Retarded, or Casimir, long-range potentials

Even if two systems consist entirely of slowly moving constituents, nonrelativistic theory may not be adequate to determine the interaction energy of the systems when they are very far apart.

Larry Spruch

Only someone with a short-range view could fail to be aware of the great importance of long-range interactions. Indeed, from the late 18th century, when Coulomb discovered that the electrostatic interaction has the same $1/r^2$ force law that Newton had found for the gravitational interaction, until perhaps the 1930s, when the strong and weak interactions began to be understood, long-range interactions largely *were* the subject of physics. By long-range interactions I mean not only those for which the potential behaves as $1/r$ for all r but those whose potentials behave asymptotically as some power of $1/r$. These originate in $1/r$ potentials and include, for example, the van der Waals $1/r^6$ interaction (as calculated nonrelativistically) between two spherically symmetric atoms at a large separation r, and multipole interactions between charge distributions. Long-range potentials therefore not only play a vital role in astrophysics via Newton's law of gravitation and a significant role in nuclear physics via Coulomb's law, but determine almost all of atomic, molecular and condensed-matter physics.

Surprisingly, as we shall see, nonrelativistic theory may not be adequate for determining the interaction potential $V(r)$ of a pair of systems that are far apart, even if all their constituents are moving slowly. If the potential originates in correlated motion of the constituents, the retardation time—the transit time of a photon—can become important, and a relativistic treatment must be used. In atomic systems, the separation beyond which the retardation time becomes important is about $137a_0$. In principle, of course, one should use relativistic quantum field theory to treat these systems; however, one can also use a much more elementary derivation[1] of the retarded potential. The retarded potential can differ in its very form from the nonrelativistic result.

Normally, the chief relativistic corrections are kinematic and dynamic and are of order v^2/c^2, with v a characteristic speed. Here I will assume that such corrections are small, and that the only relativistic correction of interest stems from the time required for two systems to communicate with one another, a consequence of the finiteness of c.

Nonrelativistic quantum theory describes well a compact entity with neutral and charged constituents whose characteristic internal speeds v are all much less than c. The same is true of the interaction of a pair of compact entities, out to rather large separations. In both cases, the relativistic corrections are merely of order v^2/c^2.

However, the situation can be quite different for the interaction of two systems at large separations—greater than or of the order of $137a_0$ for two atomic systems. The two systems might be two neutral atoms in a gas, or the ionic core of an atom and an electron in a large-radius, high-n "Rydberg" state of the same atom. Suppose that the interaction between the two systems as calculated in nonrelativistic theory (using the usual Coulombic "action at a distance") originates in correlated internal motions of the two systems. If the systems are farther apart than about $137a_0$, the retardation time can be comparable to a characteristic period of an electron in either system, so that the motions in one system cannot maintain a one-to-one phase relation with the motions in the other system, and the correlated motion cannot be maintained.

Some simple systems

To make the discussion a little more concrete, consider the five pairs of systems indicated in figure 1:

- two fixed point charges ("electrons")
- a fixed point charge and a static induced dipole moment ("atom")
- two dipoles
- a point charge and its static image in an infinite plane wall
- a dipole and its image in such a wall.

I will later comment briefly also on the force per unit area between two infinite plane parallel ideal walls at a separation z. In all these cases the separation between the two systems is large compared with the size of the individual particles or atoms. The walls are plane ideal conductors whose surface charges adjust instantaneously to external fields. An atom can, for the moment, be characterized completely by the static electric-dipole polarizability α: In the presence of a static uniform electric field $\mathbf{E}$ an atom develops a dipole moment μ equal to $\alpha\mathbf{E}$. (In this article, α will *not* denote the fine-structure constant $e^2/\hbar c$, or $1/137$.) For simplicity, I will assume that the atoms have spherically symmetric ground states, that is, that their dipole moments are entirely induced.

In the expressions for potentials I

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$E \sim \frac{\mu}{r^3}$

↑ ↑

$\mu E = \alpha E^2 \sim \frac{1}{r^6}$

$V \sim \frac{\mu\mu}{r^3}$

will generally ignore signs and factors of order unity. This will enable us to concentrate on physical concepts and save a considerable amount of nervous energy. Not not only do we avoid irritating questions about factors of 4π and the factors of 2 associated with double counting and with the distinction between permanent and induced multipole moments, but we also need not worry about evaluating dimensionless integrals known to be of order unity, and we need not bother with some very messy details involving the infinite number of modes of the vacuum fluctuation field. The weakness of this approach lies not in its being cavalier, for that can be corrected, but rather in its giving the correct potential only at asymptotically large separations.

I will begin by considering the nonrelativistic quantum approximations for the potentials; even though these are well known, they will prove useful for studying how the interactions behave when retardation effects are accounted for.

Electron–electron. For two fixed electrons separated by a distance r, the potential is of course

$$V_{\mathrm{ee}}(r) = e^2/r$$

Electron–atom. For an electron and an atom separated by a fixed distance r that is large compared with a_0, the electron's Coulomb field $\mathbf{E}$ generates a dipole moment $\boldsymbol{\mu}$ in the atom. Because the separation is large, the field is approximately uniform and has magnitude e/r^2 over the volume of the atom. The interaction energy of the induced dipole moment with the external field is of order $\boldsymbol{\mu}\cdot\mathbf{E}$, so that

$$\begin{aligned} V_{\mathrm{ea}}(r) &= \boldsymbol{\mu}\cdot\mathbf{E} \\ &= \alpha E^2 \\ &= \alpha e^2/r^4 \end{aligned} \qquad (1)$$

Atom–atom. For two atoms separated by a distance r that is large compared with a_0, the interaction is the angle-dependent dipole–dipole interaction, proportional to $\boldsymbol{\mu}$, $\boldsymbol{\mu}'$ and r^{-3}. The instantaneous dipole moments $\boldsymbol{\mu}$ and $\boldsymbol{\mu}'$ have magnitudes of order ea_0. The mean value of the interaction energy vanishes because one must average over all orientations of each dipole moment. However, the interaction does have an effect; in second-order perturbation theory one finds

$$V_{\mathrm{aa}}(r) = \frac{[\boldsymbol{\mu}\cdot\boldsymbol{\mu}'/r^3]^2}{\Delta\mathscr{E}}$$

Here $\Delta\mathscr{E}$ is a characteristic excitation energy of the combined system; its value is typically on the order of e^2/a_0. The potential thus is

$$\begin{aligned} V_{\mathrm{aa}}(r) &= [(ea_0)^2/r^3]^2\,(a_0/e^2) \\ &= (e^2/a_0)(a_0/r)^6 \end{aligned} \qquad (2)$$

This is the justly famous London–van der Waals r^{-6} interaction. (Only rather recently have I begun to derive particular pleasure from the knowledge that Johannes van der Waals was not all that young when he published many of his results. He was already 36 years old when he wrote his thesis, which contained the seminal ideas on the thermodynamics of gases, and he did much important work thereafter.)

Electron–wall. For an electron at a fixed distance z from a wall, the interaction is of course equivalent to the interaction of the electron with its image charge:

$$V_{\mathrm{e\,wall}}(z) = e^2/z$$

Atom–wall. For an atom at a fixed distance z from a wall, the interaction is again equivalent to the interaction of the atom with its image. The dominant component is the interaction of the instantaneous atomic dipole with its image dipole. The orientation of the latter is completely determined by the orientation of the former, and the expectation value of the interaction energy does not vanish when it is averaged over all orientations of the atomic dipole. Thus, unlike in the atom–atom case, the interaction does not vanish in first-order perturbation theory but is given by

$$\begin{aligned} V_{\mathrm{a\,wall}}(z) &= |\boldsymbol{\mu}|^2/z^3 \\ &= (ea_0)^2/z^3 \end{aligned}$$

There is of course no wall–wall interaction in the nonrelativistic approximation. "Of course" is the wrong phrase. It is almost as "obvious" in the relativistic quantum context that there is no wall–wall interaction, but that isn't true. More on this "off the wall" effect later.

These results are clearly only approximate, even within the context of nonrelativistic quantum mechanics. Making the models somewhat more realistic means introducing corrections. Thus, for example, for an electron in a Rydberg state of a neutral atom, there are, in addition to the Coulomb potential, the polarization potential of equation 1 due to the dipole polarizability of the core and a term originating in the quadrupole polarizability of the core. One can also consider the effects of the outer electron's motion as a perturbation. The dominant nonadiabatic, or "dynamic," contribution, to be considered more fully later, is of order

$$V_{\mathrm{ea}}^{\mathrm{dyn}}(r) = \left(\frac{e^2/a_0}{\Delta\mathscr{E}}\right)^2 \left(\frac{a_0}{r}\right)^5 \frac{e^2}{r} \qquad (3)$$

where $\Delta\mathscr{E}$ is a characteristic excitation energy of the core, on the order of e^2/a_0. This interaction potential is a measure of the inability of the core electrons to follow the motion of the distant electron. It will be useful to compare the dynamic contribution with the relativistic effects. First we make a classical nonrelativistic detour.

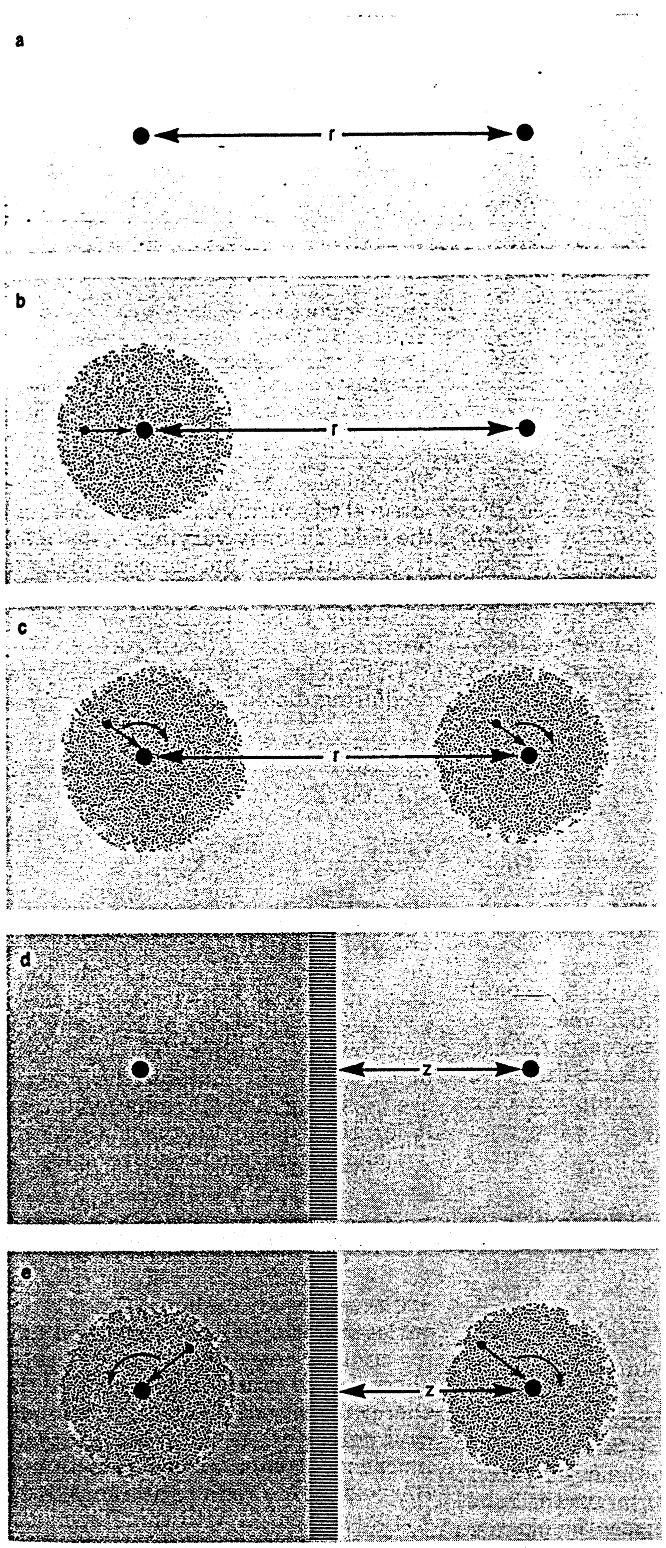
A digression: Classical mechanics

The results listed above are based on quantum mechanics. Considering the same systems classically, but still nonrelativistically, changes the results for the atom–atom and atom–wall interactions, which originate in correlated internal motions. The two effects are similar, so I consider only the atom–atom interaction. In classical theory an atom has no lowest energy level; instead one can model[2] an "atom" as a three-dimensional harmonic oscillator consisting of a "nucleus" and an "electron" coupled by a spring with stiffness constant k. The leading atom–atom interaction is, as before, the dipole–dipole term

$$e^2(\mathbf{r}_1\cdot\mathbf{r}_2 - 3z_1z_2)/r^3$$

The line joining the nuclei of the two atoms (which are separated by a large fixed distance r) defines the z axis; the positions of the electrons within the ith atom are $\mathbf{r}_i$.

The total Hamiltonian is then the sum of the kinetic energies and the



Systems. **a:** Two fixed point charges ("electrons"). **b:** A fixed point charge and a static induced dipole moment (in an "atom"). **c:** Two dynamically correlated dipoles. Semiclassically, these can be considered to be rotating at the same frequency with a fixed phase relationship; quantum mechanically, the excitations are correlated. **d:** Point charge and a conducting planar wall; the charge interacts with its image. **e:** A dipole and a wall; the dipole and its image are correlated—semiclassically they counterrotate. Figure 1

total potential energy

$$U(\mathbf{r}_1, \mathbf{r}_2, r) = \tfrac{1}{2}k({r_1}^2 + {r_2}^2) - e^2(\mathbf{r}_1 \cdot \mathbf{r}_2 - 3z_1z_2)/r^3$$

Note that this potential energy can be written as the sum of three terms, U_x, U_y and U_z, each of which contains only one component of the internal coordinates; this property allows one to separate the problem into three independent problems, one for each coordinate.

The contributions of the two terms are on the order of kd^2 for the internal energy and e^2d^2/r^3 for the dipole term, where d is the amplitude of the oscillations. Because r is large, their ratio, e^2/kr^3, is small, and the potential is positive. In fact, one can see from examining the potentials U_x, U_y and U_z that for large r each is strictly nonnegative for all values of the coordinates, so that U is always nonnegative. The atom–atom ground-state energy at large r is therefore the same as its value for two isolated ground-state atoms; that is, the atom–atom interaction vanishes at large r, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are equal to zero in the stable ground state. The interpretation is simple: An isolated classical atom in its ground state has a zero dipole moment not only on average but at each instant, and when two classical atoms are far apart, the energy required to displace each electron through a distance d in each atom—namely, twice $kd^2/2$—is more than is gained from the dipole–dipole interaction, which is of order $-e^2d^2/r^3$.

Now consider the two atoms quantum mechanically: To compare the classical and quantum-mechanical results, let us choose the spring constant k to be e^2/a_0^3, so that the ground-state amplitude is a_0. For the quantum-mechanical atom there is a van der Waals interaction, even though, as we have seen, there is none classically. The difference comes from the uncertainty principle, that is, from the zero-point motion of the electron in the atoms. Viewed semiclassically, the expectation value $\langle e\mathbf{r}_i(t)\rangle$ of the dipole moment of an electron in the ith atom vanishes, as it does classically, but—unlike the classical result—the instantaneous value of $e\mathbf{r}_i(t)$ is not zero. Thus, it's not necessary to generate dipole moments in the individual atoms—at a great cost in energy—to develop an atom–atom interaction; the two atoms need merely correlate their dipole moments, which can be done with less energy than that gained from the attraction of the correlated dipole moments. I will return to correlation effects later. The explanation of interatomic attraction, whose existence van der Waals had already noted (from the thermodynamic properties of gases) back in 1873, was one of the earliest successes of quantum theory.

$$k a_0^2 = \frac{e^2}{a_0}$$

Retardation effects

John Wheeler was probably the first to realize that retardation might play a significant role in long-range quantum-mechanical atom–atom interactions, but his 1941 abstract[3] disappeared from view, as if sucked in by one of the black holes for whose description Wheeler is noted. Independently, Hendrik B. G. Casimir and his students began calculations on retardation effects in 1948; these were subsequently continued[4–6] by others. In his charming semi-popular autobiography, Casimir states[7] that his work on what are now called Casimir effects is "of some theoretical significance." I would replace "some" by a much stronger adjective.

I now present an elementary version that contains all of the essential physics of these calculations—improving slightly upon an argument published[1] previously with Edward J. Kelsey. As I have mentioned, the results for each potential are good to within a numerical constant of order unity, and the calculations can be modified readily to yield the constants exactly. The net charges, masses and dynamic polarizabilities of the interacting systems are their only relevant properties. To the extent that the polarizabilities can be determined classically, quantum-mechanical aspects of the behavior of the systems never enter. Indeed the essential idea is to proceed entirely classically, treating the electromagnetic field relativistically, until the last step; relativistic quantum field theory is employed only in that last simple step, in which we quantize the energy of the modes of vibration of the electromagnetic field. In these calculations, the only relativistic effects enter through the electromagnetic field. There are no dynamical relativistic effects; that is, all particles have speeds much less than c. The individual systems considered here are small enough that the transit time across each system for electromagnetic signals is negligible compared with all relevant characteristic times; the transit time need not be negligible for sufficiently large separations of the interacting systems, at which it may prove necessary for some systems to build in the wave properties of electromagnetic radiation.

Consider two polarizable systems situated at $\mathbf{x}_1$ and $\mathbf{x}_2$. For generality (and because it will prove handy later on), suppose the systems are in the presence of a background electric field, which can be decomposed into Fourier components $\mathbf{E}_0(\omega,\mathbf{x})\sin\omega t$. Each system is characterized by its dynamic electric dipole polarizability, $\alpha_i(\omega)$ (when the limit $\alpha_i(0)$ exists, denote it by α_i). In the presence of the background field, each atom develops a dipole moment $\boldsymbol{\mu}_i(\omega,t)$ given by $\alpha_i(\omega)\mathbf{E}_0(\omega,\mathbf{x}_i)\sin\omega t$. The leading term in the interaction of the two systems is the interaction of the two oscillating dipoles, $\boldsymbol{\mu}_1(\omega,t)$ and $\boldsymbol{\mu}_2(\omega,t)$. This interaction (whose form is an extension of the form for two static dipoles) is $\boldsymbol{\mu}_1(\omega,t)\cdot\mathbf{E}_{2\to1}(\omega,t)$, where $\mathbf{E}_{2\to1}(\omega,t)$ is the field at $\mathbf{x}_1$ due to the dipole at $\mathbf{x}_2$.

To ensure that all results remain finite, assume that everything is enclosed in a volume $\mathscr{V}$ with dimensions very large compared with r, the separation $|\mathbf{x}_2-\mathbf{x}_1|$ of the systems; r, in turn, is very large compared with the dimensions of either system. The density of modes of the electromagnetic field is given by the standard form (in polar coordinates)

$$N(\omega)\mathrm{d}\omega = 2\mathrm{d}^3\omega\,\mathscr{V}/c^3$$
$$= 2\omega^2\mathrm{d}\omega\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi\,\mathscr{V}/c^3$$

The interaction of the two systems is then

$$V(\mathbf{x}_1,\mathbf{x}_2,t) = \int_0^\infty \boldsymbol{\mu}_1(\omega,t)\cdot\mathbf{E}_{2\to1}(\omega,t)N(\omega)\mathrm{d}\omega \qquad (4)$$

If $\mathbf{E}_0(\omega,\mathbf{x})$ is a smoothly varying function of ω and $\mathbf{x}$, a physical argument indicates that the integral can be cut off at frequencies ω on the order of c/r. For wavelengths much larger than the separation of the systems, the electric field is almost the same at $\mathbf{x}_1$ as at $\mathbf{x}_2$, and the integrand in equation 4 is a slowly varying function of the frequency and thus contributes to the potential V. For wavelengths c/ω much less than r, on the other hand, the fields $\mathbf{E}_0(\omega,\mathbf{x}_1)$ and $\mathbf{E}_0(\omega,\mathbf{x}_2)$ are quite different, so that the integrand is a strongly oscillating function of the frequency; as a result these terms cancel each other out, contributing nothing to the integral. The precise manner in which the cutoff is introduced should not affect the form of the interaction and should not greatly affect the numerical result. The simplest technique is to cut the integral off sharply at $\omega = c/r$. Because the field is slowly varying in space for the frequencies that do contribute to the integral, $\mathbf{E}_0(\omega,\mathbf{x}_2)$ can be approximated by $\mathbf{E}_0(\omega,\mathbf{x}_1)$ and $\cos\omega r/c$ is approximately unity (see figure 2).

The field $\mathbf{E}_{2\to1}$ generated at $\mathbf{x}_1$ by the oscillating dipole at $\mathbf{x}_2$ is proportional to

$$\frac{\boldsymbol{\mu}_2-3\mu_{2z}\hat{z}}{r^3}+\frac{\dot{\boldsymbol{\mu}}_2-3\dot{\mu}_{2z}\hat{z}}{cr^2}+\frac{\ddot{\boldsymbol{\mu}}_2-\ddot{\mu}_{2z}\hat{z}}{c^2r}$$

where the z axis lies along the line connecting $\mathbf{x}_1$ and $\mathbf{x}_2$. The first two terms result in contributions to the integrand in equation 4 that are each proportional to $1-3\cos^2\theta$, where θ is the angle between the field $\mathbf{E}_0$ and the z axis; on averaging over all (equally probable) orientations of $\mathbf{E}_0$, their net contribution vanishes. The only term in $\mathbf{E}_{2\to1}$ that contributes to the integral over ω is then the $1/r$ "radiation term." It is proportional to $\alpha_2(\omega)\mathbf{E}_0(\omega,\mathbf{x}_1)(\omega^2/c^2r)$ and yields, on time averaging,

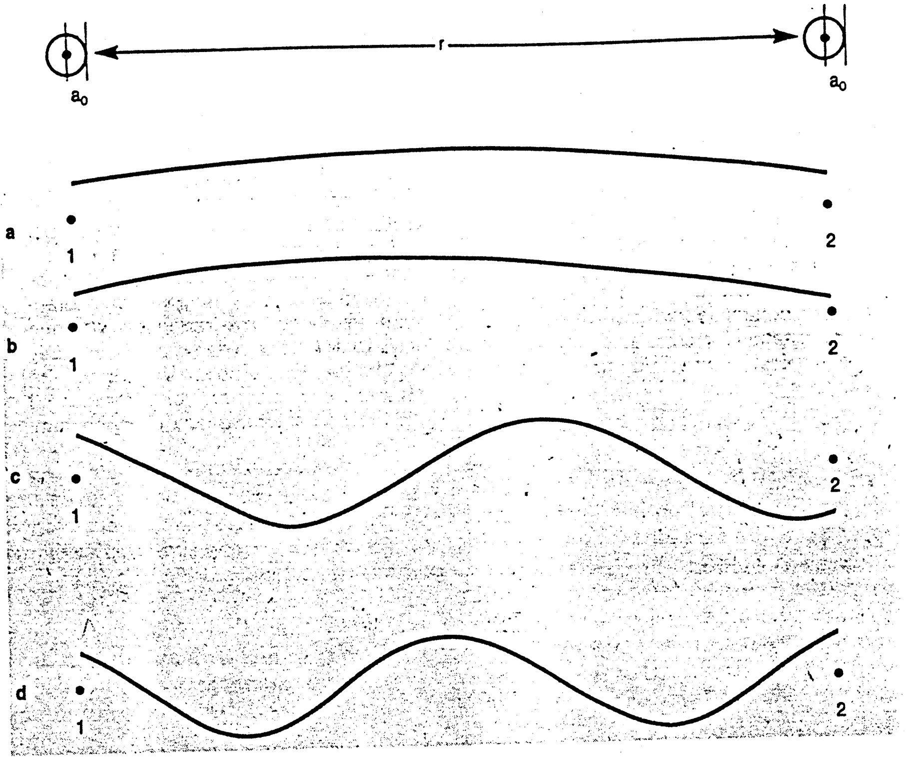
$$V(\mathbf{x}_1,\mathbf{x}_2) = \frac{\mathscr{V}}{c^5r}\int_0^{c/r}\alpha_1(\omega)\alpha_2(\omega)\omega^2|\mathbf{E}_0(\omega,\mathbf{x}_1)|^2\omega^2\mathrm{d}\omega$$

I have already assumed that $\mathbf{E}_0(\omega,\mathbf{x})$ varies smoothly with ω and $\mathbf{x}$ and that its orientations are all equally probable; I now assume further that the energy density of the mode of frequency ω, namely $|\mathbf{E}_0(\omega,\mathbf{x})|^2$, has a value $u(\omega)$ independent of $\mathbf{x}$. The interaction of two polarizable systems at a separation r large compared with the dimensions of either, located within a volume $\mathscr{V}$ and far from any surface of $\mathscr{V}$, is then

$$V^{\text{class}}_{\text{pol pol}}(r) = \frac{\mathscr{V}}{c^5r}\int_0^{c/r}\alpha_1(\omega)\alpha_2(\omega)u(\omega)\omega^4\mathrm{d}\omega$$

a result that Maxwell could have derived, and perhaps did.

The quantum version follows immediately on making $\mathbf{E}_0$ the field of vacuum fluctuations (it is already assumed to have all the right properties); in that case the energy $\mathscr{V}u(\omega)$ in a mode of the field is simply $\hbar\omega$ (actually ½$\hbar\omega$, at a temperature of absolute zero, but we're neglecting factors of ½). The



Contributions of electromagnetic waves to the interaction between two "atoms" depend on the wavelength. **a, b:** For wavelengths much longer than the separation r of the atoms, the electric field has nearly the same value at each atom; the long-wavelength contributions to an integral over wavelengths thus interfere constructively. **c, d:** For wavelengths much shorter than the separation, the field values at the two atoms can be quite different and vary significantly with wavelength; contributions to an integral over wavelengths from nearby values thus interfere destructively, and their net contribution is small. Figure 2

basic result thus has the remarkably simple form

$$V_{\text{pol pol}}(r) = (\hbar/c^5 r)\int_0^{c/r} \alpha_1(\omega)\alpha_2(\omega)\omega^5 \mathrm{d}\omega \qquad (5)$$

Of course, this simple expression is valid only asymptotically: Higher-multipole radiation and multiple scattering of electromagnetic waves—that is, the exchange of more than two photons—are significant at all but the largest distances.

To obtain the interaction potentials for the electron–electron, electron–atom and atom–atom interactions one need merely insert the appropriate expressions for the polarizabilities.

As before, a suitable model of an atom is an electron and nucleus forming a simple harmonic oscillator whose energy $\hbar\omega_0$ is a characteristic atomic energy e^2/a_0. The polarizability $\alpha(\omega)$ is then $(e^2/m)(\omega_0{}^2 - \omega^2)^{-1}$, which, for frequencies far below resonance, simplifies to $a_0{}^3$. Because the range of integration in equation 5 is cut off at c/r, the value of $\alpha(\omega)$ is constant throughout the range of integration when the separation r is much larger than c/ω_0, or about $137a_0$. Note that this condition is equivalent to requiring that the retardation time r/c be large compared with the natural period of the system—or that r be much larger than the characteristic wavelength of the photons emitted by the atom. For a free electron, the resonance frequency is zero, so that the polarizability is $e^2/m\omega^2$.

$\frac{c}{\omega_0} = \frac{c}{e^2/\hbar a_0} = \frac{\hbar c}{e^2} \cdot a_0$

These values for the polarizabilities can now be inserted into equation 5. The results are

$$V_{\text{ee}}(r) = \frac{\hbar e^4}{c^3 m^2 r^3} \qquad (6)$$

$$V_{\text{ea}}(r) = \frac{\hbar e^2 \alpha}{mcr^5} \qquad (7)$$

$$V_{\text{aa}}(r) = \frac{\hbar c \alpha_1 \alpha_2}{r^7} \qquad (8)$$

where α is equal to $a_0{}^3$ for the harmonic-oscillator atom. The interaction for the electron–atom pair can be applied to an electron–ion pair with the electron bound in a high Rydberg state, even though the range of integration of ω includes the orbital frequency of the electron in that state.

There is an even simpler derivation of the forms of the potentials. For low-frequency photons the electron–photon and atom–photon interactions are characterized by the charge e and mass m of the electron and the polarizability α of the atom. (We ignore magnetic moments and assume the nucleus to be infinitely massive.) The interactions are the results of two-photon exchanges. Because the effect of an electron–photon interaction is proportional to e, the potential must contain a factor e^2, one e for each photon exchanged, if an electron is one of the two interacting systems. A polarizability factor α accounts for the interaction of an atom with two photons. (See figure 3.) The quantization of the electromagnetic fields of the two photons introduces, as was shown, a factor $\hbar$. If one is willing to forgo both insight into the domain of validity of the results and knowledge of numerical coefficients, one can resort to dimensional analysis to obtain the remaining dependence (on r, c and m) of the retarded interactions. Equations 6, 7 and 8 then follow easily. The starting point for the electron–atom pair, for example, is

$$V_{\text{ea}}(r) = e^2\alpha\hbar f(r,c,m)$$

I noted earlier that classical "atoms" do not attract one another at separations much beyond a_0, the (nonrelativistic) van der Waals r^{-6} interaction being a consequence of the uncertainty principle for particles. On the other hand, the (retarded) Casimir r^{-7} atom–atom interaction, which is valid for r larger than about $137a_0$, can be thought of as having its origins in vacuum fluctuations, that is, in the uncertainty principle for electromagnetic fields.

Refinements

In addition to the vacuum fluctuations of the electric field, there are of course also vacuum-fluctuating magnetic fields, and these induce magnetic dipole moments. Furthermore, the dipole moments induced by the vacuum fluctuations of the fields radiate both electric and magnetic fields. The net effect, as shown[8] by Gerald Feinberg and Joseph Sucher, is that the electric polarizability must be replaced by a linear combination of the electric and magnetic dipole polarizabilities of the atoms. For example, for two hydrogen atoms both in their ground states, α is $\frac{9}{2}a_0{}^3$ and the magnetic polarizability is about $123a_0{}^3$; the magnetic term dominates at sufficiently large distances. The magnetic polarizability of a hydrogen atom is so large because the energy difference between the ground state and the first excited state, which involves a spin flip, is so small—it corresponds to the famous 21-cm line of hydrogen. But the magnetic Casimir potential is valid only for distances much larger than this 21-cm characteristic wavelength. Feinberg and Sucher, long among the leaders in long-range interactions, therefore refer to their conceptually very interesting result as "academic."

A quick, if very crude, method of estimating the electron–wall and

$a_0 = \frac{\hbar^2}{me^2}$

$-\omega^2 x_\omega + \omega_0^2 x_\omega = \frac{eE_\omega}{m}$

$\omega << \omega_0 = \frac{e^2}{\hbar a_0}$

$\hbar^2 a^2 = a^3$

Retarded potentials

In the chart below, the wall–wall entry is a force per unit area; all other entries are potentials. The values of d and $\Delta\mathscr{E}$ are characteristic atomic dimensions and excitation energies; they are generally on the order of a_0 and e^2/a_0, respectively. The static dipole-moment polarizability (α, α_1 or α_2) is generally on the order of $a_0{}^3$.

The potentials are of three sorts:

- ▶ Static potentials (red) involve no correlated excitation (no correlated motions in a semiclassical picture) and are valid for all distances beyond a few a_0.
- ▶ Nonrelativistic dynamic potentials (blue) are based on two-body Coulomb action-at-a-distance interactions, that is, assuming that the speed of light is infinite; they originate in correlated excitations (or, semiclassically, motions) and cannot be sustained at large distances if c is finite.
- ▶ Retarded potentials (purple) are calculated with finite c and a quantized electromagnetic field; they originate in interactions involving low-frequency photons only. Unlike in the dynamic potentials, only the charge e or the polarizability α and the separation, r or z, enter (along with $\hbar$, c and m); the characteristic size d and energy $\Delta\mathscr{E}$ do not enter.

In the cases not involving atoms or ions, the retarded effects are valid down to a few a_0; in the others the effects first become valid at large distances, where they replace the dynamic potentials. To obtain the gravitational analog of the electron–electron interaction, replace both factors of e^2 by Gm^2; to obtain the gravitational–electromagnetic interference term in the interaction, replace only one factor of e^2 with Gm^2.

The expressions below ignore signs and dimensionless factors of order unity.

	$a_0 \lesssim r \ll 137a_0$	$137a_0 \ll r$
electron–electron	$\longleftarrow \quad \frac{e^2}{r} + \frac{e^2}{r}\frac{e^2/mc^2}{r}\frac{\hbar/mc}{r} \quad \longrightarrow$	
electron–ion	$\frac{e^2}{r} + \frac{\alpha e^2}{r^4} + \frac{\alpha e^2}{r^4}\left(\frac{a_0}{r}\right)^2\frac{e^2/a_0}{\Delta\mathscr{E}}$	$\frac{e^2}{r} + \frac{\alpha e^2}{r^4} + \frac{\alpha e^2}{r^4}\frac{\hbar/mc}{r}$
atom–atom	$\frac{e^2}{r}\frac{\alpha d^2}{r^5}$	$\frac{\hbar c\alpha_1\alpha_2}{r^7}$
electron–wall	$\longleftarrow \quad \frac{e^2}{z} + \frac{e^2}{z}\frac{\hbar/mc}{z} \quad \longrightarrow$	
atom–wall	$\frac{e^2d^2}{z^3}$	$\frac{\hbar c\alpha}{z^4}$
wall–wall	$\longleftarrow \quad \frac{\hbar c}{z^4} \quad \longrightarrow$	

atom–wall interactions is to replace the wall by a conducting sphere of radius z, with the electron or atom at a distance z from the nearest point on the sphere. (The sphere is near enough to the atom or electron to resemble a wall, at least roughly.) The interaction between the sphere and the electron or atom is, roughly, just the dipole–dipole interaction we have discussed. (The retention of only the dipole–dipole interaction is not unreasonable, as the relevant values of $c/z\omega$ are of order unity.) A conducting sphere has a static polarizability of z^3. Equation 5 then yields

$$V_{\text{e wall}}(z) = (e^2\hbar/mcz^2) \qquad (9)$$

$$V_{\text{a wall}}(z) = \alpha\hbar c/z^4 \qquad (10)$$

A far better approach for obtaining these two potentials is to note that the time-averaged energy of a polarizable system located at $\mathbf{x}$ is, in the presence of a background field $\mathbf{E}_0(\omega,\mathbf{x})\sin\omega t$, $\alpha(\omega)\mathbf{E}_0{}^2(\omega,\mathbf{x})$, or $\alpha(\omega)u(\omega,\mathbf{x})$. The quantum self-energy of an isolated system, obtained by replacing $u(\omega,\mathbf{x})\mathscr{V}$ by $\hbar\omega$, is

$$\mathscr{E} = \int_0^\infty \alpha(\omega)u(\omega,\mathbf{x})N(\omega)\mathrm{d}\omega$$

$$= (\hbar/c^3)\int_0^\infty \alpha(\omega)\omega^3\mathrm{d}\omega$$

which is infinite.

At a distance z, much greater than a_0, from an ideal wall, a vacuum fluctuation with a frequency much larger than c/z is hardly affected by the presence of the wall, while a fluctuation with a frequency much less than c/z is greatly affected. Although the self-energy $\mathscr{E}(z)$ of the polarizable system at a distance z from the wall is also infinite, it is the difference $\mathscr{E} - \mathscr{E}(z)$, that is, the change in the energy of interaction of the system with all of the modes, that represents the interaction of the polarizable system with the wall. The contributions to this difference from frequencies large compared with c/z roughly cancel, while the contributions from frequencies below c/z are roughly comparable to one another and to their differences. As a result, the interaction potential of a polarizable system and a wall is approximately

$$V_{\text{pol wall}}(z) = (\hbar/c^3)\int_0^{c/z} \alpha(\omega)\omega^3\mathrm{d}\omega$$

Insertion of the appropriate forms of $\alpha(\omega)$ yields equations 9 and 10.

Wall–wall interaction. The fact that approximating a wall by a conducting sphere gives the correct result for $V_{\text{pol wall}}$ encourages one to go one step further, to obtain the wall–wall interaction from that of two atoms by approximating each wall by a sphere of radius z and placing the spheres so that their closest points are a distance z apart. Because the walls are infinite, we must determine the force per unit area, which we determine from the potential by dividing by an area as well as a length; the only relevant dimension is z, so the appropriate factor must be of order z^3. Making the appropriate substitutions in $V_{\text{a a}}/z^3$ gives

$$(\mathscr{F}/\mathscr{A})_{\text{wall wall}} = \hbar c/z^4$$

a result first obtained by Casimir. As $\hbar$, c and z are the only relevant quantities—the electron plays no role in our ideal wall model, so neither e nor m can appear—this last result can be deduced on dimensional grounds alone. The physical origin of the force between the walls lies in the variation with z of the modes of oscillation of the vacuum fluctuations. One expects that as the separation between the walls varies, the energy in the vacuum fluctuations between the walls will vary, giving rise to the Casimir force. This expectation was confirmed,[9] though not to high accuracy, by M. J. Sparnaay and others. The wall–wall force, perhaps one of the most beautiful problems in physics, is an astonishingly direct physical effect of vacuum fluctuations.

Murium. The ratio of the retarded potential to the Coulomb potential for an electron interacting with an ideal wall (infinite, plane, perfectly conducting and impenetrable to the electron) at a large distance z is of order $\hbar/(mcz)$. I will argue later that that ratio remains[10] valid for z down to a few times the Bohr radius a_0, where it is of the order of the fine-structure constant $e^2/\hbar c$. This suggests—as is indeed true—that an electron and its image in an ideal wall can form a bound system—"murium"—with a fractional change in energy of order $e^2/\hbar c$. Compare this change in energy with the Lamb shift, that is, the energy associated with the radiative corrections to the $n = 2$ level of hydrogen, which is roughly of order $(e^2/\hbar c)^3$ times the binding energy. The present effect is larger by a factor of order $(\hbar c/e^2)^2$, or 10 000! (This is an exclamation mark, not a factorial sign.)

Unfortunately, when the ideal wall is replaced by a realistic model, the relative energy change is reduced to order $(e^2/\hbar c)^3$ for murium. The ideal wall is nonetheless conceptually very interesting and the difference between the radiative corrections to murium and hydrogen can be understood readily. Thus, the leading term in the Lamb shift is also of order $e^2/\hbar c$, but this term is canceled by the equivalent shift in energy for a free electron, the vacuum fluctuations being the same close to and far from the proton; that is, the mass is "renormalized." (The dominant contribution to the Lamb shift originates in slight differences in recoil between bound and free electrons.) An electron near an ideal conductor does *not* see the same vacuum fluctuations as an isolated electron, because the field must satisfy boundary conditions on the conductor. The energy changes in the electron close to and far from the wall are each of order $e^2/\hbar c$, but with different coefficients, and the net effect remains of order $e^2/\hbar c$. The calculation of the energy shift of murium is one of the simplest calculations in all of quantum electrodynamics.

Gravity. Gravitational fields have both profound differences from and great similarities to electromagnetic fields. There is no gravitationally neutral system and therefore no gravitational analog of the electrically neutral atom, but the quantum corrections to the Coulombic two-point-charge and Newtonian two-point-mass interactions are similar in form. Thus, the gravitational quadrupole moment $Q(\omega)$ induced in a point mass by vacuum fluctuations $h(\omega)$ in the gravitational field has the same frequency dependence as the electric dipole moment $\mu(\omega)$ induced in a point charge by electric vacuum fluctuations $E(\omega)$, and the gravitational and electrical fields generated by $Q(\omega)$ and $\mu(\omega)$ have the same dependence on r and ω. We need therefore merely replace $(e^2)^2$ in $V_{\rm e\,e}$ by $(Gm^2)^2$ to obtain the two-graviton-exchange contribution $V_{\rm m\,m}(r)$ to the corrections to Gm^2/r.

A much larger and more interesting correction occurs if both particles are charged. There is a mass-independent interference between the exchange of one graviton and one photon. Its form follows from the replacement of only one e^2 in $V_{\rm e\,e}$ by Gm^2, and is given by

$$V_{\rm em\,em}(r) = Ge^2\hbar/c^3r^3$$

The gravitational corrections are, of course, far too small to be of more than conceptual interest.

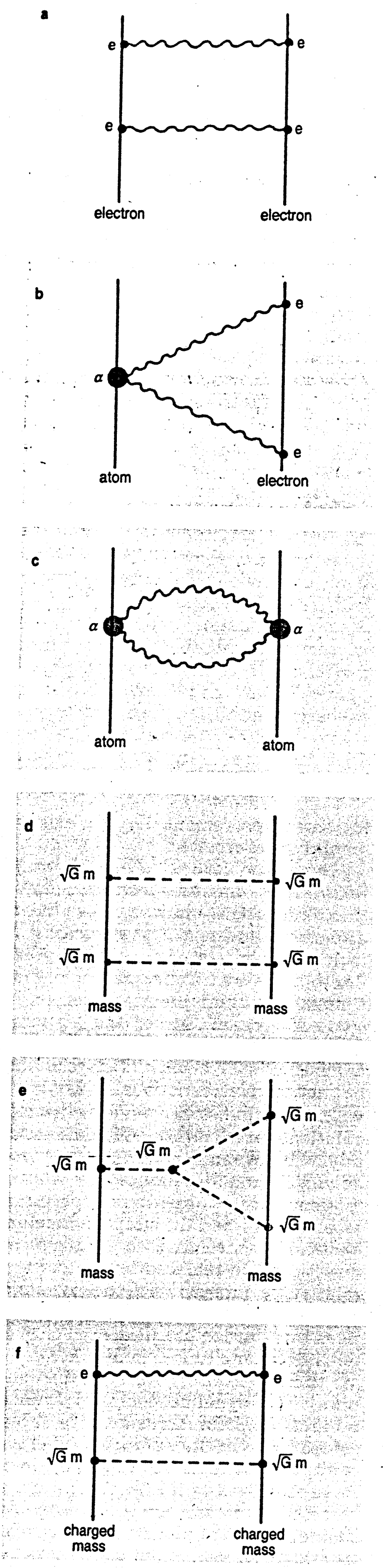
Static versus dynamic potentials

Do any of these potentials have measurable effects? In fact they do. The r^{-7} atom–atom interaction has been detected for atoms in colloidal suspensions; it would be extremely difficult to detect it for just two interacting atoms. The r^{-5} electron–atom interaction has not yet been seen, but it will be far easier to detect[5] for a helium atom with one electron in a high Rydberg state than for scattering of electrons by He$^+$, because energies can be measured far more accurately than cross sections. The electron–helium ion case is the prime candidate for accurate confirmation of a retarded potential. (Because retardation effects increase with atomic number, one might study heliumlike Rydberg atoms. Further, a mu-mesic helium atom, consisting of an alpha particle, a muon in the 1s state and an electron, also shows significant retardation effects, even when the electron is in its 1s state.)

Current experiments[11] on He Rydberg states have not quite attained the high values for the quantum numbers n and l desired—one wants n^2a_0 larger than $137a_0$, and l close to n, so that the electron spends almost all its time at the asymptotic distances for which equation 7 is valid. However, one need not restrict the analysis to quantum levels with n^2a_0 above $137a_0$ and l close to n. A thorough relativistic quantum-field-theoretic evaluation of the two-photon contribution to the electron–ion interaction for all distances r beyond a few a_0 has recently been achieved.[12] (James F. Babb and I have reproduced the basic result using the Schrödinger–Maxwell theory.) A variety of corrections have been estimated,[12] and the first possible high-accuracy verification of a retarded potential awaits a slight further improvement in the experimental measurement.

Domains of validity. The following suggestive remarks—they are anything but proofs—may be of use in an attempt to understand the domains in which the nonrelativistic and retarded interactions contribute. We must distinguish, within the nonrelativistic context, between "static" and "dynamic" potentials. The static potentials are adiabatic, involve correlated positions but not correlated motions, and remain valid—for all distances—when the calculations are performed relativistically. The dynamic potentials are nonadiabatic and depend on correlated motions, which are altered for large separations when the simple action-at-a-distance nonrelativistic Coulomb interactions are replaced by the correct relativistic interactions; the dynamic potentials are replaced at large separations by retarded potentials. For systems involving atoms (only for atoms are there dynamic potentials), the nonrelativistic dynamic potential cannot remain valid for transit times large compared with the appropriate period of either system, that is, for separations large compared with $137a_0$, because the correlated motion can no longer be sustained; on the other hand, the relativistic retarded potential cannot be

Interactions. These Feynman-type diagrams show electron–electron (**a**), electron–atom (**b**), and atom–atom (**c**) electromagnetic interactions; two contributions to the mass–mass interaction (**d, e**); and an interference term between the gravitational and electromagnetic interactions between two charged masses (**f**). An electron "vertex" introduces a factor e; an atom vertex introduces an electric-dipole polarizability factor α; and a gravitational vertex introduces a factor $\sqrt{G}\,m$. Figure 3



valid for separations much smaller than $137a_0$, for then one cannot validly approximate the polarizability of the atom by its value at zero frequency. For the electron–electron, electron–wall and wall–wall systems, there is no dynamic potential, and the retarded potential can be expected to be valid down to a few Bohr radii. The results are summarized in the box on page 42.

To see this more concretely, consider a helium atom with one electron in a Rydberg (high-n) state. In the lowest approximation the core electron sees a charge of $2e$ while the Rydberg electron sees a screened charge of very nearly e. The dominant interaction is of course given by the Coulomb potential. The lowest-order correction is an r^{-4} potential that arises when one assumes the Rydberg electron is fixed—one is thus ignoring nonadiabatic corrections—so that the core has an arbitrary amount of time in which to adjust to the field of the electron by developing a static dipole moment; the transit time is then irrelevant.

Stated differently, in nonrelativistic theory the leading contributions to the interaction energy of the electron–ion pair beyond the Coulomb term come, as I have said, from second-order perturbation theory. These contain an energy denominator $\Delta\mathcal{E}$ that consists of sums of energy differences $\mathcal{E}_u - \mathcal{E}_0$ of core states and $\mathcal{E}_v - \mathcal{E}_n$ of the Rydberg electron. Because the core excitation energy $\mathcal{E}_u - \mathcal{E}_0$ is large compared with the significant Rydberg electron excitation energies,

$$\frac{1}{\Delta\mathcal{E}} = \frac{1}{\mathcal{E}_u - \mathcal{E}_0} - \frac{\mathcal{E}_v - \mathcal{E}_n}{(\mathcal{E}_u - \mathcal{E}_0)^2} + \dots$$

The first term in the series contributes $\alpha e^2/r^4$ to the potential and does not involve excitation of the Rydberg electron from its initial state. The second term, which generates the nonadiabatic r^{-6} term, involves simultaneous excitation of the core electron and the Rydberg electron; we interpret this as correlated motion, which cannot be sustained at large r if c is finite.

An idea that failed. Retarded potentials have hardly been of compelling practical importance. However, it appears that throughout the history of physics, theories with elegance and intrinsic interest—retarded potentials have a full measure of both—have often turned out to be surprisingly significant. The possibility, suggested[13] by Casimir, of determining the value of the fine-structure constant $e^2/\hbar c$ by assuming that the stability of the electron depends upon vacuum fluctuations thus aroused considerable interest and provides a beautiful example of what one might hope to do with retarded potentials. Unfortunately, more detailed calculations do not support the hope of computing $e^2/\hbar c$ from stability considerations alone.

Take as a model of an electron an ideal conductor in the form of a hollow sphere of radius R with its charge e distributed over the surface. The outward Coulomb pressure is $C'e^2/R^4$, with C' a known positive dimensionless constant. There is also a radiation pressure P generated by vacuum fluctuations. As in the case of the wall–wall interaction, the pressure can depend only on $\hbar$, c and R. On dimensional grounds, the pressure must have the form $-C''\hbar c/R^4$, with C'' a dimensionless constant to be determined by detailed calculation. (To calculate the pressure, consider compressing or expanding the sphere. As R is changed, the energy associated with vacuum fluctuations both inside and outside the shell changes; the *net* effect determines

P.) If the pressure is inward, that is, if C'' is positive, as one might expect, vacuum fluctuations can stabilize the electron by counterbalancing the electrostatic repulsion. The ratio is independent of the radius, and balance is achieved if the ratio of the constants, C''/C', is equal to the fine-structure constant $e^2/\hbar c$. One can thus hope to achieve stabilization of the electron and a determination of $e^2/\hbar c$.

The constant C''—indeed, even its sign—is far from simple to evaluate. It was first evaluated[14] years after Casimir's suggestion, by Timothy Boyer. Unfortunately, it turns out that C'' is negative, a result Boyer described as "melancholy."

Related developments

Even if electromagnetic fluctuations have failed to provide a simple model of the electron, vacuum fluctuations of other fields may help us understand the structure of hadrons. In quantum chromodynamics hadrons are assumed to consist of quarks (fermions) and gluons (vector bosons), which are confined within the nucleon by their interactions. At sufficiently short range, gluons do not interact (a property referred to as asymptotic freedom). In what is called the "bag model" of confinement (see the article by Gerald Brown and Mannque Rho, PHYSICS TODAY, February 1983, page 24), the "color magnetic permeability" μ of the external (normal) vacuum is infinite, while the vacuum within the bag is characterized by $\mu = 1$; as an approximation to asymptotic freedom, the gluons within the bag do not interact. The mass of the quark is neglected. There is thus a correspondence between a gluon field within the bag and the quantum-electrodynamic field for a spherical cavity imbedded in a perfect conductor. (That there are eight color fields but only one electric field is a trivial matter—one need merely multiply the QED result by 8. But the difference between the shell in the Casimir model of the electron, with its fields internal and external to the shell, and the cavity with only internal fields leads to serious difficulties.) The only parameters in the problem are $\hbar$, c and the radius a of the bag, and on dimensional grounds the energy contribution associated with vacuum fluctuations, if finite, must be[15] proportional to $\hbar c/a$.

Another field in which the sort of arguments I have presented here may become useful is higher-dimensional models of the universe. There has, for example, recently been enormous interest in adaptations of the Kaluza–Klein five-dimensional cylinder world model. If an additional dimension is periodic (that is, if the additional coordinate axis is a loop rather than a line), and if its period is extremely small, one might easily be unaware of its existence. A charge in such a universe may experience a Casimir effect from the extra dimension—something akin to the wall–wall effect for an extremely small separation—that could be huge.

* * *

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