Recalculations of Long-Range van der Waals Potentials

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The long-range van der Waals forces between a particle and a conducting wall, and between two polarizable particles are calculated including contributions from both electric and magnetic polarizabilities. The techniques applied here of using quantum zero-point energy or semiclassical force and energy expressions have been used previously only for the case of purely electrically polarizable particles. A particle with an induced magnetic dipole moment may be repelled from a conducting wall while one with an induced electric dipole moment is attracted. The general retarded two-particle van der Waals potential obtained is identical with that found by Feinberg and Sucher from dispersion-theoretic calculations.

I. INTRODUCTION

The retarded van der Waals force between two neutral particles with nonvanishing electric polarizability was calculated by Casimir and Polder¹ in 1948. More recently, Feinberg and Sucher² have used dispersion theory to obtain expressions for the general long-range van der Waals force between two particles, including effects of both electric and magnetic polarizability. In this paper, we wish to show that the general expression may also be obtained by natural extensions of techniques previously used in recalculations of van der Waals forces due to purely electric polarizability - specifically, by the use of quantum zeropoint energy,³ and by the use of semiclassical energy expressions or of the Maxwell stress-energy tensor.4

In the original investigation of Casimir and Polder, the motivation arose from the suggestion of Overbeek⁵ that the stability of lyophobic colloids required that the long-range van der Waals forces between neutral unpolarized particles should fall off faster than the R^{-6} suggested by London's calculation of the Coulomb contribution to the van der Waals force. The direct physical application of calculations of retarded van der Waals forces seems to have become more remote with the passage of time. The attitude in the present account is that it is interesting to see the consistency in the widely differing approaches to the calculations through electrodynamics.

In Sec. II, Casimir's zero-point energy approach is employed as the basis for calculations. The long-range force between a polarizable particle and a conducting wall is found to be attractive for an electrically polarizable particle but may be repulsive for a magnetically polarizable one. Next the general retarded potential of Feinberg and Sucher is reproduced for two polarizable particles. In Sec. III a recalculation of the forces is sketched based on Maxwell's stress-energy tensor or, what is seen to be equivalent, on semiclassical energy expressions.

II. CASIMIR'S METHOD: QUANTUM ZERO-POINT ENERGY

Since we wish to obtain long-range electromagnetic forces between objects, it is sufficient to consider the interactions through the radiation field. However, in noncovariant quantum field theory, we may assign a zero-point energy $\frac{1}{2}\hbar\omega$ to each normal mode of frequency ω in the radiation field. Thus the interaction between objects may be understood as being due to a position-dependent change in the natural frequencies ω , and the resultant change in the zero-point energy of the electromagentic radiation field. The zero-point energy of the system depending on the separation R is the potential function U(R) for the long-range force between two particles.

It is clear that with this point of view, we hope to approach the calculation of potential functions by way of changes in the frequencies of the normal modes. Now the frequencies of the quantum radiation field are identical with those for the corresponding classical field, and hence we may compute the changes in frequencies due to the position of objects in classical theory, and then apply these frequency shifts to the quantum zeropoint energy.⁶ Specifically, let us consider a cavity with conducting walls and a neutral polarizable particle. Before the particle is introduced, the electric and magnetic fields of frequency ω are given by the real parts of

$$\vec{\mathcal{E}}_{0\omega}(\vec{\mathbf{x}},t) = \vec{\mathbf{E}}_{0\omega}(\vec{\mathbf{x}}) \exp(-i\omega_0 t),$$

$$\vec{\mathcal{R}}_{0\omega}(\vec{\mathbf{x}},t) = -i\vec{\mathbf{H}}_{0\omega}(\vec{\mathbf{x}}) \exp(-i\omega_0 t),$$
(1)

and after the introduction of the particle, the frequency of this mode is shifted to $\omega_0 + \delta \omega$ and the fields are

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$$\vec{\delta}_{\omega}(\vec{\mathbf{x}},t) = [\vec{E}_{0\omega}(\vec{\mathbf{x}}) + E_{1\omega}(\vec{\mathbf{x}})] \\ \times \exp[-i(\omega_0 + \delta\omega)t],$$

$$\vec{\mathbf{x}}_{\omega}(\vec{\mathbf{x}},t) = -i[\vec{H}_{0\omega}(\vec{\mathbf{x}}) + \vec{H}_{1\omega}(\vec{\mathbf{x}})] \\ \times \exp[-i(\omega_0 + \delta\omega)t].$$
(2)

The Maxwell curl equations for (1) and (2) may be combined to give

$$\operatorname{curl}\vec{\mathbf{E}}_{1} = \frac{\delta\omega}{c} \vec{\mathbf{H}}_{0} + \frac{\omega_{0}}{c} \vec{\mathbf{B}}_{1} + \frac{\delta\omega}{c} \vec{\mathbf{B}}_{1},$$

$$\operatorname{curl}\vec{\mathbf{H}}_{1} = \frac{\delta\omega}{c} \vec{\mathbf{E}}_{0} + \frac{\omega_{0}}{c} \vec{\mathbf{D}}_{1} + \frac{\delta\omega}{c} \vec{\mathbf{D}}_{1},$$
(3)

dropping the common subscript ω on the fields. Multiplying the first equation by \vec{H}_0 , the second by \vec{E}_0 , adding and integrating over all space, we have

$$(\delta\omega/c)\int (H_0^2 + E_0^2)d^3x$$

= $\int (\vec{H}_0 \cdot \text{curl}\vec{E}_1 + \vec{E}_0 \cdot \text{curl}\vec{H}_1)d^3x$
- $(\omega_0/c)\int (\vec{H}_0 \cdot \vec{B}_1 + \vec{E}_0 \cdot \vec{D}_1)d^3x,$ (4)

where we have neglected the term involving the product of $\delta \omega$ and the perturbing field as involving second-order quantities. Now using the identity,

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$$div(\vec{H}_{0} \times \vec{E}_{1} + \vec{E}_{0} \times \vec{H}_{1})$$

$$= -\vec{H}_{0} \cdot curl\vec{E}_{1} + \vec{E}_{1} \cdot curl\vec{H}_{0}$$

$$-\vec{E}_{0} \cdot curl\vec{H}_{1} + \vec{H}_{1} \cdot curl\vec{E}_{0}, \qquad (5)$$

to transform the first term on the right, again using Maxwell's equations for the unperturbed fields assuming there are no free charges or currents, Eq. (4) becomes

$$\delta\omega \int (H_0^2 + E_0^2) d^3x$$

= $-\omega_0 \int d^3x [\vec{H}_0 \cdot (\vec{B}_1 - \vec{H}_1) + \vec{E}_0 \cdot (\vec{E}_1 - \vec{D}_1)].$
(6)

If the fields \overline{E}_0 and \overline{H}_0 do not change significantly over the dimensions of the particle, (i.e., for wavelengths significantly longer than the dimensions of the particle), then we may approximate the right-hand side in terms of the value of the fields at the centers of the particles and the total dipole moments so that

$$- \delta\omega/\omega_0 = 4\pi (\vec{E}_0 \cdot \vec{P} + \vec{H}_0 \cdot \vec{M}) / \int (E_0^2 + H_0^2) d^3x$$

= $4\pi (\alpha E_0^2 + \beta H_0^2) / \int (E_0^2 + H_0^2) d^3x, \quad (7)$

where α and β are the electric and magnetic polarizabilities, respectively. The Eq. (7) is the desired approximate connection between the classical unperturbed fields and the shift in frequency $\delta\omega$.

Polarizable Particle and Conducting Wall

The style of calculation involved will be illustrated first by the evaluation of the force between a conducting wall and a polarizable particle of electric polarizability α and magnetic polarizability β . As indicated earlier, the potential function is

$$U(R) = \sum_{i=1}^{1} \hbar \omega_{R} - \sum_{i=1}^{1} \hbar \omega_{\infty}, \qquad (8)$$

which is the difference in zero-point energy of the electromagnetic radiation field when the particle is a distance R from the wall and when the particle is a large distance from the wall. Since both the sums give formally divergent series, we will introduce a cutoff in the wavelength, for example the cutoff function $\exp(-\lambda\omega/c)$, and will allow $\lambda \rightarrow 0$ at the end of the calculation. Now since an examination of Eq. (7) indicates that $\delta\omega_R$ and $\delta\omega_{\infty}$ average to the same value for high frequencies, and also

$$\langle \omega \rangle \equiv \langle \omega_0 + \delta \omega \rangle = \text{const} \times \langle \omega_0 \rangle,$$

we may by redefining λ employ the cutoff $\exp(-\lambda\omega_0/c)$. But then this allows us to subtract term by term in the summations of (8) giving

$$U(R) = \sum_{n=1}^{\infty} \hbar(\delta \omega_R^n - \delta \omega_\infty) \exp(-\lambda \omega_0^n/c).$$
 (9)

We will omit the exponential cutoff in all expressions until the final evaluation of integrals where its smoothing is required. We should remark that physically there is no occasion for a cutoff. The polarizability of a particle becomes vanishingly small as the frequency increases. Equivalently, the approximation used in Eq. (7) that the wavelength of the unperturbed radiation is long compared to the dimensions of the particle breaks down as the frequencies ω increase. However, it is interesting to see that the result of Eq. (9) is independent of any cutoff, and in effect it is only the longer wavelengths which contribute to the potential function so that it is appropriate to regard α and β as constants corresponding to the static polarizabilities.

For a cubic box of length L, the unperturbed fields are

$$\vec{\mathbf{E}}_{0\omega\lambda} = \operatorname{const}[\hat{i}\epsilon_{\chi}(\vec{\mathbf{k}},\lambda)\cos k_{\chi}x\sin k_{y}y\sin k_{z}z + \hat{j}\epsilon_{y}(\vec{\mathbf{k}},\lambda)\sin k_{\chi}x\cos k_{y}y\sin k_{z}z + \hat{k}\epsilon_{z}(\vec{\mathbf{k}},\lambda)\sin k_{\chi}x\sin k_{y}y\cos k_{z}z], \quad (10)$$

$$\vec{\mathrm{H}}_{0\omega\lambda} = k^{-1} \vec{\nabla} \times \vec{\mathrm{E}}_{0\omega\lambda}, \qquad (11)$$

with $k_x = l\pi/L$, $k_y = m\pi/L$, $k_z = n\pi/L$, l, m, n, integers. The waves are transverse, $\vec{k} \cdot \hat{\epsilon} (\vec{k}, \lambda) = 0$; and the polarization vectors are normalized,

$$\hat{\epsilon}(\mathbf{k},\lambda)\cdot\hat{\epsilon}(\mathbf{k},\lambda')=\delta_{\lambda\lambda'}$$

When we substitute these expressions into Eq. (7), we will find terms which are squares of sines and cosines. In the case where the argument is not $k_{\chi}R$, with R the distance of the particle to the wall of the cube taken at x = 0, the argument will be rapidly varying with k since it will involve a large distance and hence the function averages to $\frac{1}{2}$. Thus maintaining the explicit \sin^2 or \cos^2 terms only for argument $k_{\chi}R$, Eq. (9) becomes

$$U(R) = -\frac{1}{2}\hbar c \sum_{\vec{k},\lambda} \frac{k4\pi}{(2V/8)4} \left\{ \alpha [\epsilon_x^{\ 2}(\cos^2 k_x R - \frac{1}{2}) + (\epsilon_y^{\ 2} + \epsilon_z^{\ 2})(\sin^2 k_x R - \frac{1}{2})] + \beta [\frac{(\vec{k}x\hat{\epsilon})^{\ 2}}{k^2}(\sin^2 k_x R - \frac{1}{2})] + \beta [\frac{(\vec{k}x\hat{\epsilon})^{\ 2}}{k^2}(\sin^2 k_x R - \frac{1}{2})] + \frac{(\vec{k}\times\hat{\epsilon})^{\ 2} + (\vec{k}\times\hat{\ell})^{\ 2}}{k^2}(\cos^2 k_x R - \frac{1}{2})] \right\}, (12)$$

with the first contribution from the electric polarizability and the second from the magnetic. The initial minus sign comes from the sign of Eq. (7) and the factor of 2V/8 from the integral in the denominator. The factor of 4 in the denominator arises from the $(\frac{1}{2})^2$ contributions of \sin^2 and \cos^2 functions in the y and z directions, while the subtractions of $\frac{1}{2}$ come from the \sin^2 and \cos^2 functions in the x direction of $\delta\omega_{\infty}$.

Carrying out the polarization sums in $\boldsymbol{\lambda}$ with

$$\sum_{\lambda=1}^{2} \epsilon_{\chi}^{2}(\vec{k}, \lambda) = 1 - k_{\chi}^{2}/k^{2},$$

$$\sum_{\lambda=1}^{2} [\vec{k} \times \hat{\epsilon}(\vec{k}, \lambda)]_{\chi}^{2} = k^{2} - k_{\chi}^{2},$$
(13)

noting the equations for the transverse character and normalization, and using the trigonometric half-angle formulae, the expression becomes

$$U(R) = \frac{2\pi\hbar c}{V} \left(\alpha - \beta\right) \sum_{\mathbf{k}} \left(\frac{k_x^2}{k} \cos 2k_x R\right) \quad . \quad (14)$$

For a large normalization box, we may replace the sum by an integral. Casimir³ has indicated how to evaluate the expression, and we will provide some detail later in the case of two particles. The result here is

$$U(R) = -(3/8\pi)(\hbar c/R^4)(\alpha - \beta).$$
(15)

Thus if the polarizabilities are both positive, the electric polarizability gives an attraction of the particle toward the wall, but the magnetic polarizability causes repulsion.

Two Polarizable Particles

We now turn to the long-range potential between two neutral polarizable particles. The style of calculation parallels that given above for a particle and conducting wall. We consider the situation of a conducting cavity containing particle A into which we introduce particle B. The second particle shifts the frequencies of the normal modes of oscillation of the electromagnetic radiation, and hence changes the quantum zero-point energy $\sum \frac{1}{2}\hbar\omega$. The potential function for the long-range force between the particles is given by the change in this zero-point energy.

The unperturbed fields required in our analysis are now

where here $\vec{E}_{0\omega}$, $\vec{H}_{0\omega}$ stand for the free fields in the cavity and \vec{E}_{ω}' , \vec{H}_{ω}' correspond to the fields radiated by the induced electric and magnetic dipoles of particle A. The system corresponds to a closed universe in which there are standing waves, and hence we must take the average of the retarded and advanced radiated waves. Thus owing to an electric dipole $\vec{p} \exp(-i\omega t)$, the fields are

$$\vec{\delta}_{\vec{p}\omega}'(\vec{x},t) = [\vec{p}F - \hat{n}(\hat{n}\cdot\vec{p})G]\exp(-i\omega t), \qquad \vec{\mathcal{R}}_{\vec{p}\omega}'(\vec{x},t) = i(\hat{n}\times\vec{p})I\exp(-i\omega t), \qquad (17)$$

with

$$G = k^{3} [\cos kr/kr - 3\sin kr/(kr)^{2} - 3\cos kr/(kr)^{3}].$$
(18)

The contributions from a magnetic dipole \vec{m} are found by substituting in the above equation $\vec{p} \rightarrow \vec{m}$, $\vec{E} \rightarrow \vec{H}$, $\vec{H} \rightarrow -\vec{E}$.

 $I = k^{3} \left[\sin kr / kr + \cos kr / (kr)^{2} \right], \quad F = k^{3} \left[\cos kr / kr - \sin kr / (kr)^{2} - \cos kr / (kr)^{3} \right],$

Again in obtaining the potential U(R), we are dealing with divergent series for which we introduce a cutoff $\exp(-\lambda\omega/c)$. In the present case, the change in frequencies $\delta\omega$ due to the interactions between the two particles averages to zero in ω and vanishes as $R \rightarrow \infty$. The shift in frequencies related to attractions to the walls were seen to go to a common value which was a multiple of the frequency ω_0 of the normal modes in the empty box. Hence we may again redefine the cutoff parameter λ , use a cutoff function $\exp(-\lambda\omega_0/c)$, and subtract frequencies under the summation sign. As we have noted, $\delta\omega_{\infty}$ arising from

the interaction of particles vanishes. Using Eq. (7) with the fields having subscripts zero there standing for the unperturbed fields with subscripts u in Eq. (16), we have for the two-particle potential

$$U(R) = \sum \frac{1}{2} \hbar \delta \omega_R = -\frac{1}{2} \hbar c \sum_{\vec{k}, \lambda} \frac{k4\pi}{(2V/8)} \left\{ \alpha_B [\vec{E}_{0\omega}(\vec{x}_B) + \vec{E}_{\omega}'(\vec{x}_B)]^2 + \beta_B [\vec{H}_{0\omega}(\vec{x}_B) + \vec{H}_{\omega}'(\vec{x}_B)]^2 \right\}$$

- (interaction of particle *B* and wall)

$$= \frac{-8\pi nc}{V} \sum_{\vec{k},\lambda} k[\alpha_B^2 \vec{z}_{0\omega}(\vec{x}_B) \cdot \vec{z}_{\omega}'(\vec{x}_B) + \beta_B^2 \vec{H}_{0\omega}(\vec{x}_B) \cdot \vec{H}_{\omega}'(\vec{x}_B)], \qquad (19)$$

keeping terms to first order in the dipole fields and removing the particle-wall potential found in the previous calculation.

Substituting for the radiated fields from Eqs. (7) and (8) with the induced dipoles given to lowest order by

$$\vec{p} = \alpha_A \vec{E}_{0\omega} (\vec{x}_A), \quad \vec{m} = -i\beta_A \vec{H}_{0\omega} (\vec{x}_A), \tag{20}$$

and assuming the particles both lie along the x axis a distance R apart, the potential becomes

$$U(R) = \frac{-16\pi\hbar c}{V} \sum_{\vec{k},\lambda} \{ \alpha_B \alpha_A [\vec{E}_{0\omega}(\vec{x}_B) \cdot \vec{E}_{0\omega}(\vec{x}_A) kF - \vec{E}_{0\omega x}(\vec{x}_B) \vec{E}_{0\omega x}(\vec{x}_A) kG]$$

$$- \alpha_B \beta_A \vec{E}_{0\omega}(\vec{x}_B) \cdot [\hat{i} \times \vec{H}_{0\omega}(\vec{x}_A)] kI - \beta_B \alpha_A \vec{H}_{0\omega}(\vec{x}_B) \cdot [\hat{i} \times \vec{E}_{0\omega}(\vec{x}_A)] kI$$

$$+ \beta_B \beta_A [\vec{H}_{0\omega}(\vec{x}_B) \cdot \vec{H}_{0\omega}(\vec{x}_A) kF - \vec{H}_{0\omega x}(\vec{x}_B) \cdot \vec{H}_{0\omega x}(\vec{x}_A) kG] \}.$$
(21)

Now the expressions (10), (11) are substituted for the fields in the empty cavity. For example,

$$\vec{\mathbf{E}}_{0\omega x}(\vec{\mathbf{x}}_{B}) \cdot \vec{\mathbf{E}}_{0\omega x}(\vec{\mathbf{x}}_{A}) = \epsilon_{x}^{2} \cos k_{x}(x_{A}+R) \cos k_{x}x_{A} \sin^{2}k_{y}y_{A} \sin^{2}k_{z}z_{A} = \frac{1}{8}\epsilon_{x}^{2}(\vec{\mathbf{k}},\lambda) \cos k_{x}R,$$
(22)

where we have replaced \sin^2 , \cos^2 , and $\sin \times \cos$ functions not involving the distance R by their average values. Performing analogous simplifications for the remaining terms,

$$U(R) = \frac{-2\pi\hbar c}{V} \sum_{\vec{k},\lambda} \left((\alpha_A \alpha_B + \beta_A \beta_B) [kF - \epsilon_x^2(\vec{k},\lambda)kG] \cos k_x R + (\alpha_A \beta_B + \alpha_B \beta_A) kI \frac{k_x}{k} \sin k_x R \right).$$
(23)

It is worth remarking that although the original formulation of the problem was asymmetric between particles A and B, the potential has now been brought into a symmetric form as must be the case.

The polarization sum may be evaluated by again noting Eq. (13). Assuming the enclosing box used for the "universe" is quite large, the sum over \vec{k} may be replaced by an integral $\frac{1}{8}(V/\pi^3)\int_{-\infty}^{\infty} d^3k$. We change to polar coordinates and carry out the angular integrations,

$$U(R) = -\left(\alpha_{A}\alpha_{B} + \beta_{A}\beta_{B}\right)\frac{\hbar c}{\pi} \int_{0}^{\infty} dk \, k^{6} \left(\frac{\sin 2kR}{(kR)^{2}} + \frac{2\cos 2kR}{(kR)^{3}} - \frac{5\sin 2kR}{(kR)^{4}} - \frac{6\cos 2kR}{(kR)^{5}} + \frac{3\sin 2kR}{(kR)^{6}}\right) \\ -\left(\alpha_{A}\beta_{B} + \alpha_{B}\beta_{A}\right)\frac{\hbar c}{\pi} \int_{0}^{\infty} dk \, k^{6} \left(-\frac{\sin 2kR}{(kR)^{2}} - \frac{\cos 2kR}{(kR)^{3}} + \frac{\sin 2kR}{(kR)^{4}}\right).$$
(24)

At this point, we reintroduce the exponential cutoff function mentioned in connection with Eq. (19). The integrals may be calculated easily. For example,

$$\int_{0}^{\infty} dk \sin ak \exp(-\lambda k) = \operatorname{Im} \int_{0}^{\infty} dk \exp[(-\lambda + ia)k] = -\operatorname{Im} (-\lambda + ia)^{-1} + a^{-1}, \quad \text{as } \lambda \to 0.$$
(25)

Evaluating the remaining integrals analogously with the use of partial integrations, we arrive at the result,

$$U(R) = \left[-23(\alpha_A \alpha_B + \beta_A \beta_B) + 7(\alpha_A \beta_B + \alpha_B \beta_A)\right] \hbar c / 4\pi R^7.$$
⁽²⁶⁾

This expression is identical with that obtained by Feinberg and Sucher² from dispersion-theory techniques.

III. SEMICLASSICAL METHODS OF CALCULATION

It has been pointed out, 7 that noncovariant freefield quantum electrodynamics is equivalent to classical electrodynamics on which there is superimposed a random walk in the normal coordinates of the field. This understanding emphasizes the possibility of using traditional classical methods in electromagnetic theory with a final averaging suitable for the random walk. In a calculation of the quantum electromagnetic attraction between two conducting parallel plates, it was shown that it is perfectly feasible and sometimes not inconvenient to use the Maxwell stress-energy tensor for the evaluation of these quantum forces. As a further reminder of this approach, we will show that the same techniques may be applied here.

The force on an object in classical electromagnetic theory is given by the relation

$$\frac{d}{dt} \left(\vec{\mathbf{P}}_{\text{mechanical}} + \vec{\mathbf{P}}_{\text{field}} \right) = \oint_{S} d\sigma \, \hat{n} \cdot \vec{T}, \quad (27)$$

with S a surface surrounding the object and where \overline{T} is the Maxwell stress-energy tensor

$$\overline{T} = \left[\vec{E} \, \vec{E} + \vec{H} \, \vec{H} - \frac{1}{2} \, \vec{I} \, (E^2 + H^2) \right] / 4\pi \,. \tag{28}$$

In the present case, we may take the surface S as a sphere immediately surrounding a particle. Just as in Sec. II, the electric and magnetic fields may be regarded as given by an unperturbed part and a part due to the perturbation of the fields on introducing the particle on which we wish to compute the force. The perturbing field will be given by the (near-field) dipole field due to the polarized particle. Under the assumption that the particle dimension is small compared to the wavelength of the standing waves, the unperturbed field at the surface s may be expanded about the center of the particle as

$$\vec{\mathcal{E}}_{0}(\vec{\mathbf{x}},t) \cong \vec{\mathcal{E}}_{0}(\vec{\mathbf{x}}_{1},t) + r(\hat{n} \cdot \vec{\nabla}_{1}) \vec{\mathcal{E}}_{0}(\vec{\mathbf{x}}_{1},t), \qquad (29)$$

where r is the radius of the spherical surface S and \hat{n} the outward pointing normal. Then substituting into Eq. (27) and easily carrying out the integrals of the form

$$\oint_{S} d\sigma n_{i} n_{j}, \quad \oint_{S} d\sigma n_{i} n_{j} n_{k} n_{l},$$

we obtain precisely the expected classical result,

$$F_{i} = -\vec{p} \cdot \vec{\partial}_{i} \vec{\mathcal{E}}_{0} - \vec{m} \cdot \vec{\partial}_{i} \vec{\mathcal{K}}_{0}, \qquad (30)$$

for the force on a dipole in an inhomogeneous electromagnetic field. Remembering that the dipoles are induced, and dropping higher-order terms in the perturbation, this gives

$$F_{i} = -\alpha \vec{\mathcal{S}}_{0} \cdot \vartheta_{i} \vec{\mathcal{S}}_{0} - \beta \vec{\mathcal{K}}_{0} \cdot \vartheta_{i} \vec{\mathcal{K}}_{0}, \qquad (31)$$

or
$$\vec{F} = -\vec{\nabla}(\frac{1}{2}\alpha \vec{\mathcal{E}}_0 \cdot \vec{\mathcal{E}}_0 + \frac{1}{2}\beta \vec{\mathcal{E}}_0 \cdot \vec{\mathcal{E}}_0).$$
 (32)

At this point, we may introduce the expressions for the fields and arrive at the force obtained from the potentials (15) and (26). Alternatively, we may note that the force of Eq. (32) is obtained from the potential

$$U(R) = \frac{1}{2} \alpha \vec{\mathcal{E}}_0 \cdot \vec{\mathcal{E}}_0 + \frac{1}{2} \beta \vec{\mathcal{K}}_0 \cdot \vec{\mathcal{H}}_0 + \text{const}, \qquad (33)$$

and may substitute into this expression. Thus in the present case, the use of the Maxwell stressenergy tensor is merely a long way of arriving at the classical energy expression. In the calculation of the force between two conducting parallel plates, no expression comparable to (33) is available and the use of the stress-energy tensor represents the only obvious semiclassical approach.

In the following evaluation of the potential (33), we may regard the fields equally well as classical fields subject to a random walk or as quantum fields. Free electromagnetic fields in an enclosure with conducting walls are given by⁸

$$\vec{\mathcal{E}}_{0}(\vec{\mathbf{x}},t) = \sum_{\vec{\mathbf{k}},\lambda} \left(\frac{4\pi}{V}\right)^{1/2} \dot{q}_{\vec{\mathbf{k}}\lambda}(t) \vec{\mathbf{f}}_{\vec{\mathbf{k}}\lambda}(\vec{\mathbf{x}}),$$
$$\vec{\mathcal{E}}_{0}(\vec{\mathbf{x}},t) = -c \sum_{\vec{\mathbf{k}},\lambda} \left(\frac{4\pi}{V}\right)^{1/2} q_{\vec{\mathbf{k}}\lambda}(t) \vec{\nabla} \times \vec{\mathbf{f}}_{\vec{\mathbf{k}}\lambda}(\vec{\mathbf{x}}), \quad (34)$$

where the $f_{\vec{k}\lambda}(\vec{x})$ are functions satisfying

$$-\operatorname{curl}\operatorname{curl}\vec{\mathbf{f}}_{\vec{\mathbf{k}}\lambda} + k^{2}\vec{\mathbf{f}}_{\vec{\mathbf{k}}\lambda} = 0, \qquad (35)$$

with $\hat{n} \times \tilde{f}_{k\lambda} = 0$ on the walls of the enclosure. For the normalizations indicated, the average values or expectation values for treatments regarding the q and \dot{q} as subject to a random walk or as quantum operators, respectively, are

$$\langle q_{\vec{k}\lambda}^{(t)} q_{\vec{k}'\lambda}^{-} , (t) \rangle = \frac{1}{2} (\hbar/\omega)^{\delta} (\vec{k}\lambda) (\vec{k}'\lambda'),$$

$$\langle \dot{q}_{\vec{k}\lambda}^{-} (t) \dot{q}_{\vec{k}'\lambda}^{-} , (t) \rangle = \frac{1}{2} \hbar \omega^{\delta} (\vec{k}\lambda) (k'\lambda').$$

$$(36)$$

Returning to substitute these expressions into (33) for U(R),

$$U(R) = \frac{\alpha}{2} \frac{4\pi}{V} \sum_{\vec{k}\lambda} \sum_{\vec{k}'\lambda'} \langle \dot{q}_{\vec{k}\lambda}(t) \dot{q}_{\vec{k}'\lambda}(t) \rangle$$

$$\times \vec{f}_{\vec{k}\lambda}(\vec{x}) \cdot \vec{f}_{\vec{k}'\lambda}(\vec{x})$$

$$+ \frac{\beta}{2} c^2 \frac{4\pi}{V} \sum_{\vec{k}\lambda} \sum_{\vec{k}'\lambda'} \langle q_{\vec{k}\lambda}(t) q_{\vec{k}'\lambda}(t) \rangle$$

$$\times [\operatorname{curl} \vec{f}_{\vec{k}\lambda}(\vec{x}) \cdot \operatorname{curl} \vec{f}_{\vec{k}'\lambda}(\vec{x})] + \operatorname{const}$$

$$= \frac{\pi}{V} \hbar c \sum_{\vec{k}\lambda} k \left(\alpha \vec{f}_{\vec{k}\lambda}(\vec{x}) \cdot \vec{f}_{\vec{k}\lambda}(\vec{x}) + \frac{\beta}{k^2} \operatorname{curl} \vec{f}_{\vec{k}\lambda}(\vec{x}) \cdot \operatorname{curl} \vec{f}_{\vec{k}\lambda}(\vec{x}) \right) + \operatorname{const.} (37)$$

But $f_{\vec{k}\lambda}(\vec{x})$ is exactly what has been called the unperturbed $\vec{E}_{0\omega}(\vec{x})$ in Sec. II and

$$\operatorname{curl} \vec{\mathrm{f}}_{\vec{\mathrm{k}}\lambda}(\vec{\mathrm{x}}) = k \vec{\mathrm{H}}_{0\omega}(\vec{\mathrm{x}}).$$

Hence we recognize that Eq. (37) is exactly

$$U(R) = \sum \frac{1}{2} \hbar \,\delta\omega + \text{const}, \qquad (38)$$

where $\delta \omega$ is given by Eq. (7). The analysis now coincides exactly with that given in Sec. II. For a single particle and a conducting wall, the unperturbed fields are the free electromagnetic fields in vacuum, Eqs. (10) and (11). For two particles, the second particle is the perturbing particle and the unperturbed field is the free electromagnetic field together with the field radiated by the first particle.

IV. SUMMARY

The long-range van der Waals force between two polarizable particles has been computed by at least four distinct methods. The earliest method, that of Casimir and Polder, obtained the force between electrically polarizable particles using quantum-electromagnetic perturbation theory. Feinberg and Sucher obtained the general expression for the retarded van der Waals force from an entirely different approach through dispersion theory. The use of quantum zero-point energy, which has been extended in the present paper, was discovered by Casimir when searching for an explanation of the simplicity of the perturbation theory results. Finally, we have seen that the semiclassical use of the Maxwell stress-energy tensor or dipole energy expressions may be made the basis for the general calculation of these quantum forces.

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⁴E. A. Power, <u>Introductory Quantum Electrodynamics</u> (Elsevier Publishing Co., Inc., New York, 1965); T. H. Boyer, Phys. Rev. <u>174</u>, 1631 (1968). ⁵E. J. W. Verwey and J. Th. G. Overbeek, <u>Theory of</u> the Stability of Lyophobic Colloids (Elsevier Publishing Co., Inc., Amsterdam, 1948).

⁶The argument leading to Eq. (7) for the classical frequency shift is given by H. B. G. Casimir, Philips Res. Rept. <u>6</u>, 162 (1951). The zero-point-energy technique appears in Ref. 3.

⁷See the author's work in Ref. 4.

⁸See references in 4. Power has given evaluations of the electric polarizability contributions of the potential of Eq. (33) from the point of view of quantum electrodynamics.

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²G. Feinberg and J. Sucher, J. Chem. Phys. <u>48</u>, 3333 (1968).

³H. B. Casimir, J. Chim. Phys. <u>46</u>, 407 (1949). Professor Casimir suggested that the methods of this paper might allow extension to give the magnetic terms (letter to Professor Feinberg, communicated to the author by Professor Sucher).