Energy-level shifts in atoms between metallic planes

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The vacuum fluctuations of the electric field will shift the energy levels of an atom between two neutral, conducting planes. We have calculated these shifts in hydrogen atoms, and numerical values for the shifts of the lowest levels are given.

I. INTRODUCTION

Modifications of the quantum fluctuations in the vacuum due to boundaries have recently attracted a lot of interest.¹⁻³ Since the original work of Casimir⁴ on the electromagnetic zero-point energy between two parallel, perfectly conducting planes the role of vacuum fluctuations in quantum-field theories has changed dramatically. Despite the fact that the tiny Casimir force between neutral conductors is one of the few macroscopic manifestations of vacuum fluctuations and a fascinating test of quantum concepts, these phenomena have been regarded by many as a mere curiosity. The fundamental importance of the vacuum structure first came to light in the wake of the spectacular developments in elementary particle physics over the last two decades.

One of the key concepts which lead to the unified theory of electromagnetic and weak interactions is spontaneous symmetry breaking, which can be regarded as a vacuum condensation phenomenon. In the presence of an external field the effective potential can develop a nontrivial minimum which gives a scalar field a nonvanishing vacuum expectation value,⁵ thus breaking the symmetry. This is analogous to the Casimir effect where the one-loop effective potential, which is the vacuum energy, changes from its vanishing free-space value because the propagators are modified by the presence of the boundaries.

More directly related to the Casimir effect are the calculations of the vacuum energy⁶ and fermion condensate⁷ in hadron models. The hadrons are pictured as "bags" or cavities in the vacuum,² the inside and outside being associated with different phases of the quantumchromodynamic (QCD) vacuum. Finally, it has long been clear that vacuum fluctuations play an important role in field theories on curved background spaces,¹ which serve as a prelude to fully quantized theories of gravity and also are important in cosmology and unification schemes.

One attempt in this direction are the recently revitalized Kaluza-Klein theories,⁸ which try to account for gauge symmetries simply as spatial symmetries of extra, compact dimensions. The vacuum energy associated with these dimensions are *a priori* enormous, and a detailed understanding of the vacuum structure of the theory seems to be required in order to explain the observed smallness of the cosmological constant, as well as other features of the Kaluza-Klein scenario.

It should be clear from the above that not only the vac-

uum energy but all aspects of vacuum fluctuations are of physical importance and should be studied. Even the investigations of the original Casimir configuration are deficient in this respect. We intend to try to remedy this situation by shifting attention from the global properties previously studied, to the local variation of the field fluctuations between the planes.

From a practical point of view, the electromagnetic field fluctuations are easier to observe experimentally than those of other theories. The Casimir force between two plates has been found to be in agreement with direct measurements.9 We propose instead to use an atom placed between the plates as a sensitive local probe of the field fluctuations. As a first step in this direction we have recently calculated the electromagnetic field fluctuations outside one conducting plane and their perturbations of the ener-gy levels of a nearby atom.¹⁰ The results are in agreement with a similar calculation by Power and Thirunamachandran,¹¹ who have developed a general formalism for quantum electrodynamics (QED) in a cavity. In addition, they have applied this formalism to the investigation of spontaneous emission by an excited atom in the presence of a conducting wall. Closely related work on spontaneous emission from atoms in conducting cavities was recently discussed by Kleppner,¹² and is currently under experimental investigation by Vaidyanathan et al.¹

Here we will consider the effects of the electromagnetic vacuum fluctuations on an atom placed between two conducting parallel planes. We will first explicitly calculate how the electric and magnetic field fluctuations vary between the planes. In contrast to the energy density whose constant value is known from the value of the Casimir force, the field fluctuations are found in the next section to depend strongly on the distance from the planes and actually diverge when one approaches one of the planes. This result is obtained under the assumption that the planes are perfectly conducting at all frequencies. Technical aspects of these mode sum calculations can be found in the Appendix.

The energy-level shifts of one atom placed in this fluctuating field is calculated in Sec. III. We find that when the atom is close to one of the plates the interaction energy is simply the one corresponding to the classical dipoledipole interaction. We explicitly exhibit this by also calculating the classical interaction of a dipole with two neutral plates by the method of images.

Numerical values for the shifts of the lowest levels of

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hydrogen are given in Sec. IV, where we also provide the atomic matrix elements necessary for calculating the shift of an arbitrary energy level.

II. VACUUM FLUCTUATIONS

Two perfectly conducting plates are placed in the x-y plane at z=0 and z=L; see Fig. 1. If n is the unit vector normal to the planes, the electric and magnetic fields will satisfy the usual boundary conditions at both plates

$$\mathbf{n} \times \mathbf{E} = \mathbf{n} \cdot \mathbf{B} = 0 \ . \tag{2.1}$$

We choose to work in the Coulomb gauge so that the electromagnetic potential A^{μ} satisfies $\nabla \cdot \mathbf{A} = 0$. For our problem we can then also choose $A^0 = 0$, so that in the vacuum between the plates we have

$$\mathbf{E} = -\mathbf{A}, \quad \mathbf{B} = \nabla \times \mathbf{A} \ . \tag{2.2}$$

It is convenient to expand the vector potential in terms of its transverse electric eigenmodes $(E_z=0)$ and transverse magnetic eigenmodes $(B_z=0)$. Because of symmetry the wave vector $\mathbf{k} = (k_x, k_y, k_z)$ can be decomposed in a transverse wave vector $\mathbf{k}_T = (k_x, k_y)$ and a longitudinal part $k = k_z$. These wave numbers can be used to label the solutions of the wave equation.

The transverse electric modes which respect the boundary condition (2.1) can be written as

$$\mathbf{A}_{k\mathbf{k}_{T}}^{E}(\mathbf{x}) = \nabla \times \mathbf{U}_{k\mathbf{k}_{T}}^{E}(\mathbf{x}) , \qquad (2.3a)$$

while the transverse magnetic modes can be written as

$$\mathbf{A}_{k\mathbf{k}_{T}}^{M}(\mathbf{x}) = \nabla \times \left[\nabla \times \mathbf{U}_{k\mathbf{k}_{T}}^{M}(\mathbf{x})\right], \qquad (2.3b)$$

where the potentials are

$$\mathbf{U}_{k\mathbf{k}_{T}}^{E}(\mathbf{x}) = N\mathbf{e}_{z}\sin(kR)e^{i\mathbf{k}_{T}\cdot\mathbf{x}_{T}}, \qquad (2.4a)$$

$$\mathbf{U}_{k\mathbf{k}_{T}}^{M}(\mathbf{x}) = \frac{N}{i\omega} \mathbf{e}_{z} \cos(kR) e^{i\mathbf{k}_{T} \cdot \mathbf{x}_{T}}$$
(2.4b)

and $\mathbf{x} = (\mathbf{x}_T, \mathbf{R}) = (x, y, z)$.

Only a discrete set of longitudinal wave numbers

$$k = \frac{n\pi}{L}, \quad n = 0, 1, 2, \dots,$$
 (2.5)



FIG. 1. Electromagnetic field is confined between two perfectly conducting parallel plates with separation L. survive, and the energy is therefore quantized

$$\omega = [\mathbf{k}_T^2 + (n\pi/L)^2]^{1/2} . \qquad (2.6)$$

The normalization factor N in the potentials (2.4) is determined by the normalization condition

$$\int d^3x \mathbf{A}_{n\mathbf{k}_T}^{\lambda^*}(\mathbf{x}) \cdot \mathbf{A}_{n'\mathbf{k}_T}^{\lambda'}(\mathbf{x}) = 4\pi^2 \delta_{\lambda\lambda'} \delta_{nn'} \delta(\mathbf{k}_T - \mathbf{k}_T') , \quad (2.7)$$

which gives

$$N = \frac{1}{k_T} \left[\frac{1}{L} \right]^{1/2} \tag{2.8a}$$

for n=0, and

$$N = \frac{1}{k_T} \left[\frac{2}{L} \right]^{1/2} \tag{2.8b}$$

for n > 0.

Hence the vector potential is given by

$$\mathbf{A}(\mathbf{x},t) = \sum_{\lambda = E,M} \sum_{n=0}^{\infty} \int \frac{d^2 k_T}{(2\pi)^2} \frac{1}{\sqrt{2\omega}} \times [a_{n\mathbf{k}_T}^{\lambda} \mathbf{A}_{n\mathbf{k}_T}^{\lambda}(\mathbf{x})e^{-i\omega t} + \text{c.c.}] . \quad (2.9)$$

We now promote this classical field to a field operator by canonical quantization. This is achieved as usual by turning the Fourier coefficients in (2.9) into operators satisfying the commutation relation

$$[a_{n'\mathbf{k}_{T}'}^{\lambda'}, a_{n\mathbf{k}_{T}}^{\lambda\dagger}] = 4\pi^{2}\delta_{\lambda\lambda'}\delta_{nn'}\delta(\mathbf{k}_{T} - \mathbf{k}_{T}'), \qquad (2.10)$$

all other commutators being zero. The operator $a_{n\mathbf{k}_T}^{\lambda^{\intercal}}$ $(a_{n\mathbf{k}_T}^{\lambda})$ creates (destroys) a photon of polarization λ and wave vector $(\mathbf{k}_T, n\pi/L)$. The vacuum state $|\Omega\rangle$ is defined by

$$a_{nk_{\pi}}^{\lambda} | \Omega \rangle = 0 , \qquad (2.11)$$

which means that there are no real photons present in this state. This implies that $\langle \Omega | \mathbf{E} | \Omega \rangle = \langle \Omega | \mathbf{B} | \Omega \rangle = 0$ as expected in a vacuum.

However, it is now straightforward to verify that the fluctuation of the transverse component of the electric field is given by

$$\langle \mathbf{E}_{T}(\mathbf{R},t) \cdot \mathbf{E}_{T}(\mathbf{R},t') \rangle \equiv \langle \Omega | \mathbf{E}_{T}(\mathbf{R},t) \cdot \mathbf{E}_{T}(\mathbf{R},t') | \Omega \rangle$$

$$= \frac{1}{L} \sum_{n=1}^{\infty} \int \frac{d^{2}k_{T}}{(2\pi)^{2}} (\omega + k^{2}/\omega)$$

$$\times \sin^{2}(kR)e^{i\omega(t'-t)} .$$

$$(2.12)$$

In order to make this integral well defined we employ Schwinger's method of imaginary time splitting, i.e., let $t'-t=i\tau$. As shown in the Appendix, in the limit $\tau \rightarrow 0$ we obtain

$$\langle E_{x}^{2} \rangle = \langle E_{y}^{2} \rangle = \frac{1}{2} \langle \mathbf{E}_{T}^{2} \rangle = \frac{1}{\pi^{2} \tau^{4}} + \frac{\pi^{2}}{48L^{4}} [F(\theta) - \frac{1}{15}],$$

(2.13)

where $\theta = \pi R / L$ and the function

$$F(\theta) = \frac{3}{\sin^4 \theta} - \frac{2}{\sin^2 \theta}$$
(2.14)

is displayed in Fig. 2.

The first term in (2.13) is a divergence due to the free

field fluctuations. Since this is of no physical interest it can be dropped and we obtain the renormalized fluctuations due solely to the presence of the plates

$$\langle : E_{x}^{2} : \rangle = \langle : E_{y}^{2} : \rangle = \frac{\pi^{2}}{48L^{4}} [F(\theta) - \frac{1}{15}].$$
 (2.15)

The fluctuation in the longitudinal component of the field is calculated in a similar way, while taking care to include the TEM mode (n=0) with its special normalization (2.8a):

$$\langle E_{z}(\mathbf{x},t)E_{z}(\mathbf{x},t'=t+i\tau)\rangle = \frac{1}{4\pi L} \int_{0}^{\infty} d\omega \,\omega^{2} e^{-\omega\tau} + \frac{1}{L} \sum_{n=1}^{\infty} \int \frac{d^{2}k_{T}}{(2\pi)^{2}} (\omega - k^{2}/\omega) \cos^{2}(kR) e^{-\omega\tau}$$

$$= \frac{1}{\pi^{2}\tau^{4}} + \frac{\pi^{2}}{48L^{4}} [F(\theta) + \frac{1}{15}] .$$
(2.16)

A similar calculation of the fluctuations in the magnetic field gives

$$\langle :B_{x}^{2}: \rangle = \langle :B_{y}^{2}: \rangle = -\langle :E_{z}^{2}: \rangle ,$$

$$\langle :B_{z}^{2}: \rangle = -\langle :E_{x}^{2}: \rangle .$$

$$(2.17)$$

The energy density in the region between the plates is therefore

$$\langle :T_{00}:\rangle = \frac{1}{2} \langle :(\mathbf{E}^2 + \mathbf{B}^2):\rangle = -\frac{\pi^2}{720L^4}$$
 (2.18)

Notice that while the field fluctuations vary between the plates, the energy density is a constant. A simple argument will now give us the entire energy-momentum tensor. The only geometrical objects present in our problem, from which we can construct physical tensors, are the metric $g_{\mu\nu}$ with nonvanishing elements $g_{ii} = 1 = -g_{00}$,

FIG. 2. Function $F(\theta)=3/\sin^4\theta-2/\sin^2\theta$ which describes the field fluctuations between the plates.

and the vector normal to the plates $n_{\mu} = (0, \mathbf{n})$. Remembering that $T_{\mu\nu}$ must be symmetric and traceless (at least in the absence of conformal anomalies which is the case here), the unique tensor is therefore by (2.18)

$$\langle :T_{\mu\nu}: \rangle = \frac{\pi^2}{720L^4} (g_{\mu\nu} - 4n_{\mu}n_{\nu}) .$$
 (2.19)

Reading off the pressure on one of the plates

$$\langle :T_{zz}: \rangle = -\frac{\pi^2}{240L^4}$$
, (2.20)

we see that this result is in complete agreement with Casimir's result.⁴

The field fluctuations close to one plate are obtained by expanding (2.15) and (2.16) in powers of R for small values of R,

$$\langle :E_x^2: \rangle = \langle :E_y^2: \rangle = \frac{1}{16\pi^2 R^4} + O(R^2/L^6) , \qquad (2.21)$$

$$\langle :E_z^2: \rangle = \langle :E_x^2: \rangle + \frac{\pi^2}{360L^4}$$
 (2.22)

The results for one plate are now obtained by letting L go to infinity.

III. ENERGY-LEVEL SHIFTS

As discussed in the Introduction the alteration of the mode structure of the vacuum due to the plates can be detected by an atom placed between the plates. We regard the atom as a local probe of the field fluctuations calculated in the preceding section. The change of the spectrum of the atom in the presence of the plates can be used to read off the fluctuations as a function of position between the plates.

The fluctuations in the magnetic field **B** will cause a perturbation of the energy eigenstates proportional to eB/m, where m is the electron mass, while the fluctua-



tions in the electric field cause a perturbation $er \cdot E$. Since the atomic radius r is of the order $(\alpha m)^{-1}$, where $\alpha = e^2/4\pi = \frac{1}{137}$ is the fine-structure constant, we can ignore the magnetic perturbation in the following.

Furthermore, since the vacuum expectation values of the fields vanish, there will be no shift of the energy levels to first order in perturbation theory. In second order the fluctuating electric field contributes a shift

$$\Delta \epsilon_n = e^2 \sum_{m,k} \frac{|\langle n | \mathbf{r} \cdot \mathbf{E} | m, k \rangle|^2}{\epsilon_n - \epsilon_m - \omega_k} , \qquad (3.1)$$

where ω_k is the energy of the photon in the *k*th radiation mode.

If in the summation over allowed atomic states $|m\rangle$ we isolate the states $|n'\rangle$ degenerate in energy with the state $|n\rangle$ under consideration, we can write

$$\Delta \epsilon_n = \Delta \epsilon_n^{(1)} + \Delta \epsilon_n^{(2)} , \qquad (3.2)$$

with

$$\Delta \epsilon_n^{(1)} = -e^2 \sum_{n',k} \frac{|\langle n | \mathbf{r} \cdot \mathbf{E} | n', k \rangle|^2}{\omega_k}$$
(3.3)

and

$$\Delta \epsilon_n^{(2)} = e^2 \sum_{\substack{m \ (\neq n'), k}} \frac{|\langle n | \mathbf{r} \cdot \mathbf{E} | m, k \rangle|^2}{\epsilon_n - \epsilon_m - \omega_k} .$$
(3.4)

The first sum (3.3) can be separated into a product of an atomic factor and a radiation factor

$$\Delta \epsilon_n^{(1)} = -e^2 \sum_i \sum_{n'} |\langle n | x_i | n' \rangle|^2 \sum_k \frac{|\langle \Omega | E_i | k \rangle|^2}{\omega_k} ,$$
(3.5)

where the first summation is over the three spatial directions.

The radiation factors

$$\langle E_i^2/\omega \rangle \equiv \sum_k \frac{|\langle \Omega | E_i | k \rangle|^2}{\omega_k}$$
(3.6)

can be evaluated by the same techniques used to calculate the field fluctuations. As shown in the Appendix we obtain

$$\langle E_x^2/\omega \rangle = \langle E_y^2/\omega \rangle = \frac{1}{3\pi^2 \tau^3} + \frac{F_-(R)}{64\pi L^3}$$
, (3.7a)

$$\langle E_z^2/\omega \rangle = \frac{1}{3\pi^2 \tau^3} + \frac{F_+(R)}{32\pi L^3} ,$$
 (3.7b)

with

$$F_{\pm}(R) = (L/R)^3 + \zeta(3, R/L) + \zeta(3, -R/L) \pm 2\zeta(3) ,$$
(3.8)

where the ζ functions are defined in the Appendix.

Ignoring the free field divergence as usual, we are left with the energy-level shift

$$\Delta \epsilon_{n}^{(1)} = -\frac{e^{2}}{64\pi L^{3}} \sum_{n'} \left[\left(\left| \left\langle n \mid x \mid n' \right\rangle \right|^{2} + \left| \left\langle n \mid y \mid n' \right\rangle \right|^{2} \right) F_{-} + 2 \left| \left\langle n \mid z \mid n' \right\rangle \right|^{2} F_{+} \right] + 2 \left| \left\langle n \mid z \mid n' \right\rangle \right|^{2} F_{+} \right]$$
(3.9)

due to the degenerate states $|n'\rangle$. These give rise to a permanent electric dipole moment $\mathbf{p} = e\mathbf{r}$ of the atom, and we will in a moment see that $\Delta \epsilon_n^{(1)}$ represents the interaction energy between the dipole and its images in the planes. For atoms without permanent dipole moments, however, only the second term (3.4) contributes to the level shifts.

Let us first study $\Delta \epsilon_n^{(2)}$ near one of the plates. Since the mode sum (3.4) is dominated by the terms with $\omega R \sim 1$, we will find $\omega_k \gg \epsilon_n - \epsilon_m$ in a region sufficiently near the left plate. In this region the two terms $\Delta \epsilon_n^{(1)}$ and $\Delta \epsilon_n^{(2)}$ therefore take the same form. Using completeness of the atomic states, we find

$$\Delta \epsilon_n = -\frac{e^2}{64\pi L^3} [\langle n \mid (x^2 + y^2) \mid n \rangle F_- + 2\langle n \mid z^2 \mid n \rangle F_+], \qquad (3.10)$$

where in spherical coordinates the matrix elements can be found in the literature.¹⁴ This result is simply the quantum-mechanical version of the classical interaction energy V between an atomic dipole \mathbf{p} and its induced images in the plates. A simple image construction suffices to calculate V. Thus, the two primary images of \mathbf{p} in the plates will themselves induce new dipoles in the opposite plate and so on *ad infinitum*. Notice that the induced dipole is oriented so that the field lines are normal to the image plane, as required by the boundary conditions. The interaction energy U of \mathbf{p} with any of these images \mathbf{p}' is given by

$$U(d) = \frac{1}{8\pi d^3} [\mathbf{p} \cdot \mathbf{p}' - 3(\mathbf{p} \cdot \mathbf{n})(\mathbf{p}' \cdot \mathbf{n})], \qquad (3.11)$$

where d is the distance between p and p'. Summing over all images, we find

$$V = -\frac{e^2}{64\pi L^3} [(x^2 + y^2)F_- + 2z^2F_+], \qquad (3.12)$$

in complete agreement with the corresponding quantummechanical expression (3.10).

In the opposite limit $\omega_k \ll \epsilon_n - \epsilon_m$ away from the plates, we can ignore ω_k in the denominator of Eq. (3.4) for $\Delta \epsilon_n^{(2)}$. Factoring out the radiation contribution $\langle : E_i(R)E_j(R): \rangle$ which was calculated in Sec. II, we see that the shifts are determined by the zero-frequency electric dipole polarizabilities

$$\alpha_{i} = 2e^{2} \sum_{m \ (\neq n)} \frac{|\langle n | x_{i} | m \rangle|^{2}}{\epsilon_{m} - \epsilon_{n}} .$$
(3.13)

This part of the energy-level shift can now be written in

the diagonal basis of atomic states as

$$\Delta \epsilon_n^{(2)} = -\frac{\pi^2}{96L^4} \{ (\alpha_x + \alpha_y) [F(\theta) - \frac{1}{15}] + \alpha_z [F(\theta) + \frac{1}{15}] \} .$$
(3.14)

In the limit $L \rightarrow \infty$ we recover the expression valid for an atom outside one plate

$$\Delta \epsilon_n^{(2)} = -\frac{1}{32\pi^2 R^4} (\alpha_x + \alpha_y + \alpha_z) \tag{3.15}$$

as first derived by Casimir and Polder.¹⁵

The sum of the polarizabilities α_i for hydrogenlike atoms has recently been determined analytically by Leutwyler¹⁶ and Voloshin¹⁷ in connection with the energy-level shifts in charmonium due to vacuum fluctuations in the chromoelectric field. Their results can be written as

$$\alpha_{x} + \alpha_{y} + \alpha_{z} = 16\pi a^{3} n^{6} A_{nl} , \qquad (3.16)$$

where $a = (\alpha m)^{-1}$ is the Bohr radius and the dimensionless numbers A_{nl} are of order one. For n=1 we recover the usual second-order Stark shift of the ground state

$$\Delta \epsilon_{100}^{(2)} = -9\pi a^3 \langle :\mathbf{E}^2 : \rangle = -\frac{9\pi^3}{16} \frac{a^3}{L^4} [F(\theta) - \frac{1}{45}] . \qquad (3.17)$$

We see that at least for low values of n, the dipole-dipole term (3.9) dominates the energy-level shift $\Delta \epsilon_n$, provided the atom has a permanent dipole moment. For atoms without permanent dipole moments, the Casimir-Polder term (3.14) gives the full energy-level shift in atoms far from both plates.

As we shall see in the next section the matrix elements in (3.9) increase with the radial quantum number n only as n^4 . For sufficiently high n we can therefore not ignore the Casimir-Polder term (3.14) which grows like n^6 , even if we are studying hydrogen atoms with permanent dipole moments.

This is relevant to experiments now in progress,^{13,18} where the interactions of matter with the vacuum is stud-

ied by creating highly excited atoms. The outer electron is typically excited to $n \simeq 30$, and the atom can be treated as an excited hydrogen atom. The accidental degeneracy in the hydrogen spectrum causes it to have a permanent dipole moment, and both the terms (3.9) and (3.14) must be taken into consideration.

IV. NUMERICAL RESULTS

For not too highly excited atoms the dipole-dipole term (3.9) will dominate the energy-level shift. We will now numerically evaluate the shifts of the lowest levels of hydrogen. It is convenient to consider this perturbation to be given by the matrix elements of the operator

$$W = \sum_{n'} \left[(x_+ \mid n') \langle n' \mid x_- + x_- \mid n' \rangle \langle n' \mid x_+) F_- \right. \\ \left. + 2z \mid n' \rangle \langle n' \mid zF_+ \right], \qquad (4.1)$$

where $x_{\pm} = (x \pm iy)/\sqrt{2}$, and the sum extends over the degenerate members of the multiplet.

The level shifts are given by

$$\Delta \epsilon_n^{(1)} = -\frac{e^2}{64\pi L^3} \langle n \mid W \mid n \rangle$$
(4.2)

in a basis where W is diagonal.

In an arbitrary basis we must diagonalize the matrix representing W. Although the matrix elements of W are simpler in parabolic coordinates, W turns out to be more diagonal in the spherical basis, which we shall therefore use. An explicit calculation shows that W is nondiagonal only between states with the same azimuthal quantum number m and with orbital angular momentum l differing by $\Delta l = \pm 2$.

For the diagonal matrix elements of W we find

$$\langle n,l,m | W | n,l,m \rangle = \frac{9}{4}a^{2}n^{2} \left[\frac{n^{2} - l^{2}}{(2l-1)(2l+1)} [(l^{2} - l + m^{2})F_{-} + 2(l^{2} - m^{2})F_{+}] + \frac{n^{2} - (l+1)^{2}}{(2l+1)(2l+3)} [(l^{2} + 3l + m^{2} + 2)F_{-} + 2(l^{2} + 2l - m^{2} + 1)F_{+}] \right],$$
(4.3)

while the nondiagonal matrix elements are given by

$$\langle n, l-2, m \mid W \mid n, l, m \rangle = \frac{9}{4} a^2 n^2 \left[\frac{n^2 - l^2}{(2l-1)(2l+1)} \frac{n^2 - (l-1)^2}{(2l-3)(2l-1)} (l^2 - m^2) [(l-1)^2 - m^2] \right]^{1/2} (2F_+ - F_-) .$$
(4.4)

Because of parity invariance W does not contribute to the shift of the ground state, which therefore is given entirely by (3.17), which can be written as

$$\Delta \epsilon_{100} = -(6.5 \times 10^4 \text{ eV})(a/L)^4 [F(\theta) - \frac{1}{45}]. \qquad (4.5)$$

For the n=2 multiplet there is no mixing of states and the energy-level shifts can be read off directly from (4.3):

$$\Delta \epsilon_{200}^{(1)} = -18a^2 A (F_+ + F_-) ,$$

$$\Delta \epsilon_{210}^{(1)} = -18a^2 A F_+ ,$$

$$\Delta \epsilon_{211}^{(1)} = -9a^2 A F_- ,$$

(4.6)

where we have introduced

$$A = \frac{e^2}{64\pi L^3} = \frac{\alpha}{16L^3} \ . \tag{4.7}$$

In the n=3 multiplet the states $|300\rangle$ and $|320\rangle$ will mix. The secular matrix is

$$-\frac{81}{4}a^{2}A\begin{bmatrix}\frac{16}{3}(F_{+}+F_{-}) & \frac{4}{3}\sqrt{2}(2F_{+}-F_{-})\\\frac{4}{3}\sqrt{2}(2F_{+}-F_{-}) & \frac{2}{3}(4F_{+}+F_{-})\end{bmatrix}, \quad (4.8)$$

with eigenvalues

$$\Delta \epsilon_{3\pm}^{(1)} = -\frac{81}{4} a^2 A \left[4F_+ + 3F_- \pm (16F_+^2 - 8F_+F_- + 9F_-^2)^{1/2} \right].$$
(4.9)

We denote the corresponding eigenstates by $|3+\rangle$ and $|3-\rangle$.

The other levels within the n=3 multiplet do not mix and are given by (4.3):

$$\Delta \epsilon_{310}^{(1)} = -\frac{81}{2} a^2 A \left(4F_+ + F_- \right) ,$$

$$\Delta \epsilon_{311}^{(1)} = -\frac{27}{4} a^2 A \left(6F_+ + 15F_- \right) ,$$

$$\Delta \epsilon_{321}^{(1)} = -\frac{81}{4} a^2 A \left(2F_+ + F_- \right) ,$$

$$\Delta \epsilon_{322}^{(1)} = -\frac{81}{4} a^2 A F_- .$$

In order to display these shifts graphically we must choose a value of R. Taking for simplicity R = L/2, where, by the way, the Casimir-Polder term is minimal, we find

$$F_{+}(R = L/2) = 2(7 \pm 1)\zeta(3)$$
,

where $\zeta(3)=1.202...$ This gives for the n=2 levels in units of $\zeta(3)Aa^2$:

$$\Delta \epsilon_{200}^{(1)} = -504, \ \Delta \epsilon_{210}^{(1)} = -288, \ \Delta \epsilon_{211}^{(1)} = -108$$

and for the n=3 levels,

$$\begin{split} &\Delta \epsilon_{3\pm}^{(1)} = -81(25 \pm \sqrt{241}), \quad \Delta \epsilon_{310}^{(1)} = -3078 , \\ &\Delta \epsilon_{311}^{(1)} = -1863, \quad \Delta \epsilon_{321}^{(1)} = -891, \quad \Delta \epsilon_{322}^{(1)} = -486 \end{split}$$

These shifts are shown in Fig. 3.

The magnitude of the dipole-dipole splittings is set by the quantity

$$a^{2}A = \frac{\alpha}{16a} (a/L)^{3} = (1.70 \text{ eV})(a/L)^{3}$$



FIG. 3. Splittings due to the dipole-dipole interaction of the n=2 and n=3 multiplets in hydrogen in the middle between the plates in units of $\zeta(3)Aa^2$.

which is rather small. In terms of the Lamb shift, which is roughly given by

$$\Delta \epsilon_{\text{Lamb}} \simeq \frac{lpha^4}{a}$$
 ,

the magnitude of our splittings are

$$\Delta \epsilon_n^{(1)} \simeq n^4 (a / \alpha L)^3 \Delta \epsilon_{\text{Lamb}}$$

. (1)

and

$$\Delta \epsilon_n^{(2)} \simeq n^6 (a / \alpha L)^4 \Delta \epsilon_{\text{Lamb}}$$
.

When the atom is at a distance $R \ll L$ from either plate, then R enters these expressions instead of the plate separation L. Hence for low n the plate separation must be much less than 137 atomic radii for the wall-induced vacuum fluctuations to be larger than the Lamb shift. However, in view of the fact that shifts much smaller than the Lamb shift are detectable with present technology, and excitations to $n \simeq 30$ ($n^6 \sim 10^9$) already are attainable,¹³ we are hopeful that these wall-induced shifts will be seen. An experiment designed for this purpose is in progress.¹⁸

V. DISCUSSION AND CONCLUSION

The attractive Casimir force between two conducting, parallel plates or walls is now a well-known, macroscopic manifestation of the quantum-mechanical vacuum fluctuations of the electromagnetic field. It is usually obtained by just calculating the regularized, total energy of the field.

We have here taken a more microscopic point of view and calculated how the field fluctuations vary between the plates. It is shown that the local properties of the vacuum field fluctuations can in principle be mapped out by measuring the energy-level shifts of an atom placed between the walls. For hydrogen atoms between, but not too close to the plates, there are two contributing terms to the energy-level shifts. If the atom is not highly excited the shift is dominated by the induced dipole-dipole interaction which decreases with the plate separation L like L^{-3} , but increases with the principal quantum number n only as n^4 . We have explicitly calculated the shifts of the lowest levels and supplied the formulas necessary for calculating the shift of an arbitrary level.

For sufficiently high n, however, the Casimir-Polder term, which decreases with the plate separation like L^{-4} , but increases with n like n^6 , must be included. This part of the shift is given in terms of the polarizabilities of the atom.

Our results are obviously somewhat unrealistic. We have considered the electromagnetic field between a pair of parallel walls which are assumed to be perfectly conducting at all frequencies and perfectly plane. Such ideal walls probably do not exist. For real walls in the laboratory our results could be modified, but we will not consider these problems here. Questions of the same nature have been discussed in connection with "murium," which is an electron bound by its image charge to a wall, and the effects of vacuum fluctuations on this system.¹⁹

The generalization of our work to the finitetemperature regime is straightforward.²⁰ The atom would now in addition be subject to stimulated emission by blackbody radiation. Since we know from the calculations of Fierz²¹ and Mehra²² that the Casimir force between the plates changes rapidly with increasing temperature, we expect the same to be true for the local-field fluctuations. For plate distances less than 1 μ m the temperature effects can be ignored even at room temperature.

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APPENDIX

We start by calculating the transverse field fluctuations given by (2.12). Using $\omega^2 = \mathbf{k}_T^2 + (\pi n/L)^2$, we find

$$\langle \mathbf{E}_{T}^{2}(R) \rangle = \frac{1}{2\pi L} \sum_{n=1}^{\infty} \sin^{2}(kR) \int_{k}^{\infty} d\omega (\omega^{2} + k^{2}) e^{-\omega\tau} \quad (A1)$$

$$= \frac{1}{4\pi L} \left[\partial_{\tau}^{2} \frac{1}{\tau} + \frac{1}{\tau} \partial_{\tau}^{2} \right] \sum_{n=1}^{\infty} [1 - \cos(2kR)] e^{-k\tau}$$

$$= \frac{\lambda^{3}}{4\pi L} \left[\partial_{\epsilon}^{2} \frac{1}{\epsilon} + \frac{1}{\epsilon} \partial_{\epsilon}^{2} \right] \Sigma_{-}(\epsilon, \theta) , \qquad (A2)$$

where $\lambda = \pi/L$, $\epsilon = \lambda \tau$, $\theta = \lambda R$, and

$$\Sigma_{\pm}(\epsilon,\theta) \equiv \frac{1}{e^{\epsilon} - 1} \pm \frac{1}{2} \left[\frac{1}{e^{\epsilon + 2i\theta} - 1} + \text{c.c.} \right].$$
(A3)

The longitudinal field fluctuations given by (2.16) similarly reduce to

$$\langle E_z^2(R)\rangle = \frac{1}{2\pi L \tau^3} + \frac{\lambda^3}{4\pi L} \left[\partial_\epsilon^2 \frac{1}{\epsilon} - \frac{1}{\epsilon}\partial_\epsilon^2\right] \Sigma_+(\epsilon,\theta) .$$
 (A4)

Expanding $\Sigma_+(\epsilon, \theta)$ in powers of ϵ , we find

$$\Sigma_{\pm}(\epsilon,\theta) = \frac{1}{\epsilon} - \frac{1}{2}(1\pm1) + \frac{\epsilon}{4}S_{\pm}(\theta) - \frac{\epsilon^3}{48} \left[\frac{1}{15} \pm F(\theta)\right] + O(\epsilon^4) , \qquad (A5)$$

where

$$S_{\pm}(\theta) = \frac{1}{3} \pm \frac{1}{\sin^2 \theta} \tag{A6}$$

and

$$F(\theta) = \frac{3}{\sin^4 \theta} - \frac{2}{\sin^2 \theta} . \tag{A7}$$

Now using these expressions in (A2) and (A4) we obtain the desired results, given by Eqs. (2.15) and (2.16).

The dipole-dipole interaction is determined by the radiation factors (3.5),

$$\langle \mathbf{E}_{T}^{2}(R)/\omega \rangle \equiv \sum_{k} \frac{|\langle \Omega | \mathbf{E}_{T} | k \rangle|^{2}}{\omega_{k}}$$
$$= \frac{1}{L} \sum_{n=1}^{\infty} \int \frac{d^{2}k_{T}}{(2\pi)^{2}} \left[1 + \frac{k^{2}}{\omega^{2}} \right] \sin^{2}(kR)e^{-\omega\tau}$$
$$= \frac{1}{2\pi L} \sum_{n=1}^{\infty} k \left[1 - \cos(2kR) \right]$$
$$\times \int_{k}^{\infty} d\omega \left[\frac{\omega}{k} + \frac{k}{\omega} \right] e^{-\omega\tau} \quad (A8)$$

and

$$\langle E_z^2(R)/\omega \rangle \equiv \sum_k \frac{|\langle \Omega | E_z | k \rangle|^2}{\omega_k}$$

$$= \frac{1}{4\pi L} \int_0^\infty d\omega \, \omega e^{-\omega \tau}$$

$$+ \frac{1}{2\pi L} \sum_{n=1}^\infty k [1 + \cos(2kR)]$$

$$\times \int_k^\infty d\omega \left[\frac{\omega}{k} - \frac{k}{\omega} \right] e^{-\omega \tau}$$

These expressions can be rewritten in terms of the Σ_{\pm} introduced in (A3):

$$\langle \mathbf{E}_T^2 / \omega \rangle = \frac{\pi}{4L^3} \partial_{\epsilon}^2 \int_{\epsilon}^{\infty} \frac{dx}{x} \left[1 + \frac{\epsilon^2}{x^2} \right] \boldsymbol{\Sigma}_{-}(x,\theta)$$

= $\frac{\pi}{2L^3} \left[\int_{\epsilon}^{\infty} dx f_{-}(x) - \frac{1}{\epsilon} \partial_{\epsilon} \boldsymbol{\Sigma}_{-}(\epsilon,\theta) \right], \quad (A9)$

$$\langle E_z^2/\omega\rangle = \frac{\pi}{2L^3} \left[\frac{1}{2\epsilon^2} - \int_{\epsilon}^{\infty} dx f_+(x) + \frac{1}{\epsilon^2} \Sigma_+(\epsilon,\theta) \right],$$

(A10)

where $f_{\pm}(x) \equiv \Sigma_{\pm}(x,\theta)/x^3$.

It is convenient to study the analytically continued function

$$f_{\pm}(z,p) \equiv \frac{\Sigma_{\pm}(z,\theta)}{z^p}$$
.

We choose the contour of integration shown in Fig. 4. Since the integral over C_{ρ} vanishes when $\rho \rightarrow \infty$, we obtain



FIG. 4. Contour chosen to evaluate the integrals which determine the radiation factor in the dipole-dipole interaction term.

$$\int_{\epsilon}^{\infty} dx f_{\pm}(x,p) = (1-e^{-2\pi p i})^{-1} \left| \int_{C_{\epsilon}} dz f_{\pm}(z,p) + 2\pi i \sum_{\substack{\text{poles}\\z\neq 0}} \operatorname{Res} f_{\pm}(z,p) \right|.$$

By inserting the expansions (A5) in $f_{\pm}(z,p)$ and performing the integral over C_{ϵ} , we find

$$\lim_{p \to 3} (1 - e^{-2\pi p i})^{-1} \int_{C_{\epsilon}} dz f_{\pm}(z, p) = \frac{1}{3\epsilon^3} - \frac{1}{4\epsilon^2} (1 \pm 1) + \frac{1}{4\epsilon} S_{\pm} + O(\epsilon) .$$
(A11)

It is also straightforward to verify that

$$\lim_{p \to 3} (1 - e^{-2\pi p i})^{-1} 2\pi i \sum_{\substack{\text{poles} \\ z \neq 0}} \operatorname{Res} f_{\pm}(z, p) = -\frac{1}{8\pi^2} \{ \zeta(3) \pm \frac{1}{2} [\zeta(3, R/L) + \zeta(3, -R/L) + (L/R)^3] \} ,$$
(A12)

where the ζ functions are defined as

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}$$

and

 $\zeta(s,a) = \sum_{n=0}^{\infty} \frac{1}{(n+a)^s} \; .$

Putting it all together we finally obtain the results (3.7a) and (3.7b).

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