ldots,\mathbf{r}'_N)|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle = \frac{1}{N!}\sum_{\boldsymbol{\sigma}\in P(N)} \epsilon_{\boldsymbol{\sigma}}\, \delta^3(\mathbf{r}_1-\mathbf{r}'_{\sigma_1})\cdots\delta^3(\mathbf{r}_N-\mathbf{r}'_{\sigma_N}), \tag{20.71}$$

which is antisymmetrized via the permutation symbol.

Then, as in the bosonic Eq. (20.58), the remaining part of the mode-number Fock state is

$$\langle\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)|n_1,\ldots,n_N\rangle = \frac{1}{\sqrt{N!}}\sum_{\boldsymbol{\sigma}\in P(N)} \epsilon_{\boldsymbol{\sigma}}\, \phi_{\sigma_1}(\mathbf{r}_1)\cdots\phi_{\sigma_N}(\mathbf{r}_N). \tag{20.72}$$

Again, this corresponds to an exchange-antisymmetric state, giving the amplitude for a joint position measurement to find a fermion at each of $\mathbf{r}_1,\ldots,\mathbf{r}_N$. Again, this corresponds to the joint position density of two fermions that we considered before [Eq. (10.98)]. This is also an eigenstate of the combination (20.59) of N one-body Hamiltonians, and thus provides the fermionic counterpart to the first-quantized formalism. Note that the sum over permutations in Eq. (20.72) has the form of a determinant, due to the permutation symbol, and an antisymmetrized product of this form (not necessarily in terms of eigenmodes) is called a **Slater determinant**.

20.6 Particle-Interaction Potential

The second-quantized formalism as we have developed it so far is useful for representing states of multiple particles. However it is even better if the particles *do* something beyond things that single particles do. In particular, we would like to be able to model interactions between the particles. The simplest interaction

that we could add to the first-quantization Hamiltonian (20.2) is a two-body interaction, represented by the interaction potential $V_2(\mathbf{r}_1, \mathbf{r}_2)$:

$$\hat{H} = \sum_{j=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_j^2 + V(\hat{\mathbf{r}}_j, t) \right) + \frac{1}{2} \sum_{j \neq k=1}^{N} V_2(\hat{\mathbf{r}}_j, \hat{\mathbf{r}}_k). \tag{20.73}$$

The factor of $1/2$ in the interaction term compensates for double-counting the interactions (since the interaction potential V_2 is symmetric in its two coordinate arguments).

To translate this interaction into the second-quantization formalism, we need to adapt the basic, one-particle Schrödinger equation (20.4) to accommodate the two-body potential. The key is to realize that quantum particle, completely localized at $\mathbf{r}'$, induces a potential for any other particle as a function of $\mathbf{r}$ via the two-body potential $V_2(\mathbf{r}, \mathbf{r}')$. In the matter-wave interpretation of the one-particle Schrödinger equation, we do not necessarily have a localized particle at $\mathbf{r}'$, but rather a density $|\psi|^2$ of particles. Thus, the total potential induced by the two-body interaction follows from integration with respect to this density:

$$V(\mathbf{r}) = \int d^3r' \, V_2(\mathbf{r}, \mathbf{r}') \left| \psi(\mathbf{r}') \right|^2. \tag{20.74}$$

Adding this extra potential to the external potential in the one-particle Schrödinger equation (20.4), we obtain

$$i\hbar \dot{\psi}(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r}, t) \, \psi + \int d^3r' \, V_2(\mathbf{r}, \mathbf{r}') \left| \psi(\mathbf{r}', t) \right|^2 \psi(\mathbf{r}, t). \tag{20.75}$$

The Schrödinger equation is now *nonlinear* in the wave function. In principle, there should be no technical problems with this, for example with normalization—the nonlinear potential acts effectively as just some time-dependent potential.

Since we are just modifying the potential (adding no derivatives of the matter field), the quantization procedure carries through with no structural changes, and (20.38) becomes

$$\hat{H}(t) = \int d^3r \, \hat{\psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) + \frac{1}{2} \int d^3r' \, \hat{\psi}^\dagger(\mathbf{r}') \, V_2(\mathbf{r}, \mathbf{r}') \, \hat{\psi}(\mathbf{r}') \right) \hat{\psi}(\mathbf{r}),$$

(matter-field Hamiltonian) (20.76)

with associated Heisenberg equation of motion

$$i\hbar \dot{\hat{\psi}}(\mathbf{r}, t) = -\frac{\hbar^2}{2m} \nabla^2 \hat{\psi} + V(\mathbf{r}, t) \, \hat{\psi} + \int d^3r' \, \hat{\psi}^\dagger(\mathbf{r}', t) \, V_2(\mathbf{r}, \mathbf{r}') \, \hat{\psi}(\mathbf{r}', t) \, \hat{\psi}(\mathbf{r}, t). \tag{20.77}$$

The factor of $1/2$ in the interaction term of the Hamiltonian again compensates for double-counting in the double integral of the interaction term. Of course, we have assumed a particular ordering of the quantized operators here, **normal ordering** (all creation operators to the left, all annihilation operators to the right). As we saw in Section 20.3.2, quantizing directly into this order will miss the proper zero-point energy of the quantized collection of harmonic oscillators. Provided that this omission is acceptable, the choice of normal ordering is convenient for handling many particles. When expanded into modes, the Hamiltonian will involve combinations of mode-ladder operators like $\hat{a}_k^\dagger \hat{a}_k$ that count occupation numbers n_k as usual. The interaction term will involve combinations like $\hat{a}_j^\dagger \hat{a}_k^\dagger \hat{a}_l \hat{a}_m$; in "diagonal" cases like $\hat{a}_k^\dagger \hat{a}_k^\dagger \hat{a}_k \hat{a}_k$, by virtue of two annihilations before the compensating creations, these terms will give the occupation number in the combination $n_k(n_k - 1)$, which will sensibly give no two-body interaction in the case of either $n_k = 0$ or $n_k = 1$.

20.6.1 Equivalence to First Quantization

We should mention at this point that it is possible to directly demonstrate the equivalence of first and second quantization for the many-body problem with two-body interactions (and, by extension, higher-order

interactions). This justifies the second-quantization approach, as well as our adoption of normal ordering. Recalling the localized Fock state (20.55)

$$|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle := \frac{1}{\sqrt{N!}}\hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle, \tag{20.78}$$

for either bosons or fermions, the idea is to write an arbitrary (Schrödinger-picture) state as a superposition of these localized Fock states as

$$|\Psi(t)\rangle = \int d^3r_1\cdots d^3r_N\,|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\,\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t). \tag{20.79}$$

Now the evolution of this state goes in the Schrödinger picture according to the Schrödinger equation

$$i\hbar|\dot{\Psi}(t)\rangle = \hat{H}|\Psi(t)\rangle \tag{20.80}$$

via the second-quantized Hamiltonian (20.76) at $t = 0$

$$\hat{H} = \int d^3r\,\hat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) + \frac{1}{2}\int d^3r'\,\hat{\psi}^\dagger(\mathbf{r}')\,V_2(\mathbf{r},\mathbf{r}')\,\hat{\psi}(\mathbf{r}')\right)\hat{\psi}(\mathbf{r}). \tag{20.81}$$

By writing out the Schrödinger equation, making the state explicit in terms of the creation operators in Eq. (20.78), and commuting the annihilation operators all the way to the right, it is possible show that the wave function $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N,t)$ satisfies the first-quantized Schrödinger equation in terms of the many-body Hamiltonian (20.73)

$$\hat{H} = \sum_{j=1}^{N}\left(-\frac{\hbar^2}{2m}\nabla_j^2 + V(\hat{\mathbf{r}}_j,t)\right) + \frac{1}{2}\sum_{j\neq k=1}^{N} V_2(\hat{\mathbf{r}}_j,\hat{\mathbf{r}}_k). \tag{20.82}$$

This argument gives the direct equivalence between first and second quantization for interacting particles, and it is reasonably obvious that this argument carries through for three-body, four-body, and higher interactions. The details of this proof make for an excellent exercise (Problem 20.4). Since particle number is explicitly conserved in first quantization by the structure of Hilbert space, this also implies that particle number is a constant of the motion in second quantization, which means $[\hat{H},\hat{N}] = 0$ (this is obvious without interactions, and maybe somewhat less so with interactions). However, this is specific to this particular interaction, which involves the number-density operator $\hat{\psi}^\dagger(\mathbf{r}')\,\hat{\psi}(\mathbf{r}')$. In other cases (notably, in relativistic systems and for quasiparticles), the particle number may not be conserved.

20.6.2 Chemical Potential

With the quantized matter field, the particle number is no longer conserved. Given that the second-quantized evolution of a state is equivalent to the first-quantized counterpart, the state evolution at least preserves the particle number, even with two-body interactions. However, in an experiment it is useful to think of having a definite number N of particles, and it would be useful to have that more explicitly reflected in the formalism here.

To see a simple way to do this, let's return to the classical Lagrangian (20.5) for the matter field, which we can rewrite in the form

$$L = \int d^3r\,\psi^*\left(i\hbar\partial_t + \frac{\hbar^2}{2m}\nabla^2 - V(\mathbf{r},t)\right)\psi. \tag{20.83}$$

The ordinary wave function would be normalized to unity, but as the basis for multiparticle theory, we can think of this being normalized to the total particle number N:

$$\int d^3r\,\psi^*\psi = N. \tag{20.84}$$

The idea is then to use a Lagrange multiplier μ to implement this equation as a constraint, adding the term $\mu(\int d^3r\,\psi^*\psi - N)$ to the Lagrangian. The Lagrangian thusly modified is

$$L = \int d^3r\,\psi^*(\mathbf{r})\left(i\hbar\partial_t + \frac{\hbar^2}{2m}\nabla^2 - V(\mathbf{r},t) + \mu\right)\psi(\mathbf{r}) - \mu N. \tag{20.85}$$

Then the Hamiltonian (20.18) is modified to

$$H(t) = \mu N + \int d^3r\,\psi^\dagger(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) - \mu\right)\psi(\mathbf{r}) \tag{20.86}$$

after also eliminating the canonical momentum in favor of ψ^*. As a bit of a technical point, it is common to drop the constant offset μN from the Hamiltonian, as it will not affect the dynamical evolution. Since we are still in first quantization at this point, dropping the energy offset can be effected formally by the unitary transformation

$$U(t,0) = e^{i\mu N t/\hbar}, \qquad \psi \longrightarrow \psi\, e^{i\mu N t/\hbar}, \tag{20.87}$$

via the Hamiltonian transformation (1.133), which means the energy offset is equivalent to a (global) phase factor of the wave function. Redefining the wave function to include this phase factor, we can ignore it completely.

The (second) quantization procedure goes through as before, including with two-body interactions, and the counterpart to (20.76) becomes

$$\hat{H}(t) = \int d^3r\,\hat{\psi}^\dagger(\mathbf{r})\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) - \mu + \frac{1}{2}\int d^3r'\,\hat{\psi}^\dagger(\mathbf{r}')\,V_2(\mathbf{r},\mathbf{r}')\,\hat{\psi}(\mathbf{r}')\right)\hat{\psi}(\mathbf{r}).$$

(matter-field Hamiltonian with chemical potential) (20.88)

The difference from before is effectively a shift in the potential energy by $-\mu$. Is this really useful? Consider that we have basically redefined the Hamiltonian by making the replacement

$$\hat{H} \longrightarrow \hat{H} - \mu\hat{N}. \tag{20.89}$$

Since $[\hat{H},\hat{N}] = 0$ as we noted above this quantity can be well defined, with value $E - \mu N$. Suppose that we consider the variation of this constant quantity, which should vanish:

$$\delta E - \mu\,\delta N = 0 \tag{20.90}$$

We can rewrite this statement as

$$\mu = \frac{\delta E}{\delta N}, \tag{20.91}$$

which gives the Lagrange multiplier the physical interpretation as the energy associated with increasing the particle number by one (holding the potential and the state otherwise fixed). We can thus identify the Lagrange multiplier as the **chemical potential**. Again, since particle number here is variable in principle, in statistical mechanics we are dealing with the grand canonical ensemble. And in the grand canonical ensemble, $\hat{H} - \mu\hat{N}$ is the operator that replaces $\hat{H}$ in the partition function $Z = \mathrm{Tr}\exp[-\beta(\hat{H} - \mu\hat{N})]$ and density operator $\rho = \exp[-\beta(\hat{H} - \mu\hat{N})]/Z$, as compared to the canonical ensemble that applies in first quantization.

As an example of the chemical potential, creating a particle in a particular field mode requires an energy equal to the zero-point energy of the associated harmonic oscillator. The chemical potential would thus be equal to this zero-point energy. For this reason, the zero-point energy of the Hamiltonian can be absorbed into the chemical potential, which further justifies the adoption of normal order and ignoring the associated energy offsets as discussed in Sections 20.3.2 and 20.6. Also, in the case of having fermions filling up the lowest N energy levels in a potential well up to energy E_F (the **Fermi energy**), the chemical potential is simply $\mu = E_\mathrm{F}$. The latter example shows that the chemical potential is a useful concept when there is a background density of particles. In problems with relatively few particles, it may be appropriate to omit the chemical potential altogether.

One last comment regarding transforming away the energy offset μN. It may seem odd that the Lagrange multiplier in the Hamiltonian (20.88) no longer appears with the explicit particle number N—that is, simply adopting this Hamiltonian may seem to try to constrain the number of particles to zero. However, note that the constraint here cannot fix a particular particle number on its own. For the constraint to work, there must be a definite particle number in the initial condition, which will then be preserved by time evolution. In Dirac's language of constraints in Section 0.5.2 or Chapter 19, this constraint is first class, and is thus associated with a gauge freedom (here, the freedom to associate μN with an offset of the Hamiltonian or with a global phase).

20.6.3 Bose–Einstein Condensation

The second-quantized formalism can be applied in a relatively simple way to **Bose–Einstein condensates (BECs)**—low-temperature boson states where a single mode has a macroscopically large occupation number. To elaborate a bit on this definition[4] of a Bose–Einstein condensate, consider the **single-particle density matrix**

$$\rho_1(\mathbf{r},\mathbf{r}';t) := \left\langle \hat{\psi}^\dagger(\mathbf{r},t)\,\hat{\psi}(\mathbf{r}',t) \right\rangle . \tag{20.92}$$

Clearly, the diagonal of this density matrix gives a measure of the density of particles in some state. To see its meaning more explicitly, suppose first that the expectation value is with respect to some N-particle state, which we may write in the form [See Eq. (20.184) in Problem 20.4]

$$|\Psi\rangle = \int d^3r_1,\ldots,d^3r_N\,|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle\,\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N). \tag{20.93}$$

That is, we have a weighted superposition in terms of the localized Fock state (20.55), where $\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)$ acts as the N-body wave function in first quantization (in the Schrödinger picture). Then writing out the Fock state in terms of creation operators, we can consider the action of $\psi(\mathbf{r},t)$ on this Fock state, commuting it to the right N times to obtain [this is part of the solution to Problem 20.4]

$$\begin{aligned}\hat{\psi}(\mathbf{r})\,|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle &= \hat{\psi}(\mathbf{r})\,\hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle \\ &= \sum_{k=1}^{N}\Big[\hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)\Big]_{-k}|0\rangle\,\delta^3(\mathbf{r}-\mathbf{r}_k),\end{aligned} \tag{20.94}$$

where the subscript "$-k$" means to delete the kth factor in the product. Then using the inner product (20.57),

$$\langle\Psi(\mathbf{r}'_1,\ldots,\mathbf{r}'_N)|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle = \frac{1}{N!}\sum_{\boldsymbol{\sigma}\in P(N)}\delta^3(\mathbf{r}_1-\mathbf{r}'_{\sigma_1})\cdots\delta^3(\mathbf{r}_N-\mathbf{r}'_{\sigma_N}), \tag{20.95}$$

but with $(N-1)$-particle states, we finally obtain the alternate form

$$\rho_1(\mathbf{r},\mathbf{r}';t) = N\int d^3r_2,\ldots,d^3r_N\;\Psi^*_{\rm s}(\mathbf{r},\mathbf{r}_2,\ldots,\mathbf{r}_N,t)\,\Psi_{\rm s}(\mathbf{r}',\mathbf{r}_2,\ldots,\mathbf{r}_N,t) \tag{20.96}$$

for the density matrix, in terms of the explicitly symmetrized wave function

$$\Psi_{\rm s}(\mathbf{r}_1,\ldots,\mathbf{r}_N,t) := \frac{1}{\sqrt{N!}}\sum_{\sigma\in P(N)}\Psi(\mathbf{r}_{\sigma_1},\ldots,\mathbf{r}_{\sigma_N},t). \tag{20.97}$$

Thus, the single-particle density matrix is a reduced density matrix, in the sense of a partial trace taken over all the other coordinates, with particle symmetrization appropriate for bosons. Since this density matrix

[4] This is the definition given by A. J. Leggett, *Quantum Liquids: Bose condensation and Cooper pairing in condensed-matter systems*, (Oxford, 2006), Sections 2.1–2.2 (ISBN: 0198526431). There he also discusses the relation to alternate definitions of Bose condensation, in terms of an order parameter, or in terms of off-diagonal long-range order.

is Hermitian, it can be diagonalized in terms of an orthonormal basis of eigenfunctionss, which we can call $\varphi(\mathbf{r},t)$ with corresponding eigenvalues $n_j(t)$:

$$\rho_1(\mathbf{r},\mathbf{r}';t) = \sum_j n_j(t)\,\varphi_j^*(\mathbf{r},t)\,\varphi_j(\mathbf{r}',t). \tag{20.98}$$

These eigenfunctions are not, in general, the single-particle eigenfunctions unless there are no interparticle interactions. The eigenvalues, however, can be interpreted as occupation numbers for the corresponding mode. Now consider the largest eigenvalue, and call it N_0. If the fraction N_0/N is of order $1/N$, then there is just an ordinary boson gas, and N_0/N is called the **condensate fraction**. In N_0/N is of order 1, however, then there is a Bose condensate occupying the corresponding mode (if multiple eigenvalues are of order 1, then there is a multi-component condensate). The $\varphi_0(\mathbf{r},t)$ eigenfunction of the condensate acts something like a wave function for the condensate, and colloquially it is often referred to as such. Also, since $\sqrt{N_0}\,\varphi_0(\mathbf{r},t)$ increases sharply as the condensate starts to form (the condensation is a second-order phase transition), it is also often called the **order parameter** of the condensate.

20.6.3.1 Mean-Field Theory: Gross–Pitaevskii Equation

Bose condensates are commonly realized in ultracold, dilute atomic gases where two-body interactions are dominant. At low temperatures, the atomic wavelengths are much larger than the scale of the atom–atom potential, and it is a good approximation to replace the interaction potential by a **contact potential**.[5] In one dimension, the contact potential can be written as a simple delta-function potential,

$$V_2(x_1,x_2) = g\,\delta(x_1-x_2). \tag{20.99}$$

(In three dimensions this potential must be regularized to handle the $1/r$ divergence associated with spherical waves; see Section 16.2.3.3 for the regularization and Section 16.2.3.4 for the relation of the g parameter to the scattering length a.) Proceeding in one dimension, with this contact potential the Heisenberg equation of motion following from the Hamiltonian in Eq. (20.88) can be written

$$i\hbar\dot{\hat{\psi}}(x,t) = -\frac{\hbar^2}{2m}\nabla^2\hat{\psi} + V(x,t)\,\hat{\psi} - \mu\hat{\psi} + g\,\hat{\psi}^\dagger\,\hat{\psi}\,\hat{\psi}. \tag{20.100}$$

At sufficiently low temperature, the condensate is nearly pure, meaning that there are few atoms in non-condensate modes, and consequently the number of atoms in the condensate is fairly well defined. In this regime it is a good approximation to replace the field operator $\hat{\psi}$ by its mean value $\langle\hat{\psi}\rangle \equiv \psi$, effectively ignoring quantum fluctuations in the particle number. This is an example of a **mean-field theory**, where the complexity of an interacting quantum field theory is greatly simplified through the approximation of replacing an operator by a mean value, something that may or may not yield accurate results. Dropping the expectation brackets, the Heisenberg equation becomes the classical wave equation

$$i\hbar\dot{\psi}(x,t) = -\frac{\hbar^2}{2m}\nabla^2\psi + V(x,t)\,\psi - \mu\psi + g\,|\psi|^2\,\psi, \tag{20.101}$$

(Gross–Pitaevskii equation)

which is the Schrödinger equation plus a nonlinear potential that is proportional to the atomic density. This equation is the **Gross–Pitaevskii equation**,[6] which is widely used in modeling dilute-gas BECs (the generalization to three dimensions is the obvious one). Here, the classical field ψ acts as an effective wave function for the condensate. From the definition in Section 20.6.3.1, we can identify ψ (at last approximately) with the order parameter $\sqrt{N_0}\,\varphi_0(\mathbf{r},t)$. For $g > 0$ the nonlinear potential produces an effective repulsion,

[5] This is a simplification; for a more precise discussion of the contact-potential approximation, see Yvan Castin, "Bose-Einstein Condensates in Atomic Gases: Simple Theoretical Results," in *Coherent Atomic Matter Waves: Les Houches Session LXXII*, R. Kaiser, C. Westbrook, and F. David, Eds. (Springer, 2001), p. 1 (doi: 10.1007/3-540-45338-5_1) (arXiv: cond-mat/0105058).

[6] E. P. Gross, "Structure of a quantized vortex in boson systems," Il Nuovo Cimento **20**, 454 (1961) (doi: 10.1007/BF02731494); L.P. Pitaevskii, "Vortex Lines in an Imperfect Bose Gas," Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki **40**, 646 (1961) [Soviet Physics JETP **13**, 451 (1961)] (`http://www.jetp.ras.ru/cgi-bin/dn/e_013_02_0451.pdf`).

and for $g < 0$ there is an effective attraction (the repulsive case is more common as it more easily leads to stable Bose condensates). Remember that the nonlinear-potential term here is implicity proportional to the particle number N via the normalization of ψ.

Note that in the discussion here of the mean field, we have in mind that the approximate state of the Bose condensate is a coherent state,

$$\hat{\psi}|\psi\rangle = \psi|\psi\rangle, \tag{20.102}$$

where for the purposes of this discussion ψ most sensibly refers to a stationary state of Eq. (20.101). Then the mean-field replacement amount to ignoring fluctuations in both the condensate number N_0 (which is *not* conserved, as particles may be exchanged between the condensate mode and other thermally occupied modes), and fluctuations in the phase evolution. Since the relative fluctuations are of the order $1/\sqrt{N_0}$, we expect the Gross–Pitaevskii equation to be useful in the limit of large condensate number.

A variational justification of the Gross-Pitaevskii equation (20.101) goes as follows. Again, we want to simplify things by replacing the operator $\hat{\psi}$ by a function (mean field) ψ, but we do not assume it is the expectation value or that we are in a coherent state. What we would like is to pick ψ in such a way as to maximize the accuracy of the resulting theory. To do this, we can treat the selection of ψ as an optimization problem. Let's return to the Hamiltonian (20.76), assume a time-indepedent external potential $V(\mathbf{r})$, assume the contact potential (20.99), and make the replacement of $\hat{\psi}$ by ψ. This leads to the energy functional[7]

$$E[\psi, \psi^*] = \int d^3r\, \psi^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + \frac{g}{2}|\psi(\mathbf{r})|^2 \right) \psi(\mathbf{r}) \tag{20.103}$$

in terms of the mean field. Now one way to choose ψ optimally is in the case of a Bose condensate in the ground state of a trapping potential, where the energy should be minimized, subject to the constraint of constant particle number N (i.e., constant normalization). Thus, tacking on a Lagrange-multiplier term $\mu(N - \int d^3r\, \psi^*\psi)$ onto Eq. (20.103), and setting $\delta E/\delta\psi^* = 0$ yields the right-hand side of the Gross–Pitaevskii equation (20.101).

20.6.3.2 Steady State

A simple application of the Gross-Pitaevskii equation (20.101) is to a Bose–Einstein condensate in a trap (commonly, a magnetic-field ''bottle'' that confines the condensate to micron length scales. If the atomic density is relatively large, then the **Thomas–Fermi approximation** is justified—the kinetic-energy term is negligible compared to the nonlinear-potential term, so it is discarded.[8] The GPE in this regime becomes

$$i\hbar\dot{\psi}(x,t) \approx V(x,t)\,\psi - \mu\psi + g\,|\psi|^2\,\psi. \tag{20.104}$$

For a static BEC in a trap, this leads to the steady-state solution

$$|\psi(x)|^2 \approx \frac{\mu - V(x,t)}{g}, \tag{20.105}$$

so that the density profile of the BEC the same as the inverted profile of the trapping potential. (Note that the chemical potential handily takes up any offsets of the potential as required to yield a positive density.) Typically the trapping potential is parabolic near the potential minimum, and so the density profile is also parabolic (as opposed to the Gaussian density profile expected for uncondensed, thermal atoms).[9] In the first observation of a BEC in dilute atomic gases, images of the condensate after a period of free expansion (with

[7]Franco Dalfovo, Stefano Giorgini, Lev P. Pitaevskii, and Sandro Stringari, ''Theory of Bose-Einstein condensation in trapped gases,'' *Reviews of Modern Physics* **71**, 463 (1999) (doi: 10.1103/RevModPhys.71.463) (arXiv: cond-mat/9806038).

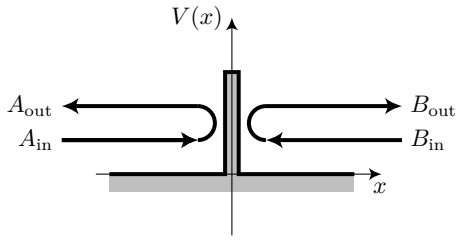
[8]This approximation in this context and the static solution was first discussed by Gordon Baym and C. J. Pethick ''Ground-State Properties of Magnetically Trapped Bose-Condensed Rubidium Gas,'' *Physical Review Letters 76*, 6 (1996) (doi: 10.1103/PhysRevLett.76.6) (arXiv: cond-mat/9508040). The ''Thomas–Fermi'' refers to an approximate, variational method for treating many electrons that focuses on the electron density as the fundamental quantity.

[9]See, for example, Figs. 8 and 9 in E. A. L. Henn, J. A. Seman, G. B. Seco, E. P. Olimpio, P. Castilho, G. Roati, D. V. Magalhães, K. M. F. Magalhães, and V. S. Bagnato, ''Bose-Einstein condensation in 87Rb: characterization of the Brazilian experiment,'' *Brazilian Journal of Physics* **38** 279 (2008) (doi: 10.1590/S0103-97332008000200012).

the trapping potential removed) could be interpreted in these same terms.[10] The atoms were trapped in an anisotropic potential well, so that there was a tightly confined direction and a loosely confined direction. A condensate evolving according to Eq. (20.104) would expand more in the tightly confined direction, because the steeper density gradients in this direction lead to stronger expansion forces (for $g > 0$). An uncondensed, thermal cloud of atoms, by contrast, would expand isotropically, because that expansion is driven by kinetic energy (which is equal in every direction by the equipartition theorem).

20.7 Mixing of Modes

As another relatively simple application of the second-quantized formalism, we will work through a toy model for scattering involving multiple particles. Suppose that we have a scattering barrier in one dimension, with two incident particles, one on each side. To see how to handle this, let's review the first-quantized version of this problem, the details of which are in Problem 2.29. In this case, we have a superposition of waves incident on the scattering potential from each side, with amplitudes A_{in} and B_{in}, scattering to outgoing waves of amplitudes A_{out} and B_{out}, as depicted schematically below.



We can then write out the ingoing waves as

$$\psi_{\text{in}}(x) = \begin{cases} A_{\text{in}} e^{ikx} & (x < 0) \\ B_{\text{in}} e^{-ikx} & (x > 0) \end{cases} \tag{20.106}$$

and the outgoing waves as

$$\psi_{\text{out}}(x) = \begin{cases} A_{\text{out}} e^{-ikx} & (x < 0) \\ B_{\text{out}} e^{ikx} & (x > 0), \end{cases} \tag{20.107}$$

where $k = \sqrt{2mE}/\hbar$ for monochromatic waves at energy E, and these solutions as written are valid outside the support of the scattering potential (i.e., outside the region where the scattering potential is nonvanishing). Then for consistency of the solutions, the outgoing amplitudes are related to the ingoing amplitudes by the matrix relation

$$\begin{bmatrix} A_{\text{out}} \\ B_{\text{out}} \end{bmatrix} = \begin{bmatrix} r & \tau' \\ \tau & r' \end{bmatrix} \begin{bmatrix} A_{\text{in}} \\ B_{\text{in}} \end{bmatrix}, \tag{20.108}$$

where r and τ refer to the reflection and transmission amplitudes, respectively, for incidence from the left-hand side, and the primed counterparts are for incidence from the right. The matrix here is unitary, and the reflection and transmission coefficients satisfy $|r|^2 + |\tau|^2 = 1$, $\tau' = \tau$, and $r'\tau^* = -r^*\tau$.

In second quantization, the amplitudes are promoted to annihilation operators $\hat{a}_{\text{in}}$, $\hat{b}_{\text{in}}$, $\hat{a}_{\text{out}}$, and $\hat{b}_{\text{out}}$, satisfying the same linear transformation:

$$\begin{bmatrix} \hat{a}_{\text{out}} \\ \hat{b}_{\text{out}} \end{bmatrix} = \begin{bmatrix} r & \tau' \\ \tau & r' \end{bmatrix} \begin{bmatrix} \hat{a}_{\text{in}} \\ \hat{b}_{\text{in}} \end{bmatrix}. \tag{20.109}$$

[10] See Fig. 2 in M. H. Anderson, J. R. Ensher, M. R. Matthews, C. E. Wieman, and E. A. Cornell, "Observation of Bose-Einstein Condensation in a Dilute Atomic Vapor," *Science* **269**, 198 (1995) (doi: 10.1126/science.269.5221.198). Also see Figs. 11 and 12 in the Henn reference in the previous footnote.

It is worth discussion for a bit the consistency of doing this, because when we developed second quantization we obtained creation and annihilation operators for modes of the single-particle Schrödinger equation. However, the ingoing and outgoing waves are not technically modes in this sense, because they do not satisfy the proper consistency conditions (e.g., boundary conditions) at the scatterer. In first quantization this is acceptable because the amplitudes must satisfy Eq. (20.108), which guarantees that the ingoing and outgoing waves occur in the right combinations to form allowed modes. It is in the same sense that the mode operators in second quantization make sense, provided that Eq. (20.109) is in force.

If we take advantage of the unitarity of the transformation matrix, it is simple to invert the linear system (20.109) and write the input operators in terms of the output operator:

$$\begin{bmatrix} \hat{a}_{\rm in} \\ \hat{b}_{\rm in} \end{bmatrix} = \begin{bmatrix} r^* & \tau^* \\ \tau'^* & r'^* \end{bmatrix} \begin{bmatrix} \hat{a}_{\rm out} \\ \hat{b}_{\rm out} \end{bmatrix}. \tag{20.110}$$

Furthermore, the creation operators are similarly related by

$$\begin{bmatrix} \hat{a}^\dagger_{\rm in} \\ \hat{b}^\dagger_{\rm in} \end{bmatrix} = \begin{bmatrix} r & \tau \\ \tau' & r' \end{bmatrix} \begin{bmatrix} \hat{a}^\dagger_{\rm out} \\ \hat{b}^\dagger_{\rm out} \end{bmatrix}, \tag{20.111}$$

relations that will be useful shortly.

20.7.1 Two-Particle Scattering

Now back to the incidence of two particles on the scattering potential, one from each side. The two-particle ingoing state is simply $\hat{a}^\dagger_{\rm in}\hat{b}^\dagger_{\rm in}|0\rangle$. Using Eqs. (20.111), we find

$$\begin{aligned} \hat{a}^\dagger_{\rm in}\hat{b}^\dagger_{\rm in}|0\rangle &= (r\hat{a}^\dagger_{\rm out} + \tau\hat{b}^\dagger_{\rm out})(\tau'\hat{a}^\dagger_{\rm out} + r'\hat{b}^\dagger_{\rm out})|0\rangle \\ &= \Big[r\tau'(\hat{a}^\dagger_{\rm out})^2 + r'\tau(\hat{b}^\dagger_{\rm out})^2 + rr'\hat{a}^\dagger_{\rm out}\hat{b}^\dagger_{\rm out} + \tau\tau'\hat{b}^\dagger_{\rm out}\hat{a}^\dagger_{\rm out}\Big]|0\rangle. \end{aligned} \tag{20.112}$$

Now the analysis differs depending on the type of particles we have on hand.

1. **Identical fermions**: The analysis for fermions is simple, owing to the property (20.65) that the square of any creation operator vanishes. Thus, the state is

$$\begin{aligned} \hat{a}^\dagger_{\rm in}\hat{b}^\dagger_{\rm in}|0\rangle &= (rr' - \tau\tau')\hat{a}^\dagger_{\rm out}\hat{b}^\dagger_{\rm out}|0\rangle \\ &= e^{i\theta}a^\dagger_{\rm out}\hat{b}^\dagger_{\rm out}|0\rangle \end{aligned} \tag{20.113}$$

   after anticommuting the operators for the different output modes. In the last step, we used that $rr' - \tau\tau'$ is the determinant of a unitary matrix (here written $e^{i\theta}$), and thus has unit modulus. This is a statement that the fermions cannot scatter into the same mode, another manifestation of the Pauli exclusion principle.

2. **Identical bosons**: For the boson case, we take advantage of the fact that creation operators for different modes to write

$$\begin{aligned} \hat{a}^\dagger_{\rm in}\hat{b}^\dagger_{\rm in}|0\rangle &= \Big[r\tau'(\hat{a}^\dagger_{\rm out})^2 + r'\tau(\hat{b}^\dagger_{\rm out})^2 + (rr' + \tau\tau')\hat{a}^\dagger_{\rm out}\hat{b}^\dagger_{\rm out}\Big]|0\rangle \\ &= \Big[r\tau(\hat{a}^\dagger_{\rm out})^2 - r^*\tau(\hat{b}^\dagger_{\rm out})^2 + \big[\tau^2 - |r|^2(\tau/\tau^*)\big]\hat{a}^\dagger_{\rm out}\hat{b}^\dagger_{\rm out}\Big]|0\rangle \\ &= \Big[r\tau(\hat{a}^\dagger_{\rm out})^2 - r^*\tau(\hat{b}^\dagger_{\rm out})^2 + e^{i2\arg\tau}\big(|\tau|^2 - |r|^2\big)\hat{a}^\dagger_{\rm out}\hat{b}^\dagger_{\rm out}\Big]|0\rangle, \end{aligned} \tag{20.114}$$

   after using $\tau' = \tau$, and $r'\tau^* = -r^*\tau$. In the last term, which represents one photon scattering into each output mode, there is a cancellation of $|r|^2$ and $\tau|^2$, and thus a suppression of this possible outcome (independent of the phases of the reflection and transmission components). The suppression

is obviously complete when the reflection and transmission components have the same magnitude. For example, if we have

$$r = \tau = \frac{1}{\sqrt{2}}, \tag{20.115}$$

then the state becomes

$$\hat{a}^\dagger_{\rm in}\hat{b}^\dagger_{\rm in}|0\rangle = \frac{1}{2}\Big[(\hat{a}^\dagger_{\rm out})^2 - (\hat{b}^\dagger_{\rm out})^2\Big]|0\rangle. \tag{20.116}$$

This says that both photons scatter into the same output mode, and each output mode is equally likely. The normalization here may seem wonky, as a superposition of two state is usually accompanied by the factor $1/\sqrt{2}$. However, the normalization here is consistent with Eq. (20.51), and should be read as the factor $1/\sqrt{2}$ for the superposition, with another factor $1/\sqrt{2!}$ because the states are doubly occupied.

3. **Distinguishable particles**: For distinguishable particles we need to modify the notation by labeling the particle types (say, 1 and 2). Putting these labels on the creation operators and dropping the ''out'' labels on the output operators, we have

$$\hat{a}^\dagger_{1,\rm in}\hat{b}^\dagger_{2,\rm in}|0\rangle = \Big[r\tau'\hat{a}^\dagger_1\hat{a}^\dagger_2 + r'\tau\hat{b}^\dagger_1\hat{b}^\dagger_2 + rr'\hat{a}^\dagger_1\hat{b}^\dagger_2 + \tau\tau'\hat{b}^\dagger_1\hat{a}^\dagger_2\Big]|0\rangle. \tag{20.117}$$

In this case the operators can commute freely, but with no special significance. The two particles scatter into the two modes completely independently, with four distinct possible outcomes.

The boson case is relatively straightforward to implement with photons, where a beam splitter takes the place of the scattering potential. In the case of a symmetric beam splitter, a pair of identical, incident photons will always ''stick together'' upon exiting the beam splitter. In quantum optics, this is known as the **Hong–Ou-Mandel effect**.[11] In principle the same effect can be observed with massive particles, in cold, degenerate gases.[12]

The above analysis is idealized, and ignores ways in which the particles could be distinguished. For example, in the case of photons the bosonic effect is only observable if the two photons have the same polarization. By changing the polarization of one of the photons, an experiment can switch easily between the distinguishable and indistinguishable cases. The same comment applies to massive particles with spin. The treatment of the modes as incoming and outgoing plane waves is another idealization of the way a real experiment would work. The state of a real particle can be reasonably modeled by a plane wave, but it will always have some finite extent, and thus some finite duration over which it will interact with the scattering potential. In order for the bosonic or fermionic effects to be manifest, both particles must be incident on the scattering potential over the same interval of time. If they are incident at widely different times, then there is an effective distinguishability due to their time of arrival. Also the wave packets of the two particles should be matched; otherwise the suppression of the glommed-together outcomes in the fermion case, or the going-separate-ways outcome in the boson case, will be reduced (depending on the overlap integral of the two wave packets).

20.7.2 Entanglement of Only One Particle

We introduced entanglement before in Sections (9.2.4) and (10.1) as a state involving two particles (e.g., two different spins), where the (first-quantized) form of the prototypical EPR/Bell state is

$$|\psi\rangle = \frac{|\uparrow\rangle_A|\downarrow\rangle_B + |\downarrow\rangle_A|\uparrow\rangle_B}{\sqrt{2}} \tag{20.118}$$

for two distinguishable, spin-$1/2$ particles A and B. It turns out that the formalism above for coupling modes is useful for answering the question, is it possible to have an entangled state involving only a *single* particle?

[11] C. K. Hong, Z. Y. Ou, and L. Mandel, ''Measurement of subpicosecond time intervals between two photons by interference,'' *Physical Review Letters* **59**, 2044 (1987) (doi: 10.1103/PhysRevLett.59.2044).

[12] An analysis in the boson case is in R. Lewis-Swan and K. Kheruntsyan, ''Proposal for demonstrating the Hong–Ou–Mandel effect with matter waves,'' *Nature Communications* **5**, 3752 (2014) (doi: 10.1038/ncomms4752).

Suppose a single particle impinges on a barrier from the left-hand side. The mode-operator relation (20.109) gives the state before and after the scattering event as

$$\begin{aligned} |\psi\rangle_{N=1} &= \hat{a}_{\text{in}}|0\rangle \\ &= \frac{1}{\sqrt{2}}\big(\hat{a}_{\text{out}} + \hat{b}_{\text{out}}\big)|0\rangle, \end{aligned} \tag{20.119}$$

in the case of equal probability of reflection or transmission, $r = \tau = 1/\sqrt{2}$. This may not look like much of an entangled state, but this state is a superposition of output Fock states,

$$|\psi\rangle_{N=1} = \frac{|1_L 0_R\rangle + |0_L 1_R\rangle}{\sqrt{2}} = \frac{|1\rangle_L|0\rangle_R + |0\rangle_L|1\rangle_R}{\sqrt{2}} \tag{20.120}$$

where we are now using the labels L and R to denote the left-going and right-going output waves, respectively. This, one must admit, strongly resembles an entangled state. On the other hand, this is the way to write this state in *second* quantization. In *first* quantization, this same state will look like a simple superposition,

$$|\psi\rangle_{N=1} = \frac{|L\rangle + |R\rangle}{\sqrt{2}}, \tag{20.121}$$

which doesn't seem very entangled at all. So which is it, entangled or not?

The answer is that it is, in fact, entangled.[13] Two see why, let's add in an extra pair of distinguishable, spin-1/2 particles A and B in the state

$$|\psi\rangle = |\uparrow_A\uparrow_B\rangle. \tag{20.122}$$

Now suppose that one is situated to the left, and the other to the right, such that each interacts with the corresponding output mode. In the case that the particle that hit the beam splitter interacts with particle A or B, suppose the interaction is such that it flips the spin of that particle. That is, our two-particle state is of the entangled form

$$|\psi\rangle = \frac{|\uparrow\rangle_A|\downarrow\rangle_B + |\downarrow\rangle_A|\uparrow\rangle_B}{\sqrt{2}}. \tag{20.123}$$

Such an interaction could happen, for example, if the beam-splitter particle carries a magnetic field strong enough to cause the right precession of the spin-1/2 particle (in which case the beam-splitter particle will also be part of the entanglement, but this can be undone by redirecting the output modes onto *another* beam splitter and making a which-way measurement on the output of that beam splitter). Alternately (and perhaps more realistically), the beam-split particle could be a photon, which gets absorbed by one or the other two-level atom to make it transition to the excited state. The crucial point is that via only *local, unitary interactions*, the state (20.119) of the first particle is translated into the entangled state (20.123). Thus, we must conclude that the single-particle state (20.119) really is entangled.

20.8 Hubbard Model

Second quantization is important in condensed-matter physics. In addition to the example of Bose–Einstein condensation in Section 20.6.3.1, we will give a brief example of how the formalism can handle many particles in a lattice potential (e.g., many electrons in a crystal lattice, or a cold, dilute gas in a lattice of laser light).

20.8.1 Lattice Potentials and Basis States

As a prelude to the many-body problem, we again need to review the corresponding details in first quantization. To keep things simple we'll stick to a particle in one dimension, in a periodic potential

$$V(x + L) = V(x), \tag{20.124}$$

[13] The argument that follows is from S. J. van Enk, "Single-particle entanglement," *Physical Review A* **72**, 064306 (2005) (doi: 10.1103/PhysRevA.72.064306) (arXiv: quant-ph/0507189), who also gives a history of this controversy.

i.e., of period L. There are two sets of useful eigenfunctions for a particle in such a potential. The first, Bloch states, we have encountered before in Section 13.3.2.1, and we will review them here.[14] The second set is complementary to the Bloch states, and it will be more useful for treating the hopping of atoms tightly bound to lattice sites.

20.8.1.1 Bloch Functions

Bloch states are extended states, akin to momentum eigenstates but with a spatially modulated amplitude. To review Bloch's theorem, let T_L be the operator that spatially translates a state by a distance L. In the position representation, the action of T_L reads

$$\langle x|T_L|\psi\rangle = \langle x+L|\psi\rangle \tag{20.125}$$

on some state $|\psi\rangle$, which implies the action

$$T_L|x\rangle = |x-L\rangle \tag{20.126}$$

on the representation basis states. Now since the potential is invariant under such translations, $T_L V(x) T_L^\dagger = V(x+L) = V(x)$, the Hamiltonian commutes with T_L, and so any energy eigenfunction must also be an eigenfunction of T_L. Since T_L is a unitary operator, the eigenvalue must have unit modulus, which we may write as e^{ikL} for some value of $k \in \mathbb{R}$. The energy eigenfunction consistent with this eigenvalue of T_L is

$$\langle x|\psi_k\rangle \equiv \psi_k(x) = e^{ikx} u_k(x), \tag{20.127}$$
(Bloch's theorem)

where $u_k(x)$ is periodic with the same period L. The index k is called the **quasimomentum**, because $\hbar k$ is analogous to the momentum of free-space plane waves. Writing out the time-independent Schrödinger equation $H|\psi_k\rangle = E_{n,k}|\psi_k\rangle$ for this eigenfunction, we have

$$\left(\frac{\hbar^2 k^2}{2m} + V(x)\right) u_k = E_k u_k. \tag{20.128}$$

Since the linear operator is real, the periodic function $u_k(x)$ is also real, and it only depends on the modulus $|k|$ of the quasimomentum, even though it may have either sign. Equation (20.127) is again **Bloch's theorem**,[15] which constrains the general form for energy eigenfunctions of periodic potentials.

Now suppose that in Bloch's theorem (20.127), we translate the quasimomentum by

$$k \longrightarrow k + \frac{2\pi n}{L} \tag{20.129}$$

for $n \in \mathbb{Z}$:

$$\psi_{k+2\pi n/L}(x) = e^{i2\pi n x/L} e^{ikx} u_{k+2\pi n/L}(x). \tag{20.130}$$

This modified Bloch state is also an eigenfunction of the translation operator T_L, with the same eigenvalue e^{ikL} as before (although in general the periodic function will now be different, and the eigenfunction will correspond to a different energy). For this reason it is conventional to decompose the quasimomentum into its integer part n, the **band index**, and the remaining fractional part k', the **reduced quasimomentum**, as

$$k = k' + \frac{2\pi n}{L}, \qquad k' \in [-\pi/L, \pi/L), \quad n \in \mathbb{Z}. \tag{20.131}$$

Since eigenvalue $e^{ikL} = e^{ik'L}$ is the same in terms of either the original or reduced quasimomentum, Bloch's theorem (20.127) may be rewritten with k' in the exponent (with a suitable redffinition of u_k). Thus,

[14] For a nice overview of this the physics of Bloch and Wannier states and their manifestations in cold-atom experiments, see Kirk William Madison, *Quantum Transport in Optical Lattices*, Ph.D. dissertation (The University of Texas at Austin, 1998) `https://raizenlab.ph.utexas.edu/pub/kirk_diss.pdf`.

[15] Felix Bloch, "Über die Quantenmechanik der Elektronen in Kristallgittern," *Zeitschrift für Physik* **52**, 555 (1929) (doi: 10.1007/BF01339455).

dropping the prime on the reduced quasimomentum, we can notate a Bloch state in terms of the band index and reduced quasimomentum thusly:

$$\psi_{n,k}(x) = e^{ikx} u_{n,k}(x). \tag{20.132}$$

The quasimomentum reduced in this way is said to be in the **first Brillouin zone**. Recalling that $u_{n,k}(x)$ only depends on $|n|$ and $|k|$ and not their signs, it is conventional to report the band index n as a nonnegative integer, with the sign in the exponent inferred from the sign of k. In fact, the Bloch states satisfy the conjugation rule

$$\begin{aligned} \psi^*_{n,k}(x) &= e^{-ikx - i2\pi nx/L} u_{n,k}(x) \\ &= e^{-ikx - i2\pi nx/L} u_{n,-k}(x) \\ &= \psi_{-n,-k}(x) \\ &=: \psi_{n,-k}(x), \end{aligned} \tag{20.133}$$

which again follows from the dependence $u_{-n,-k}(x) = u_{n,k}(x)$ of the periodic function.

The Bloch wave functions are extended and unnormalizable in the same sense as plane waves. However, the potential imposes a natural length scale, and for this reason it is common to normalize the Bloch solutions over one lattice site as

$$\int_0^L dx\, |\psi_{n,k}(x)|^2 = 1. \tag{20.134}$$

This means, for example, that if the periodic-function factors are expressed in terms of plane waves as

$$u_{n,k}(x) = \sum_j \frac{c_j(n,k)}{\sqrt{L}}\, e^{i2\pi jx/L}, \tag{20.135}$$

then the superposition coefficients must satisfy

$$\sum_j |c_j|^2 = 1. \tag{20.136}$$

However, more directly we can think of Eq. (20.134) in the limit of a free-particle, which is still a valid solution of a periodic potential. Comparing to the usual integral representation of a delta function [Eq. (1.154)],

$$\delta(p) = \frac{1}{2\pi\hbar} \int dx\, e^{ipx/\hbar}, \tag{20.137}$$

we must properly have

$$\int_{-\infty}^{\infty} dx\, \psi^*_{n',k'}(x)\, \psi_{n,k}(x) = \frac{2\pi}{L} \delta(k - k')\, \delta_{n,n'} \tag{20.138}$$

for the orthogonality relation of the Bloch solutions.

20.8.1.2 Digression: Velocity and Mass

Before continuing, it is useful to point out some interesting consequence of the Bloch solutions. Recall [Eq. (2.124)] that the probability current density may be written

$$\mathbf{j}(\mathbf{r}) = \frac{1}{m} \mathrm{Re}\big[\psi^* \mathbf{p} \psi\big]. \tag{20.139}$$

Integrating over all space changes this to the momentum expectation,

$$\int dx\, \mathbf{j} = \frac{\langle \mathbf{p} \rangle}{m} = \langle \mathbf{v} \rangle \tag{20.140}$$

which we can identify as a velocity averaged over the extent of the state. The idea is to investigate this concept of velocity in the context of Bloch states. Consider a Bloch wave function, where we suppress the band index for simplicity of notation:

$$(E_k - H)\psi_k(x) = 0. \tag{20.141}$$

Now given the Bloch theorem and its derivative,

$$\psi_k = e^{ikx}u_k(x), \qquad \frac{\partial\psi_k}{\partial k} = \left(ix + \frac{\partial_k u_k}{u_k}\right)\psi_k, \tag{20.142}$$

we can differentiate Eq. (20.141) to obtain

$$\begin{aligned}\frac{\partial E_k}{\partial k}\psi_k(x) &= (H - E_k)\frac{\partial\psi_k}{\partial k} \\ &= (H - E_k)(ix)\psi_k \\ &= -i[x, H]\psi_k - (ix)(H - E_k)\psi_k \\ &= \frac{\hbar}{m}p\,\psi_k,\end{aligned} \tag{20.143}$$

where we used the commutator $[x, H] = [x, p^2]/2m = i\hbar p/m$. Now multiplying by ψ^* on the left, we have

$$\frac{\partial E_k}{\partial k}|\psi_k|^2 = \frac{\hbar}{m}\psi_k^*\,p\,\psi_k \tag{20.144}$$

We can identify the probability current and also employ the density $\rho = |\psi_k|^2$ to find

$$\frac{1}{\hbar}\frac{\partial E_k}{\partial k} = \frac{j(x)}{\rho(x)}, \tag{20.145}$$

after dividing through by $\rho(x)$. The quantity on the left-hand side is constant, which means that $j(x)/\rho(x)$ is position-independent. If we had integrated over all space before this division, you might be tempted to intepret $\int dx\, j(x)$ as the mean velocity, but this integral diverges because the Bloch functions are unnormalizable. However, the integrals of $j(x)$ and $\rho(x)$ diverge in exactly the same way, so their *ratio* can be interpreted as the mean velocity:

$$\langle v\rangle = \frac{\int dx\, j(x)}{\int dx\, \rho(x)}. \tag{20.146}$$

Thus, the mean velocity of a Bloch state is[16]

$$\langle v\rangle = \frac{1}{\hbar}\frac{\partial E_k}{\partial k}. \tag{20.147}$$
(velocity of Bloch state)

In particular it is controlled by the energy *dispersion* (i.e., the variation of E with k). The spatial invariance of $j(x)/\rho(x)$ says that the local velocity is constant everywhere, which is a sensible thing for a stationary state. For a free particle, with $E_k = \hbar^2k^2/2m$, we find $\langle v\rangle = \hbar k/m$, as expected. However, even for Bloch states deep below the maximum height of the potential, the velocity will be nonzero—this is a manifestation of ballistic motion via tunneling. For low-energy states in deep potential wells, we would expect tunneling to occur slowly, which means that $\partial E_k/\partial k$ should be small in magnitude (with correspondingly narrow energy bands).

An external force applied to a particle in a lattice should cause it to accelerate. We can compute the acceleration from Eq. (20.146) as

$$a = \frac{d}{dt}\langle v\rangle = \frac{\partial\langle v\rangle}{\partial k}\frac{dk}{dt}. \tag{20.148}$$

Using Eq. (20.147), we find the acceleration

$$a = \frac{1}{\hbar}\frac{\partial^2 E_k}{\partial k^2}\frac{dk}{dt}. \tag{20.149}$$

[16]This velocity was given by Felix Bloch, *op. cit.*, and also by Harry Jones and Clarence Zener, "A general proof of certain fundamental equations in the theory of metallic conduction," *Proceedings of the Royal Society of London A* **144**, 101 (1934) (doi: 10.1098/rspa.1934.0036).

Now in the case of a free particle, we would have the relations $\dot{p} = \hbar\dot{k}$ and $a = \dot{p}/m$. If we assume the first relation carries over to the quasimomentum, then we could define an effective mass m^* for a Bloch state via $a = \dot{p}/m^*$, in which case[17]

$$m^* = \hbar^2 \left(\frac{\partial^2 E_k}{\partial k^2} \right)^{-1}. \tag{20.150}$$

(Bloch-state effective mass)

The effective mass is again related to energy dispersion, with a correspondingly large value for deep-in-well states.

The assumption that $a = \hbar\dot{k}/m^*$ seems reasonable based on the free-particle limit, but we should really justify it more carefully.[18] We can add a constant force F to the Bloch Hamiltonian H by changing it to $H - Fx$. Then suppose that we consider the transition amplitude from k to $k + dk$ in time dt due to this total Hamiltonian. We can write this as

$$\langle \psi_{k+dk} | U(dt, 0) | \psi_k \rangle = \frac{iF}{\hbar} \langle \psi_{k+dk} | x | \psi_k \rangle \, dt, \tag{20.151}$$

using $U(dt, 0) = -(i/\hbar)(H - Fx)\, dt$. As before, we are suppressing the band index for brevity. To compute the matrix element on the right-hand side, we can consider the matrix element of $[H, x]$:

$$(E_{k+dk} - E_k) \langle \psi_{k+dk} | x | \psi_k \rangle = \langle \psi_{k+dk} | [H, x] | \psi_k \rangle = -\frac{i\hbar}{m} \langle \psi_{k+dk} | p | \psi_k \rangle. \tag{20.152}$$

Thus,

$$\langle \psi_{k+dk} | x | \psi_k \rangle = -\frac{i\hbar}{m} \frac{\langle \psi_{k+dk} | p | \psi_k \rangle}{(\partial_k E_k)\, dk}, \tag{20.153}$$

and so the transition amplitude becomes

$$\langle \psi_{k+dk} | U(dt, 0) | \psi_k \rangle = \frac{F}{m} \frac{\langle \psi_{k+dk} | p | \psi_k \rangle}{(\partial_k E_k)\, dk/dt}. \tag{20.154}$$

Here, both the transition amplitude itself and the derivative dk/dt refer to a change dk in time dt; the only consistent solution is for this transition to happen with unit probability. That is, we should set $\langle \psi_{k+dk} | U(dt, 0) | \psi_k \rangle = \langle \psi_k | \psi_k \rangle$, and we can also replace $\langle \psi_{k+dk} | p | \psi_k \rangle$ by $\langle \psi_k | p | \psi_k \rangle$, since this leads to an ignorable correction of $O(dk)$. Now, from Eqs. (20.147) and (20.147), we have the Bloch velocity

$$\frac{\langle \psi_k | p | \psi_k \rangle}{m \langle \psi_k | \psi_k \rangle} = \langle v \rangle = \frac{1}{\hbar} \frac{\partial E_k}{\partial k}, \tag{20.155}$$

and thus Eq. (20.154) becomes

$$F = \hbar \frac{dk}{dt}. \tag{20.156}$$

This shows that the quasimomentum $\hbar k$ reacts in the same way to a constant external force as the usual momentum of the free particle.

20.8.1.3 Wannier States

For the free particle, the eigenstates are the extended plane waves, and their localized counterparts are the position eigenstates. It is useful to construct similar localized solutions in a periodic lattice, where the states would be localized about a particular lattice site. To attempt this, suppose we introduce states $|w_{n,j}\rangle$ associated with the jth lattice site, and write a Bloch state as a superposition of these lattice-site states:

$$|\psi_{n,k}\rangle = \sum_{j=-\infty}^{\infty} c_j |w_{n,j}\rangle. \tag{20.157}$$

[17] For more on the effective mass, see Neil W. Ashcroft and N. David Mermin, *Solid State Physics* (Harcourt, 1976), p. 227 (ISBN: 0030839939).

[18] Harry Jones and Clarence Zener, *op. cit.* give a longer but more precise version of this calculation in terms of a distribution of Bloch states.

Because of the translational symmetry of the Bloch states,

$$\psi_{n,k}(x+L) = \psi_{n,k}(x)\, e^{ikL}, \tag{20.158}$$

the superposition coefficients should all have the same magnitude (say, unity), differing only by a phase. Applying this same symmetry to the superposition, we have

$$\psi_{n,k}(x+L) = \sum_j c_j w_{n,j}(x+L) = \sum_j c_j w_{n,j}(x)\, e^{ikL} = \sum_j c_{j-1} w_{n,j-1}(x)\, e^{ikL}, \tag{20.159}$$

so that

$$\psi_{n,k}(x) = \sum_j c_{j-1} w_{n,j-1}(x-L)\, e^{ikL}. \tag{20.160}$$

Repeating this argument for a total of ℓ times gives

$$\psi_{n,k}(x) = \sum_j c_{j-\ell} w_{n,j-\ell}(x-\ell L)\, e^{ik\ell L}. \tag{20.161}$$

Comparing with the original series, the two are equivalent if we take

$$c_j w_{n,j}(x) = c_{j-\ell} w_{n,j-\ell}(x-\ell L)\, e^{ik\ell L}. \tag{20.162}$$

This equality is satisfied if dependence on the index j is in the form of a displacement,

$$w_{n,j}(x) \longrightarrow w_n(x-jL)m \tag{20.163}$$

and the coefficients are taken to be

$$c_j = e^{ikjL}. \tag{20.164}$$

Thus, we can write the Bloch state as

$$\psi_{n,k}(x) = \sum_j w_n(x-jL)\, e^{ikjL},$$

(Bloch state as sum of Wannier states) (20.165)

and the inverse transform is

$$w_n(x-jL) = \frac{L}{2\pi} \int_{-\pi/L}^{\pi/L} dk\, \psi_{n,k}(x)\, e^{-ikjL},$$

(Wannier state as sum of Bloch states) (20.166)

as can be verified by using Eq. (20.165) for the Bloch function and then carrying out the integral. The functions $w_n(x)$ are called **Wannier functions**,[19] and of course differ for each band index n, but otherwise are the same for each lattice site. Intuitively, for a very deep potential lattice, where the minimum of each lattice site is well approximated by a parabola, the lowest few Wannier functions are well approximated by the corresponding harmonic-oscillator eigenstates.

Since the Wannier states are defined via a unitary transform of the orthonormal Bloch basis, they are themselves orthonormal. The Wannier functions are normalized in the sense that [Problem 20.5(a)]

$$\int_{-\infty}^{\infty} dx\, w_n^2(x) = \int_0^L dx\, |\psi_{n,k}(x)|^2 \tag{20.167}$$

so that with the choice (20.134) of Bloch-function normalization, the Wannier functions are unit-normalized over all space. Note that the Wannier functions are real, owing to the transform (20.166) and the conjugation rule (20.133). The full statement of orthonormality for Wannier functions is [Problem 20.5(b)]

$$\int_{-\infty}^{\infty} dx\, w_n(x-jL)\, w_{n'}(x-j'L) = \delta_{n,n'}\, \delta_{j,j'}, \tag{20.168}$$

so that Wannier functions associated with different bands are of course orthogonal, and functions associated with different lattice sites are orthogonal as well.

[19] The pronunciation is a little tricky. The "Wann" is accented and pronounced as in "Obi-wan," and the "ier" is pronounced as "yea" as in "yea or nay." After Gregory H. Wannier, "Dynamics of band electrons in electric and magnetic fields," *Reviews of Modern Physics* **34**, 645 (1962) (doi: 10.1103/RevModPhys.34.645).

20.8.2 Hamiltonian

Now on to the model, which will be for cold collection of bosons in a periodic lattice potential (for simplicity, still in one dimension). To begin, let's return to the mode expansion (20.27), but now expressed in terms of Wannier states:

$$\hat{\psi}(x,t) = \sum_{n,j} \hat{a}_{n,j}(t)\, w_n(x - jL). \tag{20.169}$$

We will consider the limit of low temperature, where we will assume the atoms to occupy only the lowest band, and thus we can approximately write the mode expansion in terms of only $n = 0$ states,

$$\hat{\psi}(x,t) \approx \sum_{j} \hat{a}_{j}(t)\, w_0(x - jL), \tag{20.170}$$

where we have dropped the band index on the annihilation operator. Now taking the Hamiltonian (20.88) in one dimension,

$$\hat{H} = \int dx\, \hat{\psi}^\dagger(x) \bigg(-\frac{\hbar^2}{2m}\nabla^2 + V(x) - \mu + \frac{1}{2}\int dx'\, \hat{\psi}^\dagger(x')\, V_2(x,x')\, \hat{\psi}(x') \bigg) \hat{\psi}(x), \tag{20.171}$$

we can separate out the spatial components of the mode expansions into spatial intergrals. Since $w_0(x - jL)$ satisfies the one-particle, time-independent Schrödinger equation with energy E_0, we have

$$E_0 := \int dx\, w_0^*(x - jL) \bigg(-\frac{\hbar^2}{2m}\nabla^2 + V(x) \bigg) w_0(x - jL), \tag{20.172}$$

where the on-site energy is independent of j. Similarly, there are off-diagonal versions of the same quantity, which represent ''hopping'' (tunneling) amplitudes between different sites:

$$h_{jk} := -\int dx\, w_0^*(x - jL) \bigg(-\frac{\hbar^2}{2m}\nabla^2 + V(x) \bigg) w_0(x - kL). \tag{20.173}$$

The hopping matrix is Hermitian (in fact real-symmetric, since the Wannier states are real), and it only depends on the hopping distance $(j - k)$. Finally, the interaction term involves the integral

$$U_{jj'kk'} := \int dx \int dx'\, w_0^*(x - jL)\, w_0^*(x' - j'L)\, V_2(x,x')\, w_0(x' - kL)\, w_0(x - k'L). \tag{20.174}$$

In terms of these three integrals, the Hamiltonian (20.171) becomes

$$\hat{H} = (E_0 - \mu) \sum_j \hat{a}_j^\dagger \hat{a}_j - \sum_{j \neq k} h_{jk} \hat{a}_j^\dagger \hat{a}_k + \frac{1}{2} \sum_{jj'kk'} U_{jj'kk'} \hat{a}_j^\dagger \hat{a}_{j'}^\dagger \hat{a}_k \hat{a}_{k'}. \tag{20.175}$$

Now the idea is to simplify this model even more, to make it more amenable to study. First, if we assume a deep lattice potential, the hopping integrals involve Wannier functions that decay exponentially outside their potential well—and thus we can restrict the hopping coupling to nearest-neighbor lattice sites only, denoted by the summation index $\langle jk \rangle$. With uniform coupling rate h, this amounts to summing over all j, k with $h_{jk} = h(\delta_{j(k-1)} + \delta_{j(k+1)})$. Also in this regime, longer-range two-body interactions are exponentially suppressed, so we can consider only on-site interactions, making the replacement $U_{jj'kk'} \approx U\, \delta_{jk}\delta_{j'k'}\delta_{jj'}$, with the result

$$\hat{H} = (E_0 - \mu) \sum_j \hat{a}_j^\dagger \hat{a}_j - h \sum_{\langle jk \rangle} \hat{a}_j^\dagger \hat{a}_k + \frac{U}{2} \sum_j \hat{a}_j^\dagger \hat{a}_j^\dagger \hat{a}_j \hat{a}_j. \tag{20.176}$$

To clean this up a bit, we can write this Hamiltonian in terms of site-occupation numbers $\hat{n}_k := \hat{a}_k^\dagger \hat{a}_k$, and so we finally have the model Hamiltonian

$$\hat{H} = (E_0 - \mu) \sum_j \hat{n}_j - h \sum_{\langle jk \rangle} \hat{a}_j^\dagger \hat{a}_k + \frac{U}{2} \sum_j \hat{n}_j(\hat{n}_j - 1),$$

(Bose–Hubbard Hamiltonian) (20.177)

where we have used $\hat{a}^\dagger\hat{a}^\dagger\hat{a}\hat{a} = \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} - \hat{a}^\dagger\hat{a} = \hat{n}^2 - \hat{n} = \hat{n}(\hat{n}-1)$. The Hamiltonian here embodies the **Bose–Hubbard model**[20] for lattice bosons.

20.8.3 Superfluid and Insulator Phases

The Hamiltonian (20.177) has essentially three parameters: the hopping rate h, the on-site interaction energy U (generally we will assume $U \geq 0$ for a repulsive interaction), and the chemical potential $E_0 - \mu$ relative to the ground-state energy. The meaning of the first two parameters is fairly clear, but the chemical potential has a possibly counterintuitive interpretation as being related to the number of particles in the lattice. Creating the first particle only requires an energy E_0, and this is true of any other particles created in a formerly empty site. But as the lattice fills, because of the self-interaction energy, the chemical potential increases by $U/2$ in order to put the second particle into a lattice site. The chemical potential increases to U, $3U$, $6U$, $10U$, and so on above E_0 as the lattice fills to two, three, four, and five particles per site, respectively.

This scenario of the lattice sites all filling to the same number of particles may seem artificial, but in fact there is a phase transition in the Bose–Hubbard model that accomplishes exactly this. To see this intuitively, first assume that the particles can freely hop between lattice sites, $h \gg U$, such that the on-site repulsion is negligible. In this case, we have the same situation that we had with Bloch wave functions, here in the ground band: The particles can travel ballistically through the lattice via the hopping interaction. This is the **superfluid state**.

In the opposite regime, $h \ll U$, the on-site repulsion is much larger than the hopping transition rate. Since the details of the repulsion term will depend on the distribution of particles, the repulsion term will in general strongly break the translational symmetry of the lattice potential, and we no longer expect Bloch tunneling to occur. When many particle are added to the lattice at vanishingly low temperature, the tendency is to fill any empty site to minimize the energy, to the point where all sites are singly occupied. As more particles are added, the tendency is again to fill any singly occupied site until all sites are doubly occupied, and so on. Once all sites are filled with the same number of particles (for example, in the singly-occupied case), the on-site repulsion U acts as a barrier to movement, because for any particle to hop, it must acquire an extra energy $U/2$ in order to move. The on-site repulsion thus produces a gap to conducting states, and this configuration is called the **Mott insulator state**.[21] In between these two parameter extremes there is a phase transition between the two states, which turns out to be a second-order transition.[22]

[20] After J. Hubbard, "Electron Correlations in Narrow Energy Bands," *Proceedings of the Royal Society of London* **276** 238 (1963) (doi: 10.1098/rspa.1963.0204), who proposed a model for interacting electrons in a lattice. The boson version of the model is more tractable than the original.

[21] For the mean-field analysis, see Matthew P. A. Fisher, Peter B. Weichman, G. Grinstein, and Daniel S. Fisher, "Boson localization and the superfluid-insulator transition," *Physical Review B* **40**, 546 (1989) (doi: 10.1103/PhysRevB.40.546); and Subir Sachdev, *Quantum Phase Transitions*, 2nd ed. (Cambridge, 2011) (ISBN: 9780521514682).

[22] The transition from superfluidity to Mott insulator was first observed by M. Greiner, O. Mandel, T. Esslinger, T. W. Hänsch, and I. Bloch, "Quantum phase transition from a superfluid to a Mott insulator in a gas of ultracold atoms," *Nature* **415**, 39 (2002) (doi: 10.1038/415039a). For cool images with single-site resolution, see W. S. Bakr, A. Peng, M. E. Tai, R. Ma, J. Simon, J. I. Gillen, S. Fölling, L. Pollet, M. Greiner, "Probing the Superfluid-to-Mott Insulator Transition at the Single-Atom Level," *Science* **329**, 547 (2010) (doi: 10.1126/science.1192368) (arXiv: 1006.0754.pdf).

20.9 Exercises

Problem 20.1

(a) Consider the localized, bosonic Fock state (20.55) of N particles,

$$|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle := \frac{1}{\sqrt{N!}}\hat{\psi}^\dagger(\mathbf{r}_1,)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle. \tag{20.178}$$

Use the normal-mode expansion for the field operators $\hat{\psi}(\mathbf{r})$, along with the bosonic commutation relations for the mode operators a_k and $a_k^\dagger$, to show that this Fock state is indeed an eigenstate of the total number operator:

$$\hat{N}|\Psi\rangle := \sum_k \hat{a}_k^\dagger \hat{a}_k|\Psi\rangle = N|\Psi\rangle. \tag{20.179}$$

(b) Indicate how the argument changes but ultimately goes through for the localized, fermionic Fock state of the same form.

Problem 20.2

(a) Considering the same localized, bosonic Fock state of N particles as in Problem 20.1, show that the inner product of two such states is [Eq. (20.57)][23]

$$\langle\Psi(\mathbf{r}'_1,\ldots,\mathbf{r}'_N)|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle = \frac{1}{N!}\sum_{\boldsymbol{\sigma}\in P(N)}\delta^3(\mathbf{r}_1-\mathbf{r}'_{\sigma_1})\cdots\delta^3(\mathbf{r}_N-\mathbf{r}'_{\sigma_N}). \tag{20.180}$$

That is, the normalization is sensibly of the form of a product of delta functions $\delta^3(\mathbf{r}_k-\mathbf{r}'_k)$, but averaging over all permutations of one of the sets of coordinates (here, the primed coordinates), as appropriate for bosons.

(b) Repeat (a), but for a localized fermionic Fock state.

$$\langle\Psi(\mathbf{r}'_1,\ldots,\mathbf{r}'_N)|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle = \frac{1}{N!}\sum_{\boldsymbol{\sigma}\in P(N)}\epsilon_{\boldsymbol{\sigma}}\,\delta^3(\mathbf{r}_1-\mathbf{r}'_{\sigma_1})\cdots\delta^3(\mathbf{r}_N-\mathbf{r}'_{\sigma_N}). \tag{20.181}$$

Problem 20.3

We wrote the second-quantized Hamiltonian in the form (20.38)

$$\hat{H}(t) = \int d^3r\,\hat{\psi}^\dagger(\mathbf{r},t)\left(-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t) + \frac{1}{2}\int d^3r'\,\hat{\psi}^\dagger(\mathbf{r}',t)\,V_2(\mathbf{r},\mathbf{r}')\,\hat{\psi}(\mathbf{r}',t)\right)\hat{\psi}(\mathbf{r},t), \tag{20.182}$$

which includes explicit time dependence via the matter-field operators. Explain why it is sensible to include this time dependence, being specific about how to think about the Hamiltonian in the Schrödinger vs. Heisenberg pictures.

Problem 20.4

Consider the localized Fock state

$$|\Psi(\mathbf{r}_1,\ldots,\mathbf{r}_N)\rangle := \frac{1}{\sqrt{N!}}\hat{\psi}^\dagger(\mathbf{r}_1)\cdots\hat{\psi}^\dagger(\mathbf{r}_N)|0\rangle, \tag{20.183}$$

[23] The text by Paul Roman, *Advanced Quantum Theory: An Outline of the Fundamental Ideas* (Addison–Wesley, 1965) (ISBN: 0201064952), is excellent and one I really respect. However, I can't resist poking a little fun here. He says, ''Using repeatedly the commutation relations (1-186) and the definition (1-180d) of the ground state Φ_0, one easily finds that,'' and then proceeds to write down the result (20.180), but missing the symmetrization over all permutations.

which could be for either bosons or fermions. Suppose that we write an arbitrary (Schrödinger-picture) state as a superposition of the Fock-basis states as

$$|\Psi(t)\rangle = \int d^3r_1, \ldots, d^3r_N \, |\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)\rangle \, \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t). \tag{20.184}$$

That is, we have defined the amplitude (wave function) by the inner product

$$\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t) = \langle \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) | \Psi(t) \rangle. \tag{20.185}$$

By considering the Schrödinger-equation evolution of $|\Psi(t)\rangle$ via the second-quantized Hamiltonian (20.38) in the Schrödinger picture (i.e., at $t = 0$),

$$\hat{H} = \int d^3r \, \hat{\psi}^\dagger(\mathbf{r}) \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t) + \frac{1}{2} \int d^3r' \, \hat{\psi}^\dagger(\mathbf{r}') \, V_2(\mathbf{r}, \mathbf{r}') \, \hat{\psi}(\mathbf{r}') \right) \hat{\psi}(\mathbf{r}), \tag{20.186}$$

show that the wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N, t)$ satisfies the first-quantized Schrödinger equation in terms of the many-body Hamiltonian (20.73)

$$H = \sum_{j=1}^{N} \left(-\frac{\hbar^2}{2m} \nabla_j^2 + V(\mathbf{r}_j, t) \right) + \frac{1}{2} \sum_{j \neq k=1}^{N} V_2(\mathbf{r}_j, \mathbf{r}_k). \tag{20.187}$$

This establishes the equivalence between first and second quantization for interacting particles (with two-body interactions).

Problem 20.5

(a) Show that the normalizations of Bloch and Wannier functions are related by

$$\int_0^L dx \, |\psi_{n,k}(x)|^2 = \int_{-\infty}^{\infty} dx \, w_n^2(x). \tag{20.188}$$

To do this, start with the expression on the left-hand side, and use the transformation to Wannier functions. Then perform a k integration over the first Brillouin zone and simplify.

(b) Now show explicitly that the Wannier functions are orthonormal according to

$$\int_{-\infty}^{\infty} dx \, w_n(x - jL) \, w_{n'}(x - j'L) = \delta_{n,n'} \, \delta_{j,j'} \tag{20.189}$$

Chapter 21

Hic Sunt Dracones

21.1 Self-Adjoint vs. Hermitian Operators

Our approach to developing the mathematical background of quantum mechanics in Chapter 0 has been relatively informal, with a definite sense of ''better to ask for forgiveness than permission.'' Well, now it's time to pay up, forgiveness-wise. That is, now that we've studied a few examples of particles in potentials, it's a good time to revisit the mathematical structure of quantum mechanics and have a hard look at some of the bits that we've been hiding under the sofa. The infinite-square-well problem in particular is a good place to being. It seems pretty basic and straightforward, easy to solve; but it is surprisingly pathological. It is, in fact, a good prototype system for studying the distinction between Hermitian and self-adjoint operators.

As an example pathology, consider a particle in an infinite square well of length L, but shifted to occupy the symmetric region $|x| < {}^{L}/_{2}$ about the origin. Consider the example wave function[1]

$$\psi(x) = \sqrt{\frac{30}{L^5}}\left(\frac{L^2}{4} - x^2\right), \qquad |x| < \frac{L}{2}, \tag{21.1}$$

of course with $\psi(x) = 0$ outside this region. With

$$H = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\partial_x^2, \tag{21.2}$$

it is straightforward to evaluate the energy expectation value:

$$\langle H\rangle = \langle\psi|H|\psi\rangle = -\frac{15\hbar^2}{mL^5}\int_{-L/2}^{L/2} dx\left(\frac{L^2}{4} - x^2\right)(-2) = \frac{5\hbar^2}{mL^2}. \tag{21.3}$$

Here, we allowed the derivatives to operate on the wave function to the right, but since the Hamiltonian is Hermitian, the same result is obtained by operating to the left. Now let's compute the second energy moment, by similarly letting the operator act to the right, which we emphasize by writing $H^2|\psi\rangle \equiv |H^2\psi\rangle$. Because $\partial_x^4\psi = 0$, we have

$$\left\langle H^2\right\rangle = \langle\psi|H^2\psi\rangle = 0\,(!), \tag{21.4}$$

which is clearly a contradiction because we must have $\left\langle H^2\right\rangle > \langle H\rangle^2$. On the other hand, since H only involves a second derivative, then $H|\psi\rangle$ in the position representation becomes

$$\langle x|H|\psi\rangle = -\sqrt{\frac{30}{m^2L^5}}\,\hbar^2, \tag{21.5}$$

[1]This example adapted from Guy Bonneau, Jacques Faraut, and Galliano Valent, ''Self-adjoint extensions of operators and the teaching of quantum mechanics,'' *American Journal of Physics* **69**, 322 (2001) (doi: 10.1119/1.1328351), who also give a nice discussion of the definitions of self-adjoint and Hermitian operators. Another nice and more detailed discussion is Cintio12 and Alessandro Michelangeli, ''Self-adjointness in quantum mechanics: a pedagogical path,'' *Quantum Studies: Mathematics and Foundations* **8**, 271 (2021) (doi: 10.1007/s40509-021-00245-x) (arXiv: 2012.14490). Another reference, particularly clearly written and with a handy library of paradoxes, is François Gieres,''Mathematical surprises and Dirac's formalism in quantum mechanics,'' *Reports on Progress in Physics* **63** 1893 (2000) (doi: 10.1088/0034-4885/63/12/201) (arXiv: quant-ph/9907069).

and recalculating the expectation value as the norm of $H|\psi\rangle \equiv |H\psi\rangle$ gives

$$\langle H^2 \rangle = \langle H\psi | H\psi \rangle = \frac{30\hbar^4}{m^2 L^5} \int_{-L/2}^{L/2} dx = \frac{30\hbar^4}{m^2 L^4}, \tag{21.6}$$

which is the correct result (it agrees, for example, with the calculation obtained by changing to the energy representation). The problem in this example is that H is not Hermitian when operating on $|H\psi\rangle$. To see this explicitly, suppose that we write out the general form of the calculation in Eqs. (21.6) and transform it into a (correct) form analogous to the one in Eqs. (21.6) through integration by parts:

$$\begin{aligned} \langle H^2 \rangle &= \langle H\psi | H\psi \rangle \\ &= \frac{\hbar^4}{4m^2} \int_{-L/2}^{L/2} dx\, \psi''(x)\, \psi''(x) \\ &= \frac{\hbar^4}{4m^2} \Big[\psi' \psi'' \Big]_{-L/2}^{L/2} - \frac{\hbar^4}{4m^2} \int_{-L/2}^{L/2} dx\, \psi'\, \psi''' \\ &= \frac{\hbar^4}{4m^2} \Big[\psi' \psi'' - \psi \psi''' \Big]_{-L/2}^{L/2} + \frac{\hbar^4}{4m^2} \int_{-L/2}^{L/2} dx\, \psi\, \psi''''. \end{aligned} \tag{21.7}$$

The last integral is analogous to the form in Eqs. (21.6), and it vanishes as before because $\psi'''' = 0$. However, there are still boundary terms, of which one vanishes because $\psi''' = 0$, and so

$$\langle H^2 \rangle = \frac{\hbar^4}{4m^2} \Big[\psi' \psi'' \Big]_{-L/2}^{L/2} = \frac{30\hbar^4}{4m^2 L^5} \Big[4x \Big]_{-L/2}^{L/2} = \frac{30\hbar^4}{m^2 L^4}, \tag{21.8}$$

in agreement with the correct result. So the failure of H here to act Hermitian is due to the boundary conditions, which induce boundary terms in conjugation when operating on $\psi''(x)$. For another good example of this kind of pathology in the infinite square well, see Problem 21.2. So what is going on here, and why should different calculations give different results, involving what would seem to be a perfectly reasonable operator and reasonable states?

21.1.1 Definitions

This discussion shows that in working with the Hermitian conjugate of an operator, it is important to consider the state on which it acts. So let's discuss this in a bit more detail and amend our simplistic prior discussion(Section 1.1.4). Before, for an operator (linear transformation) Q, we defined the Hermitian conjugate $Q^\dagger$ such that

$$\langle Q^\dagger \phi | \psi \rangle = \langle \phi | Q\psi \rangle \tag{21.9}$$

for any vectors $|\phi\rangle$ and $|\psi\rangle$ in the vector space (here, the Hilbert space $\mathscr{H}$).[2] But this definition assumes that the operator gives a sensible result when transforming any vector in the Hilbert space. For finite-dimensional spaces this is okay, but in general this is not the case (for example, multiplying a square-integrable function on $\mathbb{R}$ by e^x give s result that is not square-integrable). Thus we should define the **domain** of the operator Q by

$$\mathrm{Dom}(Q) := \{ |\psi\rangle \in \mathscr{H} : Q|\psi\rangle \in \mathscr{H} \}, \tag{21.10}$$
(domain of an operator)

so that $Q : \mathrm{Dom}(Q) \longrightarrow \mathscr{H}$. That is, the domain is a subset of $\mathscr{H}$, including only the vectors which get mapped to other vectors in the Hilbert space (i.e., vectors with sensible results under Q). Then the definition

[2] Actually, it suffices to require just $\langle Q^\dagger \psi | \psi \rangle = \langle \psi | Q\psi \rangle$ for a *single* arbitrary vector $|\psi\rangle$. Setting $|\psi\rangle = |\phi\rangle + |\chi\rangle$ and then $|\psi\rangle = |\phi\rangle + i|\chi\rangle$ in this simpler identity yields after a bit of manipulation the apparently more general condition. See Problem 1.20 for another example of this strategy.

of the **Hermitian conjugate** (or **adjoint**) $Q^\dagger$ of Q is saved by restricting the defining condition to the operator's domain,

$$\langle Q^\dagger \phi | \psi \rangle = \langle \phi | Q\psi \rangle \quad \forall_{|\psi\rangle, |\phi\rangle \in \mathrm{Dom}(Q)}, \tag{21.11}$$
(Hermitian conjugate)

so that the condition only needs to hold when it is sensible to do so. If Q is an unbounded operator (like x or p), then it turns out that $\mathrm{Dom}(Q) \subset \mathscr{H}$ (the domain is a *proper* subset of the whole space), so the distinction is nontrivial. In this case, $\mathrm{Dom}(Q)$ must be **dense** in $\mathscr{H}$ (meaning every vector in $\mathscr{H}$ must have a vector from $\mathrm{Dom}(Q)$ arbitrarily close by) in order for the adjoint to be uniquely defined.

The Hermitian conjugate has a domain of its own,

$$\mathrm{Dom}(Q^\dagger) := \{|\phi\rangle \in \mathscr{H} : Q^\dagger|\phi\rangle \in \mathscr{H} \text{ and } \langle Q^\dagger\phi|\psi\rangle = \langle \phi|Q\psi\rangle \ \forall_{|\psi\rangle \in \mathrm{Dom}(Q)}\}.$$
(domain of the adjoint) (21.12)

In English, this is the set of all vectors that are sensibly transformed by Q and can work as the bra in the adjoint-defining inner product with an arbitrary ket in the domain of Q. Note the asymmetry in the definition here, which only requires $|\psi\rangle \in \mathrm{Dom}(Q)$: In particular, the action of $Q^\dagger$ could be defined on a larger set of vectors than $\mathrm{Dom}(Q)$, so that in general $\mathrm{Dom}(Q) \subseteq \mathrm{Dom}(Q^\dagger)$. Then the operator Q is **Hermitian**[3] if

$$Q^\dagger = Q, \quad \text{with} \quad \mathrm{Dom}(Q) \subseteq \mathrm{Dom}(Q^\dagger), \tag{21.13}$$
(Hermitian operator)

when operating on states where this statement is sensible. Note the emphasis on the possibility of the adjoint's domain being the potentially larger set, $\mathrm{Dom}(Q) \subseteq \mathrm{Dom}(Q^\dagger)$. An operator is **self-adjoint** if both of these domains are identical,

$$Q^\dagger = Q, \quad \text{with} \quad \mathrm{Dom}(Q) = \mathrm{Dom}(Q^\dagger), \tag{21.14}$$
(self-adjoint operator)

so that the distinction between a Hermitian and a self-adjoint operator comes down to a specification of the operator domains. More intuitively, this again comes down to ensuring that the operations involved in a given calculation are sensible; if they aren't, the answer could well be wrong.

21.1.2 Observables

Then going back to the second axiom of quantum mechanics (Section 1.4), **observables correspond to self-adjoint operators**, not merely Hermitian operators. In the case of a self-adjoint operator Q, Q's eigenspectrum is real, and Q has a set of complete, mutually orthogonal eigenvectors. Some of the eigenvectors forming the complete basis may not necessarily belong to the Hilbert space, in which case they are called **generalized eigenvectors** (e.g., momentum eigenstates of the free particle). These statements do not necessarily hold in the case where Q is merely Hermitian.

Again, these distinctions matter for infinite-dimensional spaces. If Q is a Hermitian operator on a finite Hilbert space $\mathscr{H}$, then we can take $\mathrm{Dom}(Q) = \mathrm{Dom}(Q^\dagger) = \mathscr{H}$, and so Q is automatically also self-adjoint. The spectrum of Q is real and finite (and discrete).

21.1.3 Example: Momentum Operator for the Infinite Square Well

Let's revisit the momentum operator to make some of these new concepts concrete. We know now that it is important to specify the domain of operators when we've gotten ourselves into trouble, so let's take $\mathrm{Dom}(p)$ to be

$$\mathrm{Dom}(p) = \{\psi \in \mathscr{H} = L^2[(-L/2, L/2)] : \psi(\pm L/2) = 0\}, \tag{21.15}$$

or that is the set of all functions $\psi(x)$ on $(-L/2, L/2)$ that are square integrable, $\int_{-L/2}^{L/2} dx\, |\psi(x)|^2 < \infty$ [the set of such functions, which we are taking to be the Hilbert space, is denoted $L^2[(-L/2, L/2)]$] and obey Dirichlet boundary conditions, $\psi(\pm L/2) = 0$.

[3] Such an operator is also called **symmetric** in the more mathematical literature. The term "Hermitian" sometimes is used in a more restrictive sense than symmetric, implying also boundedness of the operator.

We want the momentum operator to be at least Hermitian, and thus $p^\dagger = p$. In an inner product, this means that we have the vanishing difference $\langle\phi|p^\dagger|\psi\rangle - \langle\phi|p|\psi\rangle = 0$. Writing this difference in the position representation,

$$\begin{aligned}\langle\phi|p^\dagger|\psi\rangle - \langle\phi|p|\psi\rangle &= \int_{-L/2}^{L/2} dx \left[\psi(i\hbar\partial_x)\phi^* - \phi^*(-i\hbar\partial_x)\psi\right] \\ &= i\hbar \int_{-L/2}^{L/2} dx\, \partial_x(\phi^*\psi) \\ &= i\hbar\Big[\phi^*(L/2)\,\psi(L/2) - \phi^*(-L/2)\,\psi(-L/2)\Big].\end{aligned} \tag{21.16}$$

The last quantity vanishes because of the Dirichlet boundary conditions we imposed on $\psi(x)$. Note that $\phi(x)$ need not satisfy the same boundary conditions as $\psi(x)$, so we see explicitly that $\mathrm{Dom}(p) \subsetneq \mathrm{Dom}(p^\dagger)$ in this case.

But the last expression in Eqs. (21.16) suggests that the Dirichlet boundaries are too restrictive. The boundary terms also vanish if we merely require

$$\psi(L/2) = e^{i\theta}\,\psi(-L/2), \qquad \phi(L/2) = e^{i\theta}\,\phi(-L/2), \tag{21.17}$$

for some phase angle θ. Note that $\phi(x)$ and $\psi(x)$ must then be treated on equal footing for the boundary terms to vanish. With this new requirement, $\mathrm{Dom}(p)$ has expanded to include functions that do not satisfy Dirichlet conditions, and $\mathrm{Dom}(p^\dagger)$ has contracted so that $\mathrm{Dom}(p^\dagger) = \mathrm{Dom}(p)$. That is, under this new requirement, p is now self-adjoint, instead of merely Hermitian. When the domain of p is extended to functions satisfying the condition (21.17), we obtain a **self-adjoint extension** of p. Formally, an **extension** of an operator Q is an operator Q' defined on a superset of $\mathrm{Dom}(Q)$, such that $Q'|\psi\rangle = Q|\psi\rangle$ whenever $|\psi\rangle \in \mathrm{Dom}(Q)$. The expanding of the domain of p and the contracting of the domain of $p^\dagger$ until they are equal is generically how self-adjoint extensions work out.

In this example, there are many possible self-adjoint extensions of the Hermitian momentum operator, parameterized by θ.[4] Different choices for θ lead to different classes of functions (i.e., domains of p), including periodic functions ($\theta = 0$) and antiperiodic functions ($\theta = \pi$). Note that both $|\phi\rangle$ and $|\psi\rangle$ must be chosen from the same class of functions to be compatible, so p is only self-adjoint with a definite choice of θ.

21.1.4 Back to the Original Example

Now let's go back to the original example of the wave function (21.1), and see how we can resolve it. One possible method to resolve the problem, very much in the physics style of fixing problems, is to forget that the wave function is confined to $(-L/2, L/2)$,

$$\psi(x) = \begin{cases} \sqrt{\dfrac{30}{L^5}}\left(\dfrac{L^2}{4} - x^2\right) & |x| < L/2 \\ 0 & |x| > L/2, \end{cases} \tag{21.18}$$

and treat it as extended to all of $\mathbb{R}$. Then the second derivative leads to a box function instead of merely a constant function,

$$\psi''(x) = \begin{cases} -\sqrt{\dfrac{120}{L^5}} & |x| < L/2 \\ 0 & |x| > L/2, \end{cases} \tag{21.19}$$

so that the next derivative has delta functions at the boundaries, and the fourth derivative has derivatives thereof:

$$\psi''''(x) = \sqrt{\frac{120}{L^5}}\Big[\delta'(x - L/2) - \delta'(x + L/2)\Big]. \tag{21.20}$$

[4] The analogy to a spontaneously broken symmetry is pointed out by Anton Z. Capri, "Self-adjointness and spontaneously broken symmetry," *American Journal of Physics* **45**, 823 (1977) (doi: 10.1119/1.11055).

Thus a corrected version of the calculation (21.4) is

$$\begin{aligned}\langle H^2\rangle &= \langle\psi|H^2\psi\rangle \\ &= \frac{\hbar^4}{4m^2}\int_{-\infty}^{\infty} dx\,\psi(x)\,\psi''''(x) \\ &= \frac{\hbar^4}{4m^2}\int_{-\infty}^{\infty} dx\,\psi(x)\Big[\delta'(x-{}^L\!/_2)-\delta'(x+{}^L\!/_2)\Big] \\ &= \frac{\hbar^4}{4m^2}\sqrt{\frac{120}{L^5}}\left[\sqrt{\frac{30}{L^3}}+\sqrt{\frac{30}{L^3}}\right] \\ &= \frac{30\hbar^4}{m^2L^4},\end{aligned} \tag{21.21}$$

yielding the correct result (21.6). Here, we used the property of the delta-function derivative (Problem 1.26) that the integral yields the derivative (with a minus sign) of the test function multiplying it. However, there is a subtle issue with how to handle the delta-function derivatives on the boundaries. Since the delta-function derivative sits at the point where the derivative changes discontinuously between $\pm\sqrt{30/L^3}$ and zero, we would typically have the delta-function derivative act in equal fractions on each region. That would mean the average values $\pm({}^1\!/_2)\sqrt{30/L^3}$ should be used, but doing so leads to the wrong answer. Instead, we should interpret the delta-function derivatives as being completely inside $(-{}^L\!/_2, {}^L\!/_2)$, so we used the values $\pm({}^1\!/_2)\sqrt{30/L^3}$ for the derivatives. The reason is that the kinked wave function (21.18) should be viewed as a limit of more reasonable (i.e., smooth) functions that still vanish for all $|x| > {}^L\!/_2$. Thus the delta functions and their derivatives arise asymmetrically with respect to the boundary points, and their effect should be strictly confined to the region $|x| < {}^L\!/_2$.

Other problems that crop up, particularly those involving energy eigenfunctions, can be resolved with slightly more general considerations. Physically, the infinite square well should be regarded as an idealized limit of a deep—but finite—well. In the arbitrarily deep limit, the energy eigenfunction is assumed to vanish in such a way that $V(x)\,\psi(x) \longrightarrow 0$ outside the well [see Problem 2.23(b)]. If the vanishing of the wave functions outside the well is taken too seriously, it can lead to missing effects that occur right at the boundary (Problem 2.24), or ones that also have contributions from outside the well (Problem 21.2).

21.1.4.1 Resolution Confined to the Finite Interval

When you start working through a lot of quantum mechanics problems, you start to think of expectation values as $\langle Q\rangle = \langle\psi|Q|\psi\rangle$ [Eq. (1.40)]. Dirac notation is designed to encourage this, and it works. Except when it doesn't.

In fact, how we *defined* the expectation value of an operator Q was in terms of its possible measured values q_n, along with the probabilities of each of these possibilities [Eq. (1.38)]:

$$\langle Q\rangle := \sum_n q_n \cdot \text{Prob}(q_n). \tag{21.22}$$

An integral can stand in for the summation as needed, of course, and *this* expectation value is correct and physically meaningful, provided that the sum/integral converges. Then we proceeded to transform this into $\langle\psi|Q|\psi\rangle$. Let's go through this carefully in the case of H^2 and the wave function (21.1) to see what can go wrong. Starting out, we have in terms of the energy eigenvalues E_n and eigenstates $|n\rangle$, and the eigenstate

projectors $P_n := |n\rangle\langle n|$ (which are all self-adjoint),

$$\begin{aligned}\langle H^2\rangle &= \sum_n E_n^2 \cdot \text{Prob}(E_n)\\ &= \sum_n E_n^2\, |\langle n|\psi\rangle|^2\\ &= \sum_n \langle\psi|P_n\, E_n^2|\psi\rangle\\ &= \sum_n \langle\psi|P_n\, H^2|\psi\rangle\\ &= \sum_n \langle\psi|P_n\, |H^2\psi\rangle\\ &= \langle\psi|H^2\psi\rangle,\end{aligned} \tag{21.23}$$

where we used the completeness of the projector eigenstates at the end. All of this seems reasonable, but the crucial part to focus on is our treatment of H^2 as a self-adjoint operator in the context $\langle n|H^2|\psi\rangle$. Let's check this carefully.

First let's start by checking the domain of the self-adjoint (i.e., observable) operator H, which is the same as the domain of p^2. Thus we check the vanishing of

$$\begin{aligned}\langle\phi|(p^\dagger)^2|\psi\rangle - \langle\phi|p^2|\psi\rangle &= -\hbar^2 \int_{-L/2}^{L/2} dx \left[\psi\phi''^* - \phi^*\psi''\right]\\ &= \hbar^2\Big[\psi\phi'^* - \phi^*\psi'\Big]_{-L/2}^{L/2},\end{aligned} \tag{21.24}$$

after an integration by parts. We can take the position-representation Hilbert space $\mathscr{H}$ to again be $L^2[(-L/2, L/2)]$, and then the boundary terms vanish if, for example, we require that $\psi(\pm L/2) = \phi(\pm L/2) = 0$, with no particular conditions on $\psi'(\pm L/2)$ or $\phi'(\pm L/2)$. That is, we take

$$\text{Dom}(H^\dagger) = \text{Dom}(H) = \{\psi \in \mathscr{H} : \psi'' \in \mathscr{H},\ \psi(\pm L/2) = 0\}. \tag{21.25}$$

Notably, the H's eigenfunctions belong to its domain, which is a good thing. Now doing the same calculation for H^2, or equivalently p^4,

$$\begin{aligned}\langle\phi|(p^\dagger)^4|\psi\rangle - \langle\phi|p^4|\psi\rangle &= \hbar^4 \int_{-L/2}^{L/2} dx \left[\psi\phi''''^* - \phi^*\psi''''\right]\\ &= -\hbar^4\Big[\psi\phi'''^* - \psi'\phi''^* - \phi^*\psi''' + \phi'^*\psi''\Big]_{-L/2}^{L/2},\end{aligned} \tag{21.26}$$

Now how to make the boundary terms vanish here? For maximum compatibility with the domain of H, we can again take $\psi(\pm L/2) = \phi(\pm L/2) = 0$ with no particular conditions on $\psi'(\pm L/2)$ or $\phi'(\pm L/2)$. The remaining boundary terms vanish if we take $\psi''(\pm L/2) = \phi''(\pm L/2) = 0$, with no particular constraints on the third derivatives. That is, H^2 is also self-adjoint with

$$\text{Dom}(H^2) = \{\psi \in \mathscr{H} : \psi'''' \in \mathscr{H},\ \psi(\pm L/2) = \psi''(\pm L/2) = 0\}. \tag{21.27}$$

This choice also ensures that the eigenfunctions of H^2 (being the same as the eigenfunctions of H) are again in its domain. This is actually essential, as we used this fact in the course of taking advantage of the action of H^2 to the left on its eigenstate projector, in Eqs. (21.23). Note that we have $\text{Dom}(H^2) \subset \text{Dom}(H) \subset \mathscr{H}$. Incidentally, the domain definition is an example of a more general definition of the domain of an operator product AB, which is

$$\text{Dom}(AB) = \{\psi \in \text{Dom}(B) : B\psi \in \text{Dom}(A)\},$$
(domain of operator product) (21.28)

which also gives the condition $\psi''(\pm L/2) = 0$ for $\mathrm{Dom}(H^2)$. While we are on the subject, the domain for a *sum* of operators is

$$\mathrm{Dom}(A+B) = \mathrm{Dom}(A) \cap \mathrm{Dom}(B), \tag{21.29}$$
(domain of operator sum)

because the sum of operators can only operate on vectors on which the individual operators make sense.

Now we can see what went wrong in the calculation (21.23). Since the second derivative (21.19) is nonvanishing at the boundaries, the wave function (21.1) is not in the domain of H^2, so writing $|H^2\psi\rangle$ is undefined for this state in the position representation. But by varying the calculation, we can save it:

$$\begin{aligned}
\langle H^2 \rangle &= \sum_n E_n^2 \, |\langle n|\psi\rangle|^2 \\
&= \sum_n \langle \psi | E_n P_n \, E_n | \psi \rangle \\
&= \sum_n \langle \psi | H P_n \, H | \psi \rangle \\
&= \sum_n \langle H\psi | P_n \, | H\psi \rangle \\
&= \langle H\psi | H\psi \rangle .
\end{aligned} \tag{21.30}$$

Since the wave function $\psi \in \mathrm{Dom}(H)$, all the operations here are well defined, and $\langle H\psi|H\psi\rangle$ yields the correct result when evaluated in the position representation, as we have seen. The symmetric splitting of H^2 here in the inner product takes advantage of the domain of H being larger than the domain of H^2.

So what do we conclude about H^2 as a self-adjoint operator in the context of this state? As an operator, H^2 is something pretty reasonable to observe (provided it has a well defined value), and the parabolic state is not so unreasonable either. Note that the state *is* outside the domain of H^2, as we have discussed. However, it is also in a subspace in which the domain of H^2 is dense, and H^2 is uniquely defined as a self-adjoint operator on this space. That is, there are arbitrarily close-by states where $\langle\psi|H^2\psi\rangle$ gives the correct answer (the sequence of truncations of the energy representation is in the domain of H^2 and converges to this state, for example).

While involving a substantial extra load of mathematical apparatus, this formal approach to treating the self-adjointness of operators manages to guide us to the correct result, while staying firmly inside the finite interior of the infinite square well.

21.2 Bad Commutators and Uncertain Uncertainties

Interestingly, for any of these self-adjoint extension of p, the commutator $[x,p] = i\hbar$—from which a great deal of the structure of quantum mechanics flows—might not even be sensible. Suppose that we specialize to the extension $\theta = 0$. Then p is self-adjoint with respect to periodic functions ψ, but $x\psi$ is no longer in $\mathrm{Dom}(p)$. So $\mathrm{Dom}([x,p])$ does not agree at all with $\mathrm{Dom}(p)$ for nontrivial functions.

The uncertainty principle, in the form (1.43)

$$V_P V_Q \geq \frac{1}{4}\Big|\langle [P,Q] \rangle\Big|^2, \tag{21.31}$$

can then run directly into problems. Let's recast this in the form of the angular coordinate ϕ and the conjugate angular momentum [Eq. (7.51)]]

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}. \tag{21.32}$$

This angular momentum is basically equivalent to p on the finite interval as treated above, but instead of Dirichlet boundary conditions, the domain of the self-adjoint operator L_z is now the set of square-integrable

functions on $[-\pi,\pi]$ with periodic boundary conditions, $\psi(\pi)=\psi(-\pi)$. Now proceeds a simple but naïve argument. The conjugate pair satisfies the commutation relation,

$$[\phi, L_z] = i\hbar, \tag{21.33}$$

which in the uncertainty principle (21.31) gives the uncertainty constraint

$$V_{L_z} V_\phi \geq \frac{\hbar^2}{4}. \qquad \text{(wrong!)} \tag{21.34}$$

However, this can't be correct. The angular variance V_ϕ is maximum for a uniformly distributed density on $[-\pi,\pi]$, when it takes the value $\pi^2/3$. However, the momentum variance V_{L_z} becomes arbitrarily small in the case of an eigenstate, in which case the uncertainty product becomes arbitrarily small.

Let's reiterate where the argument above breaks down. We already discussed the self-adjoint condition for p on a finite interval in Eqs. (21.17), and with the choice of periodic boundary conditions here in the angular representation, we have that L_z is self-adjoint with domain

$$\mathrm{Dom}(L_z) = \{\psi \in \mathscr{H} : \psi(\pi) = \psi(-\pi)\}, \tag{21.35}$$

where we are taking our Hilbert space $\mathscr{H}$ to be the set of square integrable functions on the angular interval, denoted $L^2([-\pi,\pi])$. The self-adjoint angle operator ϕ in its own representation has the wider domain

$$\mathrm{Dom}(\phi) = L^2([-\pi,\pi]). \tag{21.36}$$

Now using the definition (21.28), we can discuss the domains of the operator products. The simpler one is

$$\begin{aligned}\mathrm{Dom}(\phi L_z) &= \{\psi \in \mathrm{Dom}(L_z) : L_z\psi \in \mathrm{Dom}(\phi)\} \\ &= \{\psi \in \mathscr{H} : \psi' \in \mathscr{H} \text{ and } \psi(\pi) = \psi(-\pi)\},\end{aligned} \tag{21.37}$$

since we just need to make sure the derivative doesn't cause normalization problems. On the other hand, multiplication by ϕ changes the parity of a wave function, so $L_z\phi$ must operate on antiperiodic functions:

$$\begin{aligned}\mathrm{Dom}(L_z\phi) &= \{\psi \in \mathrm{Dom}(\phi) : \phi\psi \in \mathrm{Dom}(L_z)\} \\ &= \{\psi \in \mathscr{H} : \psi' \in \mathscr{H} \text{ and } \psi(\pi) = -\psi(-\pi)\}.\end{aligned} \tag{21.38}$$

Then using the definition (21.29), the domain of the commutator can only involve functions that vanish at the boundaries:

$$\begin{aligned}\mathrm{Dom}\big([\phi, L_z]\big) &= \mathrm{Dom}(\phi L_z) \cap \mathrm{Dom}(L_z\phi) \\ &= \{\psi \in \mathscr{H} : \psi' \in \mathscr{H} \text{ and } \psi(\pi) = \psi(-\pi) = 0\}.\end{aligned} \tag{21.39}$$

Note in particular the eigenfunctions $\psi_m(\phi) = e^{im\phi}/\sqrt{2\pi}$ for integer m are excluded from $\mathrm{Dom}([\phi, L_z])$. Since the derivation of the uncertainty principle (21.34) involved the interpretation of the expectation value as

$$\big\langle [\phi, L_z] \big\rangle = \langle \psi | [\phi, L_z] \psi \rangle, \tag{21.40}$$

then *that* version of the uncertainty principle is restricted to functions that vanish at $\phi = \pm\pi$. In that restricted sense it is actually okay; we don't have to worry about L_z having an arbitrarily narrow uncertainty. The closest we can get is that L_z^2 can be well defined, taking on values $m^2\hbar^2$ ($m \geq 1$). But this means that the state is in a superposition of L_z taking the values $\pm m\hbar$, which implies a variance $m^2\hbar^2$, and the uncertainty principle works out.

21.2.1 A More General Angle–Angular Momentum Uncertainty Principle

But then can we do better and derive an uncertainty principle that is valid over a wider domain? The answer is yes. Suppose we have observables (self-adjoint operators) P and Q, with $|\psi\rangle \in \mathrm{Dom}(P) \cap \mathrm{Dom}(Q)$. Then we should back to the Cauchy–Schwarz inequality (1.45), from which we wrote (1.46),

$$\langle\psi|P^2|\psi\rangle\langle\psi|Q^2|\psi\rangle \geq \big|\langle\psi|PQ|\psi\rangle\big|^2, \tag{21.41}$$

which is limited to the intersection of $\mathrm{Dom}(P^2)$, $\mathrm{Dom}(Q^2)$, $\mathrm{Dom}(PQ)$, and soon $\mathrm{Dom}(QP)$. But in order to preserve the larger domain $\mathrm{Dom}(P) \cap \mathrm{Dom}(Q)$ of validity, we should now more carefully write

$$\langle P\psi|P\psi\rangle\langle Q\psi|Q\psi\rangle \geq \big|\langle P\psi|Q\psi\rangle\big|^2. \tag{21.42}$$

Again we can use $|z| \geq |\mathrm{Im}z|$ for any complex number z to write

$$\langle P\psi|P\psi\rangle\langle Q\psi|Q\psi\rangle \geq \frac{1}{4}\Big|\langle P\psi|Q\psi\rangle - \langle Q\psi|P\psi\rangle\Big|^2. \tag{21.43}$$

With the replacements $P \longrightarrow P - \langle\psi|P\psi\rangle$ and $Q \longrightarrow Q - \langle\psi|Q\psi\rangle$, we obtain the uncertainty principle with more carefully defined variances as

$$\begin{aligned} V_P V_Q \;&\geq\; \frac{1}{4}\Big|\langle P\psi|Q\psi\rangle - \langle Q\psi|P\psi\rangle\Big|^2 \\ V_Q \;&:=\; \langle Q\psi|Q\psi\rangle - \langle\psi|Q\psi\rangle^2. \end{aligned}$$

(enlarged-domain uncertainty principle) (21.44)

Of course, this is equivalent to the previous uncertainty principle (1.50) for states common to both respective domains.

To apply this to the angular case, suppose that we define a second-moment function,

$$V(\phi_0) := \int_{-\pi}^{\pi} d\phi\, \psi^*(\phi - \phi_0)\, \phi^2\, \psi(\phi - \phi_0), \qquad \phi_0 \in [-\pi, \pi], \tag{21.45}$$

where $\psi(\phi)$ should be extended periodically as needed for the integral to make sense. Then the angular variance is the minimum value of this function:

$$V_\phi := \min_{\phi_0 \in [-\pi,\pi]} V(\phi_0), \tag{21.46}$$

and the value of ϕ_0 that minimizes the function acts as the ''center'' of the angular distribution, assuming it is uniquely defined.

Now we will use the uncertainty principle in the form (21.43), with $P \longrightarrow L_z - \langle\psi|L_z\psi\rangle$ and $Q \longrightarrow \phi$, interpreting the angular integration of the inner product in the sense of the definition (21.45). The quantity on the right-hand side becomes, with an integration by parts,

$$\begin{aligned} \langle L_z\psi|\phi\psi\rangle - \langle\phi\psi|L_z\psi\rangle &= -i\hbar \int_{-\pi}^{\pi} d\phi \left[\psi^{*\prime}(\phi - \phi_0)\, \phi\, \psi(\phi - \phi_0) - \psi^*(\phi - \phi_0)\, \phi\, \psi'(\phi - \phi_0)\right] \\ &= -i\hbar\psi^*\phi\,\psi\,\Big|_{-\pi}^{\pi} + i\hbar \int_{-\pi}^{\pi} d\phi \left[\psi^*\,(\phi\,\psi)' - \psi^*\,\phi\,\psi'\right] \\ &= -i2\pi\hbar\big|\psi(\pi - \phi_0)\big|^2 + i\hbar \int_{-\pi}^{\pi} d\phi\, \psi^*\,\psi \\ &= i\hbar\Big(1 - 2\pi\big|\psi(\pi - \phi_0)\big|^2\Big) \\ &= \frac{i\hbar}{2} V''(\phi_0), \end{aligned} \tag{21.47}$$

where the last equality can be verified by differentiating the definition for $V(\phi_0)$ twice. Then the uncertainty principle becomes

$$V_{L_z} V(\phi_0) \geq \frac{\hbar^2}{4}\Big|1 - 2\pi\big|\psi(\pi - \phi_0)\big|^2\Big|^2 = \frac{\hbar^2}{4}\left[\frac{1}{2}V''(\phi_0)\right]^2. \tag{21.48}$$

It should be already clear that the right-hand side can be less than $\hbar^2/4$, and it can in fact vanish in the case of a uniform angular distribution. For more general states the right-hand side can of course be written in terms of a minimizing value of ϕ_0, but then the uncertainty limit is only implicitly defined. It would be nice to have a more explicit form. This is indeed possible, and via a variational argument it can be shown from Eq (21.48) that[5]

$$V_{L_z}\,\frac{V_\phi}{[1-(3/\pi^2)V_\phi]^2} \geq \frac{\hbar^2}{4}. \tag{21.49}$$

(angular uncertainty principle)

Note that for tightly localized states, $V_\phi \ll 1$, this reduces to the naïve uncertainty principle (21.34), while in the limit $L_z \longrightarrow 0$ this relation implies that $V_\phi \longrightarrow \pi^2/3$, as appropriate for complete angular delocalization.

21.3 Harmonic Oscillator

In the harmonic oscillator, we can introduce a similar phase operator. We might think that we can write the annihilation operator in the form

$$a = e^{i\vartheta}\sqrt{n}, \tag{21.50}$$

where $n = a^\dagger a$ is the number operator, and ϑ is a phase operator. The commutator $[a, a^\dagger] = 1$ [Eq. (5.30)] implies that $[e^{i\vartheta}, n] = e^{i\vartheta}$, which is generated by

$$[\vartheta, n] = i. \tag{21.51}$$

Then the ''number–phase'' uncertainty problem appears equivalent to the angle–angular momentum problem if $n\hbar$ plays the role of L_z. However, there are some important differences between the coordinate operator ϕ and the phase operator ϑ. For example, $e^{i\phi}$ and $e^{i\vartheta}$ both act as lowering operators for the conjugate momentum/number. But the angular-momentum space is spanned by eigenfunctions of the form $e^{-im\phi}$ for all $m \in \mathbb{Z}$, while the number space is spanned by eigenfunctions of the form $e^{-in\vartheta}$ for only *nonnegative* n; this causes $e^{i\phi}$ to be unitary, but not so for $e^{i\vartheta}$.[6] Furthermore, by taking number-state matrix elements of Eq. (21.51),

$$(n - n')\langle n'|\vartheta|n\rangle = i\delta_{nn'}. \tag{21.52}$$

This equation says that the matrix elements $\langle n'|\vartheta|n\rangle$ are equal to $i\delta_{nn'}/(n-n')$, but this doesn't make sense for integer eigenvalues—it only makes sense for continuous eigenvalues like $\langle p|x|p'\rangle = i\hbar\delta(p-p')/(p-p') = -i\hbar\delta'(p-p')$.[7]

[5] A weaker form of this relation with a smaller coefficient on the right-hand side was first proposed by D. Judge, ''On the Uncertainty Relation for L_z and ϕ,'' *Physics Letters* **5**, 189 (1963) (doi: 10.1016/S0375-9601(63)96283-2), who conjectured that the inequality in the form (21.49) should hold; a more detailed treatment appeared as D. Judge, ''On the uncertainty relation for angle variables,'' *Il Nuovo Cimento* **31**, 332 (1964) (doi: 10.1007/BF02733639). The underlying commutator was discussed by D. Judge and J. T. Lewis, ''On the Commutator $[L_z, \phi]_-$,'' *Physics Letters* **5**, 190 (1963) (doi: 10.1016/S0375-9601(63)96306-0), who proposed thinking of an alternate, more complicated commutator acting on periodic, extended angular states, which produces equivalent results. The inequality in the form (21.49) was proved by a variational argument by M. Bouten, N. Maene, and P. Van Leuven, ''On an Uncertainty Relation for Angular Variables,'' *Il Nuovo Cimento* **37**, 1119 (1965) (doi: 10.1007/BF02773197). The same result was also proven by A. A. Evett and H. M. Mahmoud ''Uncertainty Relation with Angle Variables,'' *Il Nuovo Cimento* **38**, 295 (1965) (doi: 10.1007/BF02750458). who gave stronger bound as a numerically determined factor $F(V_\phi) \geq 1$ on the right hand side that varied from 1 as $V_\phi \longrightarrow 0$ to 4.375 as $V_\phi \longrightarrow \pi^2/3$). The casting of the uncertainty relation (21.48) in terms of the uncertainty principle in the form (21.44) was emphasized by K. Kraus, ''Remark on the Uncertainty between Angle and Angular Momentum,'' *Zeitschrift für Physik* **188**, 374 (1965) (doi: 10.1007/BF01326952).

[6] G. Nienhuis and S. J. van Enk, ''Spherical angle operators for quantum-mechanical angular momentum,'' *Physica Scripta* **T48**, 87 (1993) (doi: 10.1088/0031-8949/1993/T48/013).

[7] This and the following example are from W. H. Louisell, ''Amplitude and Phase Uncertainty Relations,'' *Physics Letters* **7**, 60 (1963) (doi: 10.1016/0031-9163(63)90442-6).

In a first cut, it is worth noting that an alternative way to handle the angle–angular momentum uncertainty relation is to note that the commutation relation

$$[f(\vartheta), n] = if'(\vartheta) \tag{21.53}$$

for a differentiable function f, analogous to (21.33). So in particular

$$[\sin\vartheta, n] = i\cos\vartheta, \qquad [\cos\vartheta, n] = -i\sin\vartheta. \tag{21.54}$$

Now in the angle representation, the functions $\sin\vartheta$ and $\cos\vartheta$ are periodic, and thus do not have the effect of changing the parity of a wave function. Thus the naïve uncertainty principle goes through, and we have

$$\Delta n\,\Delta\sin\vartheta \geq \frac{1}{2}|\langle\cos\vartheta\rangle|, \qquad \Delta n\,\Delta\cos\vartheta \geq \frac{1}{2}|\langle\sin\vartheta\rangle|.$$

(quadrature uncertainty relations) (21.55)

Since $\sin\vartheta$ and $\cos\vartheta$ uniquely determine ϑ (if it is well defined), then these uncertainty relations act as simpler but less direct alternatives to the inequality (21.49).

21.3.1 Pegg–Barnett States

Notwithstanding the above comments, it is desirable to have operators in standard form that obey the regular rules and uncertainty principles. These are satisfied by the **Pegg–Barnett states**,[8] defined by

$$|\vartheta_m\rangle = \frac{1}{\sqrt{s+1}}\sum_{n=0}^{s} e^{in\vartheta_m}|n\rangle \tag{21.56}$$

(localized phase state)

in terms of regular harmonic-oscillator eigenstates $|n\rangle$, where the limit $s \longrightarrow \infty$ is taken *after* the calculation (e.g., after expectation values are calculated). To construct a basis, one must choose an arbitrary ϑ_0 to use in Eq. (21.56), after which the rest of the states can be formed from the choice

$$\vartheta_m = \vartheta_0 + \frac{2\pi m}{s+1}, \qquad m \in \{0, ..., s\}. \tag{21.57}$$

Then to invert this relation,

$$|n\rangle = \sum_{m=0}^{s} |\vartheta_m\rangle\langle\vartheta_m|n\rangle = \frac{1}{\sqrt{s+1}}\sum_{m=0}^{s} e^{-in\vartheta_m}|\vartheta_m\rangle. \tag{21.58}$$

(inverse relation)

Equations (21.56) and (21.58) are sufficient to define the localized phase states.

This allows us to define a Hermitian phase operator,

$$\vartheta := \sum_{m=0}^{s} \vartheta_m|\vartheta_m\rangle\langle\vartheta_m| = \vartheta_0 + \sum_{m=0}^{s}\frac{2\pi m}{s+1}|\vartheta_m\rangle\langle\vartheta_m|. \tag{21.59}$$

(phase operator)

This operator is Hermitian, and obeys the eigenvalue equation

$$\vartheta|\vartheta_m\rangle = \vartheta_m|\vartheta_m\rangle. \tag{21.60}$$

(eigenvalue equation)

The eigenvalues of the phase operator will depend on the choice of reference phase, so that they will range from ϑ_0 to $\vartheta_0 + 2\pi s/(s+1)$.

[8] D. T. Pegg and S. M. Barnett, "Unitary Phase Operator in Quantum Mechanics," *Europhysics Letters* **6** 483 (1988) (doi: 10.1209/0295-5075/6/6/002); D. T. Pegg and S. M. Barnett, "Phase properties of the quantized single-mode electromagnetic field," *Physical Review A* **39**, 1665 (1989) (doi: 10.1103/PhysRevA.39.1665); S. M. Barnett and D. T. Pegg, "On the Hermitian optical phase operator," *Journal of Modern Optics* **36**, 7 (1989) (doi: 10.1080/09500348914550021).

Direct calculation from Eqs. (21.56), (21.57), and (21.59) leads to

$$\begin{aligned}\langle n|\vartheta|n\rangle &= \vartheta_0 + \langle n| \sum_{m=0}^{s} \frac{2\pi m}{s+1} |\vartheta_m\rangle\langle\vartheta_m|n\rangle \\ &= \vartheta_0 + \frac{2\pi}{s+1} \sum_{m=0}^{s} m |\langle n|\vartheta_m\rangle|^2 \\ &= \vartheta_0 + \frac{2\pi}{(s+1)^2} \sum_{m=0}^{s} m \\ &= \vartheta_0 + \frac{\pi s}{s+1}\end{aligned} \tag{21.61}$$

and

$$\begin{aligned}\langle n'|\vartheta|n\rangle &= \langle n'| \sum_{m=0}^{s} \frac{2\pi m}{s+1} |\vartheta_m\rangle\langle\vartheta_m|n\rangle \\ &= \frac{2\pi}{(s+1)^2} \sum_{m=0}^{s} m\, e^{i(n'-n)\vartheta_m} \\ &= \frac{2\pi}{(s+1)^2}\, e^{i(n'-n)\vartheta_0} \sum_{m=0}^{s} m\, e^{i(n'-n)2\pi m/(s+1)} \\ &= \frac{2\pi}{(s+1)^2}\, e^{i(n'-n)\vartheta_0} \frac{s+1}{e^{2\pi i(n'-n)/(s+1)} - 1} \\ &= \frac{2\pi}{s+1} \frac{e^{i(n'-n)\vartheta_0}}{e^{2\pi i(n'-n)/(s+1)} - 1} \qquad (n' \neq n).\end{aligned} \tag{21.62}$$

Typically one is interested in the limit $n, n' \ll s$, in which case we can use the commutator

$$\langle n'|\vartheta|n\rangle \approx \frac{i}{n-n'}\, e^{i(n'-n)\vartheta_0} \qquad (n' \neq n). \tag{21.63}$$

These take the place of the problematic commutator (21.52), and are completely well behaved. The expressions here suggest the commutator (21.51) is wrong, and this is true. The diagonal elements vanish,

$$\langle n|[n,\vartheta]|n\rangle = \langle\vartheta_m|[n,\vartheta]|\vartheta_m\rangle = 0, \tag{21.64}$$

while the off-diagonal elements are non-zero,

$$\langle n'|[n,\vartheta]|n\rangle = \frac{2\pi}{s+1} \frac{(n'-n)\, e^{i(n'-n)\vartheta_0}}{e^{2\pi i(n'-n)/(s+1)} - 1} \qquad (n' \neq n). \tag{21.65}$$

and

$$\begin{aligned}\langle\vartheta_{m'}|[n,\vartheta]|\vartheta_m\rangle &= (m-m')\langle\vartheta_{m'}|n|\vartheta_m\rangle \\ &= \frac{m-m'}{(s+1)^2} \sum_{n=0}^{s} \langle n|n|n\rangle\, e^{in(\phi_{m'}-\phi_m)} \\ &= \frac{m-m'}{(s+1)^2} \sum_{n=0}^{s} n\, e^{2\pi i n(m'-m)/(s+1)} \\ &= \frac{2\pi}{s+1} \frac{m'-m}{e^{2\pi i(m'-m)/(s+1)} - 1} \qquad (m' \neq m).\end{aligned} \tag{21.66}$$

For $n \ll s$ again, the number commutator becomes

$$\langle n'|[n,\vartheta]|n\rangle \approx -i(1-\delta_{nn'}) \exp[i(n'-n)\theta_0]. \tag{21.67}$$

The commutator (21.51) was derived using the classical Poisson bracket. It turns out that the corrected commutators within this formalism arise from the classical Poisson bracket, but only in the classical limit.

21.3.1.1 Exponentials of Operators

The eigenvalues of the exponential operators

$$e^{\pm i\vartheta}|\vartheta_m\rangle = e^{\pm i\vartheta_m}|\vartheta_m\rangle \tag{21.68}$$

follows from the Hermitian phase operators (21.59). Now letting it act instead on $|n\rangle$,

$$e^{i\vartheta}|n\rangle = \exp\left(i\sum_{m=0}^{s}\vartheta_m|\vartheta_m\rangle\langle\vartheta_m|\right)|n\rangle = \frac{1}{\sqrt{s+1}}\sum_{m=0}^{s}e^{-i(n-1)\vartheta_m}|\vartheta_m\rangle, \tag{21.69}$$

after using (21.59) and then (21.58). If $n > 0$ then this is the state $|n-1\rangle$, lowered by one. If $n = 0$, then the state is

$$\begin{aligned} e^{i\vartheta}|0\rangle &= \frac{1}{\sqrt{s+1}}\sum_{m=0}^{s}e^{i\vartheta_m}|\vartheta_m\rangle \\ &= \frac{1}{\sqrt{s+1}}\,e^{i(s+1)\vartheta_0}\sum_{m=0}^{s}e^{-is\vartheta_m}|\vartheta_m\rangle \\ &= e^{i(s+1)\vartheta_0}|s\rangle, \end{aligned} \tag{21.70}$$

so that ''lowering'' the state $|0\rangle$ wraps around and generates the $|s\rangle$ state. That is, the representation of the exponential is

$$e^{i\vartheta} = |0\rangle\langle 1| + |1\rangle\langle 2| + \cdots + |s-1\rangle\langle s| + e^{i(s+1)\theta_0}|s\rangle\langle 0|. \tag{21.71}$$

Then we can form Hermitian sines and cosines from these operators. For example,

$$[\cos\vartheta, \sin\vartheta] = 0 \tag{21.72}$$

follows from

$$\begin{aligned} 2\cos\vartheta = e^{i\vartheta} + e^{-i\vartheta} &= |0\rangle\langle 1| + |1\rangle\langle 0| + |1\rangle\langle 2| + |2\rangle\langle 1| + \cdots + e^{i(s+1)\theta_0}|s\rangle\langle 0| + e^{-i(s+1)\theta_0}|0\rangle\langle s| \\ 2i\sin\vartheta = e^{i\vartheta} - e^{-i\vartheta} &= |0\rangle\langle 1| - |1\rangle\langle 0| + |1\rangle\langle 2| - |2\rangle\langle 1| + \cdots + e^{i(s+1)\theta_0}|s\rangle\langle 0| - e^{-i(s+1)\theta_0}|0\rangle\langle s|, \end{aligned} \tag{21.73}$$

while the formulae

$$\begin{aligned} \langle n|\cos^2\vartheta|n\rangle = \langle n|\cos^2\vartheta|n\rangle &= \frac{1}{2} \\ \cos^2\vartheta + \sin^2\vartheta &= 1 \end{aligned} \tag{21.74}$$

follow from

$$2\cos^2\vartheta = |0\rangle\langle 0| + |1\rangle\langle 1| + \cdots + |s\rangle\langle s| = 2\sin^2\vartheta. \tag{21.75}$$

The first of Eqs. (21.74) is particularly nice, as it says the phase of the vacuum is consistent with being random.

21.3.1.2 Lowering and Raising Operators

Having the exponential operator, we can define the lowering operator as

$$\begin{aligned} a &:= e^{i\vartheta}\sqrt{n} = |0\rangle\langle 1| + \sqrt{2}|1\rangle\langle 2| + \cdots + \sqrt{s}|s-1\rangle\langle s| \\ a^\dagger &:= \sqrt{n}\,e^{-i\vartheta} = |1\rangle\langle 0| + \sqrt{2}|2\rangle\langle 1| + \cdots + \sqrt{s}|s\rangle\langle s-1|. \end{aligned} \tag{21.76}$$

(lowering and raising operator)

Note that the operator $\sqrt{n}$ removes the problematic term $e^{i(s+1)\vartheta}|s\rangle\langle 0|$. Then using

$$\begin{aligned} aa^\dagger &= |0\rangle\langle 0| + 2|1\rangle\langle 1| + \cdots + s|s-1\rangle\langle s-1| \\ a^\dagger a &= |1\rangle\langle 1| + 2|2\rangle\langle 2| + \cdots + s|s\rangle\langle s|, \end{aligned} \tag{21.77}$$

we obtain the commutator

$$[a, a^\dagger] = 1 - (s+1)|s\rangle\langle s|. \tag{21.78}$$

(commutator of a and $a^\dagger$)

The second term converts the trace to zero (as must happen for any finite-dimensional space). However, note that for any state, s can be chosen large enough to make the extra term have negligible effect.

21.3.1.3 Coherent States

We defined coherent states as

$$|\alpha\rangle = \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}}\, e^{-|\alpha|^2/2}\, |n\rangle, \tag{21.79}$$

or in terms of the phase, with $\alpha = |\alpha|\, e^{i\zeta}$,

$$|\alpha\rangle = e^{-|\alpha|^2/2} \sum_{n=0}^{\infty} \frac{|\alpha|^n\, e^{in\zeta}}{\sqrt{n!}}\, |n\rangle. \tag{21.80}$$

Then suppose we project on the family of phase states:

$$\langle \vartheta_m|\alpha\rangle = \frac{e^{-|\alpha|^2/2}}{\sqrt{s+1}} \sum_{n=0}^{\infty} \frac{|\alpha|^n\, e^{in(\zeta-\vartheta_m)}}{\sqrt{n!}}. \tag{21.81}$$

We can make progress for $|\alpha|^2 \gg 1$, where the probability density is approximately

$$P(n) = \frac{|\alpha|^{2n} e^{-|\alpha|^2}}{n!} \approx \frac{1}{\sqrt{2\pi|\alpha|^2}}\, e^{-(|\alpha|^2-n)^2/2|\alpha|^2}. \tag{21.82}$$

This is normalized such that

$$\int dn\, P(n) = 1. \tag{21.83}$$

Putting the square root of the probability density into Eq. (21.81),

$$\begin{aligned} \langle \vartheta_m|\alpha\rangle &\approx \frac{1}{\sqrt{s+1}\sqrt[4]{2\pi|\alpha|^2}} \int_{-\infty}^{\infty} dn\, e^{-(|\alpha|^2-n)^2/4r^2}\, e^{in(\zeta-\vartheta_m)} \\ &= \sqrt{\frac{2\pi}{s+1}} \sqrt[4]{\frac{4|\alpha|^2}{2\pi}}\, e^{-|\alpha|^2(\zeta-\vartheta_m)^2}\, e^{i|\alpha|^2(\zeta-\vartheta_m)}. \end{aligned} \tag{21.84}$$

This corresponds to the alternate probability density

$$P(\vartheta) = |\langle\vartheta|\alpha\rangle|^2 \approx \frac{2\pi}{s+1}\sqrt{\frac{4|\alpha|^2}{2\pi}}\, e^{-2|\alpha|^2(\zeta-\vartheta)^2}, \tag{21.85}$$

which is normalized such that

$$\int d\vartheta\, P(\vartheta)\, \frac{s+1}{2\pi} = 1, \tag{21.86}$$

where $(s+1)/2\pi$ is the density of angular states. If ϑ is sufficiently different from ϑ_0, then there is no issue with the wave packet crossing the discontinuity (a problem that also happens classically), and we can read off the mean and variance of ϑ:

$$\langle\vartheta\rangle = \zeta, \qquad V_\vartheta = \frac{1}{4|\alpha|^2}. \tag{21.87}$$

We already worked out the mean and variance of n:

$$\langle n\rangle = |\alpha|^2, \qquad V_n = |\alpha|^2. \tag{21.88}$$

What this shows is

$$V_n V_\vartheta = \frac{1}{4}, \tag{21.89}$$

i.e., that it is a minimum-uncertainty state.

21.4 Momentum and Position Operators on the Real Line

The momentum operator, when defined on the entire real line, has somewhat different issues that the same operator on a compact space. Recall that the definition of a **Hilbert space** $\mathscr{H}$ (Section 1.2) which is an inner-product space that is both normed and complete. For the sake of discussion, we will work with a specific example of a Hilbert space, $\mathscr{H} = L^2(\mathbb{R})$, the space of square-integrable functions on $\mathbb{R}$. Note that this is *not* a suitable domain of definition for the momentum operator; the **maximal domain** of definition for p is

$$\mathrm{Dom}_{\max}(p) = \{\psi \in L^2(\mathbb{R}) : \psi' \in L^2(\mathbb{R})\}. \tag{21.90}$$

Such a domain would exclude functions that behave like $|x|^{-1/4}$ near $x = 0$, for example. A smaller, useful domain of definition for the momentum operator can be defined **Schwartz space** $\mathcal{S}(\mathbb{R})$ of all infinitely differentiable functions on $\mathbb{R}$ that decay to zero as $|x| \longrightarrow \infty$ more quickly than $|x|^{-n}$ for any positive integer n (the same is then true for all derivatives). The elements of this space are called **good functions**; examples of good functions are Gaussians. The Schwarz space is an **invariant domain** of definition for p, in the sense that the map $p : \mathcal{S}(\mathbb{R}) \longrightarrow \mathcal{S}(\mathbb{R})$ is onto.

Now the momentum operator acting on $\mathcal{S}(\mathbb{R})$ has the eigenvalue equation

$$\langle x|p|p\rangle = -i\hbar\partial_x\langle x|p\rangle = p\langle x|p\rangle, \tag{21.91}$$

in the position representation, where the p in the leftmost expression is the operator defined by the center expression, and the p in the rightmost expression is the eigenvalue. We have already found that the eigenvalue equation has solutions

$$\langle x|p\rangle = \frac{1}{\sqrt{2\pi\hbar}}\, e^{ipx/\hbar}. \tag{21.92}$$

However, these functions have constant amplitude and never decay to zero, so they do not belong to $\mathcal{S}(\mathbb{R})$ or in $L^2(\mathbb{R})$—the momentum operator has no nontrivial eigenvectors in this Hilbert space, and thus no nontrivial eigenvalues.

The situation is the similarly problematic for the position operator, as we saw in Section 1.7.2. Like p, $L^2(\mathbb{R})$ is not a valid domain for x, but $\mathcal{S}(\mathbb{R})$ is an invariant domain. The position eigenstate $|x_0\rangle$ expressed in the position representation is $\langle x|x_0\rangle = \delta(x - x_0)$ which is not a function in $L^2(\mathbb{R})$, or even a function at all. So what does this mean, is there something wrong with the momentum and position operators or with this Hilbert space?

21.4.1 Distributions

To answer this, we need to develop the notion of a generalized function.[9] A **tempered distribution** is a linear, continuous functional

$$\phi : \mathcal{S}(\mathbb{R}) \longrightarrow \mathbb{C}. \tag{21.93}$$

We will refer to this loosely as a **distribution**, though a distribution usually refers to a broader definition that only requires it to be a functional on a smaller space of functions with compact support. The distributions here then act as $\phi[\psi] = c$, where $c \in \mathbb{C}$, and the good function ψ is called a **test function** that "tests" the action of the distribution. The set of all tempered distributions on $\mathcal{S}(\mathbb{R})$ is called the **dual space** to $\mathcal{S}(\mathbb{R})$, and is denoted $\mathcal{S}'(\mathbb{R})$. The action of such functionals is often written as the inner product $\langle\phi, \psi\rangle = c$, so that the inner product on an inner product space is more generally defined (than in Section 1.1.2) in terms of an inner product $\langle\phi, \psi\rangle$, where ψ is in the vector space and ϕ is in the dual space.

Any function in $L^2(\mathbb{R})$ can work as an element of $\mathcal{S}'(\mathbb{R})$ via the integral

$$\langle\phi, \psi\rangle \equiv \phi[\psi] = \int_{-\infty}^{\infty} dx\, \phi^*(x)\, \psi(x). \tag{21.94}$$

[9] A nice review appears in Ralph J. Gagnon, "Distribution Theory of Vector Fields," *American Journal of Physics* **38**, 879 (1970) (doi: 10.1119/1.1976487).

If an element of $\mathcal{S}'(\mathbb{R})$ can be written in this form, then $\phi(x)$ is said to be a **function representation** of the functional ϕ. But the range of possible functionals is broader than what can be represented in terms of integrals of functions in the sense of Eq. (21.94). One simple example of a functional with no function representation is the Cauchy principal value integral with $1/x$:

$$\langle \mathscr{P}x^{-1}, \psi\rangle \mathscr{P}x^{-1}[\psi] := \int_{-\infty}^{\infty} dx\, \frac{\psi(x)}{x} := \lim_{\epsilon\to 0^+} \int_{\mathbb{R}-(-\epsilon,\epsilon)} dx\, \frac{\psi(x)}{x}. \tag{21.95}$$

Another important example is the Dirac delta function, which Dirac wrote (colloquially)

$$\psi(a) = \int_{-\infty}^{\infty} dx\, \delta(x-a)\, \psi(x), \tag{21.96}$$

which can be regularized as needed. A person more inclined towards formal mathematics, on the other hand, would write a definition in terms of the functional

$$\langle \delta_a, \psi\rangle \equiv \delta_a[\psi] := \psi(a). \tag{21.97}$$

To revisit the connection between these two interpretations of the delta function, which we saw before in Section 1.7.2, a distribution can be thought of as an equivalence class of **regular sequences**, which are sequences of good functions ϕ_n for which the limit

$$\phi[\psi] = \lim_{n\to\infty} \int_{-\infty}^{\infty} dx\, \phi_n^*(x)\, \psi(x) \tag{21.98}$$

exists. The limit then serves as a representation of the functional ϕ. Thus the usual regularization of the delta-function integral (21.96) in terms of unit-normalized functions $\delta_n(x)$, where $\lim_{n\to\infty} \delta_n(x) = 0\,(\forall_{x\neq 0})$, can be written

$$\delta_a[\psi] = \lim_{n\to\infty} \int_{-\infty}^{\infty} dx\, \delta_n(x-a)\, \psi(x) = \psi(a). \tag{21.99}$$

This connects the pragmatic definition (21.96) to the formal definition (21.97) of the delta function in terms of distributions.

21.4.2 Generalized Eigenfunctions and Eigenvalues

The position operator thus has eigenfuctions in the sense of distributions. Since these are outside of the Hilbert space, but they belong to the dual space $\mathcal{S}'(\mathbb{R})$, they are called **generalized eigenfunctions**, and the associated eigenvalues are **generalized eigenvalues**. Formally, we can define the functional ϕ to be a generalized eigenfunction of an operator Q with associated generalized eigenvalue q if the generalized eigenvalue equation

$$\phi[Q\psi] = q\phi[\psi] \qquad \forall_{\psi\in \mathrm{Dom}[Q]} \tag{21.100}$$

(generalized eigenvalue condition)

is satisfied, where the action of the functional must hold over the whole domain of Q. In Dirac notation, this generalized eigenvalue problem reads

$$\langle \phi|Q|\psi\rangle = q\langle\phi|\psi\rangle \qquad \forall_{|\psi\rangle\in \mathrm{Dom}[Q]}. \tag{21.101}$$

In the case at hand of the position operator, we have

$$\delta_x[x\psi] = x\psi(x) = x\delta_x[\psi] \qquad \forall_{\psi\in\mathcal{S}(\mathbb{R})}, \tag{21.102}$$

and thus we have generalized eigenvectors (delta functions) belonging to $\mathcal{S}(\mathbb{R})$ and associated eigenvalues.

The momentum eigenfunctions $\phi_p(x) := \langle x|p\rangle$ define a functional in the usual inner-product sense:

$$\phi_p[\psi] = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} dx\, e^{-ipx/\hbar}\, \psi(x). \tag{21.103}$$

This functional is, of course, the Fourier transform of $\psi(x)$ evaluated at the momentum p, or more compactly, $\mathscr{F}[\psi](p)$. The function $e^{-ipx/\hbar}$ is also not in $L^2(\mathbb{R})$, but is a function representation of an element of $\mathcal{S}'(\mathbb{R})$. In the generalized eigenvalue condition (21.100), we have

$$\phi_p[p\psi] = -i\hbar\phi_p[\partial_x\psi] = -i\sqrt{\frac{\hbar}{2\pi}}\int_{-\infty}^{\infty}dx\,e^{-ipx/\hbar}\,\psi'(x) = \frac{p}{\sqrt{2\pi\hbar}}\int_{-\infty}^{\infty}dx\,e^{-ipx/\hbar}\,\psi(x) = p\phi_p[\psi] \tag{21.104}$$

after integrating by parts. Thus, the $\phi_p(x)$ are likewise generalized eigenfunctions, and the set of generalized eigenvalues is the entire real line.

These generalized eigenvalue problems thus motivate the replacement of the Hilbert space $\mathscr{H} = L^2(\mathbb{R})$ by the **rigged Hilbert space** or **Gel'fand triplet**[10]

$$\mathcal{S}(\mathbb{R}) \subset L^2(\mathbb{R}) \subset \mathcal{S}'(\mathbb{R}). \tag{21.105}$$
(rigged Hilbert space)

Here, the Hilbert space is still $L^2(\mathbb{R})$, but the domain of p and x are the (dense) subset $\mathcal{S}(\mathbb{R})$ of $L^2(\mathbb{R})$. The dual space $\mathcal{S}'(\mathbb{R})$ is a superset of the Hilbert space, and most generally contains the (physically observable) eigenvalues that are not contained in smaller spaces.

The Hilbert space ($L^2(\mathbb{R})$ here) itself *also* has a dual space, which is the space of all linear, continuous, functionals $\phi : L^2(\mathbb{R}) \longrightarrow \mathbb{C}$. So why don't we have a quadruplet to consider instead of a triplet? The **Riesz representation theorem** says that a Hilbert space and its dual are **isometric**, meaning that they are connected by a bijective **isometry** (metric-preserving function). That is, they are equivalent spaces, so we can think of elements of the dual space as always having a representation element in the Hilbert space. This of course means that $\mathcal{S}(\mathbb{R})$ is *not* a Hilbert space [in fact, it is not complete under the usual quantum-mechanical norm, $L^2(\mathbb{R})$ being the completion of $\mathcal{S}(\mathbb{R})$, although it *is* a complete space under a different metric where it is a Fréchet space].

Generally speaking, the eigenfunctions of the standard eigenvalue problem represent the discrete part of the spectrum, while the generalized eigenfunctions correspond to the continuous part. Then in general terms of the Hilbert space $\mathscr{H}$, a self-adjoint operator Q should be associated with a subspace Ω and its dual Ω' to form the rigged Hilbert space

$$\Omega \subset \mathscr{H} \subset \Omega', \tag{21.106}$$
(rigged Hilbert space)

where Ω' contains the continuous part of the spectrum of Q. The choice of Ω is clearly connected to $\mathrm{Dom}(Q)$, but Ω' is not the same as $\mathrm{Dom}(Q^\dagger)$. The subspace Ω should be chosen large enough to constrain Ω' to be "as 'near' as possible to $\mathscr{H}$," so that the generalized eigenvectors in Ω' properly characterize Q.[11] An example of a poor match comes from the momentum operator for the infinite square well, with the choice of $\mathrm{Dom}(p)$ to be the set of square-integrable functions satisfying Dirichlet boundary conditions. In this case the generalized eigenvalue problem goes through as in Eq. (21.104) but with finite integration limits. But *any value of p in the complex plane* is allowed, unlike the unbounded case (where p must be real for the integral to converge). The odd result is then that the spectrum of p is the entire complex plane with this choice of domain (in which p is Hermitian, but not self-adjoint).

21.4.3 Finite Hilbert Spaces

So, now that we have seen a number of examples of Hilbert spaces gone wrong, do they always go wrong? If Q is linear operator on a Hilbert space, everywhere defined, and $\langle\phi|Q\psi\rangle = \langle Q\phi|\psi\rangle$ for all $\phi, \psi \in \mathscr{H}$, then Q is bounded. This is called the **Hellinger–Toeplitz theorem**,[12] and is a consequence of completeness of the Hilbert space. That is, observables are Hermitian, and that makes for an incompatibility between unboundedness and being everywhere defined.

[10] I. M. Gel'fand and N. Ya. Vilenkin *Generalized Functions, Volume 4: Applications of Harmonic Analysis* (Academic Press, 1964) (ISBN: 0122795041).

[11] François Gieres, *op. cit.*

[12] Andrea Cintio and Alessandro Michelangeli, op. cit.

Even more simply, for finite Hilbert spaces, Hermitian and self-adjoint are the same; the spectrum of Q is simply all its eigenvalues. Any operator on $\mathscr{H}$ and its adjoint are defined on all of $\mathscr{H}$. That is, $\mathrm{Dom}(Q) = \mathscr{H} = \mathrm{Dom}(Q^\dagger)$.

21.5 Spectral Theorem

21.5.1 Functions of Operators

The **spectral theorem** is easy to state for operators on finite Hilbert spaces. It says that any finite Hermitian (self-adjoint) operator A may be decomposed as[13]

$$A = \sum_{n=1}^{N} \lambda_n P_n, \tag{21.107}$$
(spectral theorem, finite operators)

where the P_n are mutually orthogonal, rank-1 projectors, the λ_n are the eigenvalues of the operator A, and N is the dimension of the matrix. Because of the property $P_n^2 = P_n$, any power satisfies

$$A^m = \sum_{n=1}^{N} \lambda_n^m P_n, \tag{21.108}$$

and thus any function $f(A)$ may be defined via its power-series expansion by

$$f(A) = \sum_{n=1}^{N} f(\lambda_n) P_n. \tag{21.109}$$
(definition of function of an operator)

Thus, it is relatively straightforward to define a function of an operator, through its Taylor series.

Now we must generalize the spectral theorem to unbounded operators. A ***σ*-algebra** on the Hilbert space $\mathscr{H}$ is a collection Σ of subsets of $\mathscr{H}$ that satisfies:

1. $\mathscr{H} \in \Sigma$.
2. if $A \in \Sigma$ then $\mathscr{H} - A \in \Sigma$. (And thus $\emptyset \in \Sigma$.)
3. the union of every countable subset of Σ is an element of Σ.

The σ-algebra defines what kind of sets are measurable, because there are pathological sets that should be excluded (see the Banach–Tarski paradox). Then a **projection-valued measure** is a collection of operators $\{P_\Omega\}$, where $\Omega \in \Sigma$, satisfying

1. P_Ω is a projector (i.e., it is self-adjoint, and $P_\Omega^2 = P$) for every $\Omega \in \Sigma$
2. $P_\emptyset = 0$ for the empty set $\emptyset$
3. $P_{\mathscr{H}} = 1$, where 1 is the identity operator
4. if $\Omega = \bigcup_{n=1}^{\infty} \Omega_n$, with Ω_n and Ω_m disjoint for $n \neq m$, then $P_\Omega = \sum_{n=1}^{\infty} P_{\Omega_n}$
5. $P_{\Omega_1} P_{\Omega_2} = P_{\Omega_1 \cap \Omega_2}$ for all $\Omega_1, \Omega_2 \in \Sigma$.

In terms of this the **spectral theorem** may be written for a self-adjoint operator A,

$$A = \int_{\sigma(A)} \lambda \, dP_\lambda, \tag{21.110}$$
(spectral theorem, general)

[13] Michael Reed and Barry Simon, *Methods of Modern Mathematical Physics. I: Functional Analysis*, revised and enlarged edition (Academic Press, 1980), Chapters VII and VIII (ISBN: 0125850506).

where $\sigma(A)$ is the spectrum of A. Then we can *define* a function of A by

$$f(A) = \int_{\sigma(A)} f(\lambda)\, dP_\lambda, \tag{21.111}$$
(function of an operator)

by analogy with the finite-dimensional case. Importantly, this can only be done for a *self-adjoint* operator, because the spectral decomposition only holds in this case.

21.5.2 Stone's Theorem

Another practical consequence of A being a self-adjoint operator is **Stone's theorem**, which says that the self-adjoint generator of a unitary transform exists. If $U(t)$ is a strongly continuous one-parameter unitary group on a Hilbert space $\mathscr{H}$, then there exists a self-adjoint operator A on $\mathscr{H}$ such that $U(t) = \exp(iAt/\hbar)$. By **strong continuity**, we mean that for every real number t_0 and $|\psi\rangle \in \mathscr{H}$, then

$$\lim_{t\to t_0} U(t)|\psi\rangle = U(t_0)|\psi\rangle. \tag{21.112}$$

The operator A is called the **generator** of the transform (cf. Problem 1.16). This is another reason that observables need to be self-adjoint—so they can generate transformations.

21.6 Exercises

Problem 21.1

In addition to the angular uncertainty relation, a famous paradox that arises from the angle–angular momentum commutator (21.33)

$$[\phi, L_z] = i\hbar \tag{21.113}$$

goes as follows.[14] Suppose we write out the matrix elements in the representation of the eigenstates $|m\rangle$ of L_z:

$$\langle m|[\phi, L_z]|m'\rangle = i\hbar\langle m|m'\rangle. \tag{21.114}$$

Then letting L_z act on its eigenstates in either direction,

$$(m' - m)\hbar\langle m|\phi|m'\rangle = i\hbar\delta_{mm'}. \tag{21.115}$$

This seems to be a contradiction for $m = m'$. Explain what is wrong in this argument.

Problem 21.2

Consider a particle of mass m in an infinite square well, with the well occupying $(-L/2, L/2)$. Here is an argument for the claim that the expectation value with respect to any energy eigenstate $\langle [x^4, p^4]\rangle = 0$. Every energy eigenstate of the infinite square well has the form

$$\psi_n(x) \sim e^{in\pi x/L} \pm e^{-in\pi x/L}, \tag{21.116}$$

which is a superposition of momentum eigenstates of momentum $p_n = \pm n\pi\hbar/L$ (such that the energy $E_n = p_n^2/2m$ is well defined in terms of this momentum). In the expectation value p^4 is an even power of momentum and is therefore well defined sitting next to its eigenstate. Thus,

$$\langle x^4p^4 - p^4x^4\rangle = p_n^4\langle x^4 - x^4\rangle = 0. \tag{21.117}$$

Another way to work out this expectation value is to write

$$\langle x^4p^4 - p^4x^4\rangle = \langle x^4p^4\rangle - \text{c.c.} = 2i\,\text{Im}\,\langle x^4p^4\rangle\,. \tag{21.118}$$

But in $\langle x^4p^4\rangle$, the wave function is real, the x factors are real, and the p factors amount to an even number of derivatives times a real factor. So $\langle x^4p^4\rangle$ is purely real, and sos the original expectation value vanishes.

(a) All that may sound reasonable, and indeed it is true that $\langle [x^2, p^2]\rangle = 0$. However, show that $\langle [x^4, p^4]\rangle \neq 0$ by carefully evaluating the expectation value in the position representation, either by explicit integration by parts or by working through the commutator. To be clear, here you are interpreting the expectation value as $\langle\psi_n|[x^4, p^4]|\psi_n\rangle$, with all operators acting to the right, as $\langle\psi_n|[x^4, p^4]\psi_n\rangle$.

(b) That $\langle [x^4, p^4]\rangle \neq 0$ is something of a pathology of the infinite square well. That is, the argument above that $\langle x^4p^4\rangle$ is real should actually hold true for bound states on all of $\mathbb{R}$ where the wave functions decay to zero sufficiently quickly (say exponentially), such that boundary terms from integration by parts may be discarded. The point of this part of the problem is to work through an argument that the nonzero expectation value for the infinite square well is a pathological result, owing to a nonphysical limit taken too soon. A regularized interpretation of the problem is to compute the same expectation value for the *finite* square well, and *then* take the limit $V_0 \longrightarrow \infty$. Show explicitly that this calculation yields $\langle [x^4, p^4]\rangle = 0$ (use the results of Problem 2.23). What is missing from the calculation in (a) that leads to the pathological result?

[14] W. H. Louisell, "Amplitude and Phase Uncertainty Relations," *Physics Letters* **7**, 60 (1963) (doi: 10.1016/0031-9163(63)90442-6).

(c) Now treat this problem in a mathematically rigorous way, showing that the interpretation in (a) is not physically sensible because $[x^4, p^4]$ is not "self-adjoint" in the context of the given expectation value. (Note that $[x^4, p^4]$ is antisymmetric under conjugation and thus imaginary, so think of it as self-adjoint in the sense of being multiplied by i.) Find a physically sensible interpretation of the expectation value where it vanishes.

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