Static dipole moment of an atom or a centrosymmetric molecule near a perfect metallic surface

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The expression for the dipole moment of an atom or a centrosymmetric molecule in the vicinity of a perfect metallic surface is given at any distance. The near-zone (London) and the far-zone (Casimir) limits of these results are also considered.

I. INTRODUCTION

In recent years, there has been considerable interest concerning the behavior of atoms and molecules near surfaces. It is well known that a first consequence of the interaction of an atom (or of a molecule) with a surface is the appearance of an attractive potential energy between the two partners. Although it has been considerably less studied, the electric dispersive polarization of the initially symmetric atom (or of the considered molecule) is another consequence quite as important as the first.

In the case of *two* spherically symmetric systems, the existence of such a static dipole moment was previously pointed out by Buckingham[1] and then calculated by Byers Brown and Whisnant[2] and by Hunt.[3] Recently Galatry and Gharby[4] gave a more physical form to these earlier results by expressing them in terms of dynamical polarizabilities and hyperpolarizabilities of the two systems. In a more recent paper Craig and Thirunamachandran[5] obtained these same results by using quantum electrodynamics and one of us[6] generalized all these calculations which were only performed in the London limit (long-range polarization) by giving a general theory of the dipole moment of a pair of nonidentical systems at any distance.

All these results point to similar effects when an atom or a molecule is placed near a surface. In a recent paper, Antoniewicz[7] considered this case by studying the interaction between an adatom and its image; Linder and Kromhout[8] and Galatry and Girard[9] also presented a theory of the long-range polarization of an adatom near a solid surface. However, these papers only consider the limit case of adatoms; we then consider in this work the general problem of the appearance of a static dipole moment in the coupled system whatever the distance may be between the atom (or the molecule) and the surface. However, we restrict our study to *atoms* or *centrosymmetric molecules* near a *perfect metallic surface*.

In vacuum, calculations involving atoms or molecules interacting with radiation are generally simpler with the multipolar Hamiltonian than with the minimal coupling one.[10] Although this point is still a matter of controversy,[11] the connection between these two Hamiltonians can be formed by using a unitary transformation.[10,12–14] Such a Power-Zienau transformation can be used near a surface and, as far as we know, Babiker and Barton[15] were the first to employ it near a plasma surface (in calculations of frequency shifts). However, the formal proof of the equivalence of the two Hamiltonians in a cavity or near a metallic surface was just recently given by Power and Thirunamachandran.[16] In this work, we use the multipolar Hamiltonian. Instantaneous Coulombic interactions consequently do not appear explicitly and we only consider retarded transverse waves. To perform calculations, we have thus to define the normal modes of the electromagnetic field near the surface and then to introduce the Feynman's propagator of such modes. The definition of this propagator (Sec. II) constitutes the first result of this paper.

To calculate the dipole moment $\vec{\mu}$ of the coupled system, we proceed as Craig and Thirunamachandran[5] and we suppose that an external static electric field $\vec{E}$ is applied. If the external field is uniform, the energy shift ΔE is linear in the field and equal to $-\vec{\mu} \cdot \vec{E}$. Thus, from the calculation of the energy shift, we can deduce the desired moment $\vec{\mu}$. All these calculations are presented in Sec. III for centrosymmetric molecules. We also give their limit form in the near zone (London) and in the far zone (Casimir) limits. In Sec. IV we consider the more particular case of a spherically symmetric system (atom).

II. PRESENTATION OF OUR FORMALISM

A. Electromagnetic modes and quantization of the electromagnetic field near the surface

The electromagnetic field in a half space $z > 0$ bounded by a perfect metallic mirror ($z = 0$) can be expressed as the sum of an incident and a reflected (superscript R) plane wave. As presented in Ref. 17 and 18 such a superposition defines the elementary mode of the field in the half space. Each mode can be characterized by the wave vec-

tor of its incident part $\vec{k} \equiv (k_1, k_2, k_3 < 0)$ and by its polarization $\vec{\epsilon}(s)$ [$s = 1$ for a transverse electric mode (TE) and $s = 2$ for a transverse magnetic mode (TM)]. We can thus write

$$\vec{\mathscr{E}}(\vec{k}, s, \vec{r}) = \frac{1}{\sqrt{2}} [\vec{\epsilon}(s) e^{i\vec{k}\cdot\vec{r}} + \vec{\epsilon}^R(s) e^{i\vec{k}^R\cdot\vec{r}}] \tag{1}$$

(the scale factor $1/\sqrt{2}$ is a normalization factor). The wave vectors $\vec{k}$ and $\vec{k}^R$ of these two components are defined by

$$|k| = |k^R| = \omega/c \ ,$$
$$\vec{k}_{x(y)} = \vec{k}^r_{x(y)}, \quad k_z = -k_z^R \ , \tag{2}$$

and their polarizations $\vec{\epsilon}(s)$ and $\vec{\epsilon}^R(s)$ must verify

$$\vec{\epsilon}^R(1) = -\vec{\epsilon}(1), \quad \vec{\epsilon}^R(2) = [\vec{\epsilon}(1) \times \vec{k}^R]/|\vec{k}| \ . \tag{3}$$

It can be shown[18] that Eq. (1) forms a complete basis in the space of the field states. By combining all possible modes with arbitrary complex amplitude $u(\vec{k}, s)$ we can thus form a representation of any arbitrary electric (or magnetic) field[18]

$$\vec{E}(\vec{r}, t) = \frac{1}{(2\pi)^{3/2}} \int_{k_z < 0} d^3k \sum_{s=1}^{2} \left[\frac{\hbar\omega}{\epsilon_0} \right]^{1/2} [u(\vec{k}, s) \vec{\mathscr{E}}(\vec{k}, s, \vec{r}) e^{-i\omega t} + \text{c.c.}] \ . \tag{4}$$

By expanding the electromagnetic field in terms of these doublet modes, the energy and the impulsion parallel to the mirror is expressible as the sum of contributions from independent harmonic oscillators, one for each mode. The situation is therefore exactly the same as for the free field in vacuum and it is consequently straightforward to quantify the field in the presence of the mirror by using these modes: The complex amplitudes $u(\vec{k}, s)$ and $u^*(\vec{k}, s)$ are replaced by Hilbert space operators $u(\vec{k}, s)$ and $u^\dagger(\vec{k}, s)$ which can be given the usual interpretation of annihilation and creation operators for quantum modes.

This quantization is quite similar to the one introduced earlier by Carniglia and Mandel[19] in the case of evanescent waves near a dielectric. The importance of the formalism of doublet modes is that it permits the performance of calculations which automatically take into account the combinatorial aspects of the incident and reflected parts of the field arising from the presence of the interface. In short, the interface being included in the definition of the electromagnetic field modes, we may calculate all the possible interactions between matter and light near the surface, exactly as we do in a free field in vacuum. (Some examples of the use of these modes are given in Refs. 20—23; the first reference deals with the Cherenkov effect, the second with absorption or emission of evanescent waves and others with Raman effect near a dielectric.) In the present case, we can then introduce the Feynman's propagator of the electromagnetic mode near the mirror exactly as we do in a free field.

B. The Feynman's propagator of the mode

To calculate the Feynman propagator of the mode let us successively consider the two processes illustrated in Figs. 1(a) and 1(b). In 1(a), a mode $(\vec{k}, s)$ is emitted at time τ_1 by atom A and absorbed at time $\tau_2 > \tau_1$ by B.

Writing the dipolar emission by A as

$$\frac{1}{i\hbar} \langle b, \vec{k}s | [-D_A E(R_A)] | a, 0 \rangle = \frac{-e}{i\hbar} \left[\frac{\hbar\omega}{(2\pi)^3 \epsilon_0} \right]^{1/2} \sum_i \langle b | r_{Ai} | a \rangle \mathscr{E}_i^*(\vec{k}, s, \vec{R}_A) e^{j\omega\tau_1} \tag{5}$$

and using a similar expression for the absorption by B, the total amplitude corresponding to 1(a) can be written

$$\left[\frac{1}{i\hbar} \right]^2 e^2 \sum_{i,j} \langle b | r_{Ai} | a \rangle \langle d | r_{Bj} | c \rangle \int_{k_3 < 0} d^3k \sum_s \frac{\hbar\omega}{(2\pi)^3 \epsilon_0} \mathscr{E}_i^*(\vec{k}, s, \vec{R}_A) \mathscr{E}_j(\vec{k}, s, \vec{R}_B) e^{-i\omega(\tau_2 - \tau_1)} \ . \tag{6}$$

The propagator of the doublet mode between the two space-time points R_A, τ_1 and R_B, τ_2 corresponds to the integral of Eq. (6). Using Eqs. (21)—(27) of Ref. 18 this propagator can also be written ($\omega = c|k|$ and $\tau_2 > \tau_1$)

$$\int_{k_3 < 0} d^3k \sum_s \frac{\hbar\omega}{(2\pi)^3 \epsilon_0} \mathscr{E}_i^*(\vec{k}, s, \vec{R}_A) \mathscr{E}_j(\vec{k}, s, \vec{R}_B) e^{-i\omega(\tau_2 - \tau_1)}$$

$$= \frac{1}{2} \int d^3k \frac{\hbar\omega}{(2\pi)^3 \epsilon_0} e^{-i\omega(\tau_2 - \tau_1)} \left[\delta_{ij} - \frac{k_i k_j}{|k|^2} \right] [e^{i\vec{k}\cdot(\vec{R}_B - \vec{R}_A)} + \eta_i e^{i\vec{k}\cdot(\vec{R}_B - \tilde{\vec{R}}_A)}] \ . \tag{7}$$

In the above expression

$$\eta_i = -1 \quad \text{for } i = 1, 2$$
$$\eta_i = +1 \quad \text{for } i = 3 \tag{8}$$

and $\tilde{R}_A$ corresponds to the position vector of the image atom A, that is to say, taking the origin of the reference frame on the mirror

$$\vec{R}_A \equiv (x,y,z), \quad \widetilde{\vec{R}}_A \equiv (x,y,-z) \ . \tag{9}$$

The expression corresponding to Fig. 1(b) is quite similar to Eq. (7) after changing the sign of $\omega(\tau_2-\tau_1)$, $\vec{k}\cdot(\vec{R}_B-\vec{R}_A)$, and $\vec{k}\cdot(\widetilde{\vec{R}}_B-\vec{R}_A)$. Then with the use of the identity

$$-\frac{1}{2i\pi}2|\vec{k}|\lim_{\epsilon\to 0+}\int_{-\infty}^{+\infty}dk_0\frac{e^{-ick_0(\tau_2-\tau_1)}}{k_0^2-|k|^2+i\epsilon}=\begin{cases}e^{-ic|\vec{k}|(\tau_2-\tau_1)}, & \tau_2>\tau_1\\ e^{+ic|\vec{k}|(\tau_2-\tau_1)}, & \tau_2<\tau_1\end{cases} \tag{10}$$

and integrating on k_0, it is possible to write the two results corresponding to 1(a) and 1(b) by the same expression:

$$D_{ij}^F(R_A\tau_1,R_B\tau_2)=-\frac{1}{2}\frac{i\hbar c}{(2\pi)^2\epsilon_0}\int_{-\infty}^{+\infty}dk_0 e^{-ick_0(\tau_2-\tau_1)}[g_{ij}^F(|k_0|,R)+\eta_i g_{ij}^F(|k_0|,\widetilde{R})] \tag{11}$$

with

$$\vec{R}=\vec{R}_B-\vec{R}_A, \quad \widetilde{\vec{R}}=\widetilde{\vec{R}}_B-\vec{R}_A, \quad R\equiv|\vec{R}_B-\vec{R}_A|, \quad \widetilde{R}\equiv|\widetilde{\vec{R}}_B-\vec{R}_A| \ . \tag{12}$$

This expression is the Feynman's propagator of the mode. As for the free field in vacuum,

$$g_{ij}^F(|k_0|,\widetilde{R})=e^{i|k_0|\widetilde{R}}|k_0|^3 h_{ij}(|k_0|,\widetilde{R}) \ ,$$

$$h_{ij}(|k_0|,\widetilde{R})=\frac{1}{|k_0|\widetilde{R}}\left[\delta_{ij}-\frac{\widetilde{R}_i\widetilde{R}_j}{\widetilde{R}^2}\right]+\left[\frac{i}{|k_0|^2\widetilde{R}^2}-\frac{1}{|k_0|^3\widetilde{R}^3}\right]\left[\delta_{ij}-\frac{3\widetilde{R}_i\widetilde{R}_j}{\widetilde{R}^2}\right] \ . \tag{13}$$

In our calculations, we shall need the first derivative of $g_{ij}^F(|k_0|,\widetilde{R})$ with respect to the space coordinate. We give here its expression:

$$\frac{d}{dx_k}g_{ij}^F(|k_0|,\widetilde{R})=e^{i|k_0|\widetilde{R}}|k_0|^4\eta_k h_{kij}(|k_0|,\widetilde{R}) \ ,$$

$$h_{kij}(|k_0|,\widetilde{R})=\frac{i}{|k_0|\widetilde{R}}\frac{\widetilde{R}_k}{\widetilde{R}}\left[\delta_{ij}-\frac{\widetilde{R}_i\widetilde{R}_j}{\widetilde{R}^2}\right]-\frac{1}{|k_0|^2\widetilde{R}^2}\left[\frac{2\widetilde{R}_k}{\widetilde{R}}\left[\delta_{ij}-\frac{3\widetilde{R}_i\widetilde{R}_j}{\widetilde{R}^2}\right]+\frac{\widetilde{R}_i\delta_{jk}+\widetilde{R}_j\delta_{ik}}{\widetilde{R}}\right]$$

$$-\frac{i}{|k_0|^3\widetilde{R}^3}\left[\frac{3\widetilde{R}_k}{\widetilde{R}}\left[\delta_{ij}-\frac{5\widetilde{R}_i\widetilde{R}_j}{\widetilde{R}^2}\right]+3\left[\frac{\widetilde{R}_i\delta_{jk}+\widetilde{R}_j\delta_{ik}}{\widetilde{R}}\right]\right]$$

$$+\frac{1}{|k_0|^4\widetilde{R}^4}\left[\frac{3\widetilde{R}_k}{\widetilde{R}}\left[\delta_{ij}-\frac{5\widetilde{R}_i\widetilde{R}_j}{\widetilde{R}^2}\right]+3\left[\frac{\widetilde{R}_i\delta_{jk}+\widetilde{R}_j\delta_{ik}}{\widetilde{R}}\right]\right] \ . \tag{14}$$

It must be realized that, when the derivative is taken with respect to $\widetilde{x}$, we obtain, because of (9), (8), and (12),

$$\frac{\partial}{\partial\widetilde{x}_i}g_{jk}^F(|k_0|,\widetilde{R})=\eta_i\frac{\partial}{\partial x_i}g_{jk}^F(|k_0|,\widetilde{R}) \ . \tag{15}$$
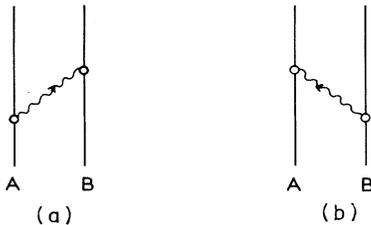
FIG. 1. Graphs corresponding to a virtual photon exchange between two systems A and B. (a) Virtual photon emitted by A is absorbed by B; (b) virtual photon is emitted by B and absorbed by A. Near a surface, the wavy line represents a virtual mode of the electromagnetic field. Feynman's propagator of the mode is obtained by adding these two cases.

III. DIPOLE MOMENT OF THE COUPLED SYSTEM "CENTROSYMMETRIC MOLECULE-SURFACE"

The dipole moment $\vec{\mu}$ of the system can be obtained by derivation of the interaction energy ΔE when an external static field $\vec{E}$ is applied,

$$\Delta E=-\vec{\mu}\cdot\vec{E}+\cdots, \quad \mu_i=-\frac{\partial\Delta E}{\partial E_i} \ . \tag{16}$$

Our first step to calculate $\vec{\mu}$ is therefore to find the R dependent part of ΔE. In the case when the system is an atom or a molecule with a center of inversion, the parity selection rules show that $\Delta E(R)$ can be obtained in the lowest order from graphs in which appear [Figs. 2(a)—2(f)] two dipole vertices ($\bigcirc$) and one quadrupole vertex ($\square$) (in this figure, the external horizontal line represents the interaction with the external static field and the wavy lines represents a virtual mode of the field).

As explained above, we have pointed out that quantization of the electromagnetic field near the surface permits us to study interactions between matter and light near the mirror exactly as we do in a free field in vacuum. There-
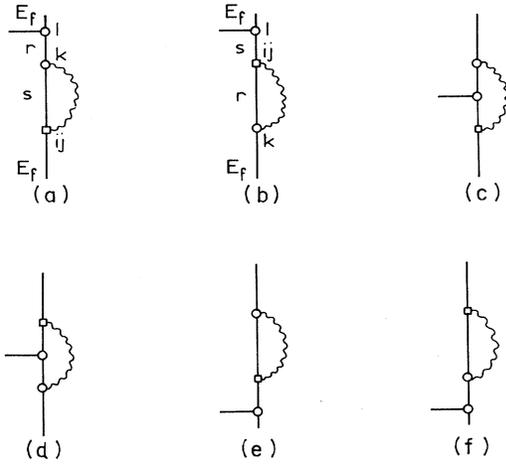
FIG. 2. Graphs corresponding to the energy shift of a spherically symmetric or of a centrosymmetric system near the metallic surface, in the presence of an external static electric field. O and □ indicate a dipolar and a quadrupolar interaction, respectively; wavy line corresponds to a virtual mode of the electromagnetic field near the surface.

fore, in such a description the attractive potential energy between the atom and the mirror is given by Fig. 3 which usually represents the self-energy of the system, and which contains, in the present case, the interaction energy with the mirror in addition to the usual self-energy terms. Using Eq. (11) the identification is immediate: The first term in (11) leads to the self-energy which diverges as expected and consequently cannot be calculated by this method; the second term corresponds to the R-dependent part of ΔE and can thus be interpreted as the interaction potential between the atom and the mirror.[24-26]

In order to calculate ΔE we have to add the contributions of all these diagrams. To be clearer we only present calculations for the first two [2(a) and 2(b)] and we use notations presented in Fig. 2: states (r,s) are the virtual states of the atom (or of the centrosymmetric molecule). Letters i,j,k,l stand for Cartesian components of quadrupole and dipole moments. The energy of the initial and of the final states is E_f.

To get the contribution of Fig. 1(a) to ΔE we have to consider external atomic lines,

$$e^{-iE_f\tau_1/\hbar} e^{iE_f\tau_3/\hbar} , \qquad (17)$$

internal atomic terms,

$$\left[-\frac{1}{2i\pi}\right] \lim_{\eta\to 0+} \int_{-\infty}^{+\infty} \frac{e^{-E'(\tau_2-\tau_1)/\hbar}}{E'+i\eta-E_r} dE' ,$$

$$\left[-\frac{1}{2i\pi}\right] \lim_{\eta\to 0+} \int_{-\infty}^{+\infty} \frac{e^{-iE''(\tau_3-\tau_2)/\hbar}}{E''+i\eta-E_s} dE'' , \qquad (18)$$

vertices,

$$-\frac{e^3}{2}\left[\frac{1}{i\hbar}\right]^3 \langle f|r_{Al}|s,m''\rangle\langle s,m''|r_{Ak}|r,m'\rangle$$

$$\times\langle r,m'|r_{Ai}r_{Aj}|f\rangle\frac{\partial}{\partial x_i} , \qquad (19)$$

an internal photonic term which reduces to the second part of Eq. (11) [since the first term does not depend on R ($R=0$) and represents the self-energy of the atom], and the external static electric field,

$$E_l . \qquad (20)$$

We do not delve into justifications of these expressions since it is clearly set forth in all electrodynamic books or papers.

The contributions of the process of Fig. 2(a) to $\Delta E(R)$ is then obtained by taking the product of Eqs. (17)—(19), (11), and (20) and by integrating on time τ_1,τ_2,τ_3, energy $E',E'',\hbar ck_0$, and summing on energy levels r,s, magnetic quantum numbers m',m'', and Cartesian coordinates i,j,k,l. Integrations on τ_1,τ_2,τ_3 give

$$(2\pi)^3\delta^T\left[\frac{E''}{\hbar}-\frac{E_f}{\hbar}\right]\delta^T\left[\frac{E'}{\hbar}+ck_0-\frac{E_f}{\hbar}\right]$$

$$\times\delta^T\left[\frac{E'}{\hbar}+ck_0-\frac{E''}{\hbar}\right] \qquad (21)$$

which expresses the energy conservation for all the lines joining at each vertex.

Making use of the above result (21) integration on E' and E'' becomes straightforward: using (18) in which only the denominators remain, noting

$$E_{fs}=E_f-E_s, \quad E_{fr}=E_f-E_r \qquad (22)$$

and using

$$\left[\delta^T\left[\frac{E_f}{\hbar}-\frac{E'}{\hbar}\right]\right]^2 = \frac{T}{2\pi}\hbar\delta^T(E_f-E') , \qquad (23)$$

the total contribution of Fig. 2(a) to ΔE can be written

$$(\Delta E)_a = \langle\phi_0|\widetilde{U}|\phi_0\rangle\frac{\hbar i}{T} = -\frac{i\hbar c}{16\pi^2\epsilon_0}\sum_{i,j,k,l}\sum_{r,s}\sum_{m',m''} E_l\frac{\partial}{\partial x_i}\int_{-\infty}^{+\infty}dk_0\frac{\mu_l^{fs}\mu_k^{sr}\theta_{ij}^{rf}}{(E_{fr}+i\eta)(E_{fs}-\hbar ck_0+i\eta)}\eta_j g_{jk}^F(|k_0|,\widetilde{R}) . \qquad (24)$$

In the above equation we note $\mu_l^{mn}=e\langle n|r_l|m\rangle$ the components of the dipole moment operator and $\theta_{kl}^{mn}=e\langle n|r_k r_l|m\rangle$ the quadrupole ones. With the use of its parity properties Eq. (24) can be written

$$(\Delta E)_a = -\frac{i\hbar c}{16\pi^2\epsilon_0}\sum_{i,j,k,l}\sum_{r,s}\sum_{m',m} E_l\mu_l^{fr}\mu_k^{rs}\theta_{ij}^{sf}$$

$$\times\frac{\partial}{\partial x_i}\int_{-\infty}^{+\infty}dk_0\frac{1}{E_{fr}+i\eta}\left[\frac{1}{E_{fs}-\hbar ck_0+i\eta}+\frac{1}{E_{fs}+\hbar ck_0+i\eta}\right]\eta_j g_{jk}^F(k_0,\widetilde{R}) . \qquad (25)$$

Integration being performed in the interval $[0, +\infty)$, $|k_0|$ can be replaced by k_0 in $g_{jk}^F(|k_0|, \widetilde{R})$.

To calculate the contribution of Fig. 2(b) we proceed, of course, in the same way. However, we have to point out two appreciable changes: on the one hand, the mode propagator is now to be written D_{kj}^F. Then with the use of Eq. (11) the R-dependent part of ΔE will now be given by $\eta_k g_{kj}$ instead of $\eta_j g_{jk}$. On the other hand, we must not lose sight of the fact that the quadrupolar interaction acts no more at the point $(x, y, -z)$ but at the point (x, y, z). Taking these two remarks into account, using Eq. (15) to calculate the derivative of g_{jk} with respect to $(\widetilde{x}, \widetilde{y}, \widetilde{z})$, Eq. (13) to be convinced that $g_{jk} = g_{kj}$, and Eq. (8) to see that $\eta_k^2 = 1$, we can write

$$\frac{\partial}{\partial \widetilde{x}_i} \eta_k g_{kj} = \eta_i \frac{\partial}{\partial x_i} \eta_k g_{kj}$$

$$= \eta_i \eta_j \eta_k \frac{\partial}{\partial x_i} \eta_j g_{jk} \ . \tag{26}$$

This allows us to write the contribution $(\Delta E)_b$ of the process of Fig. 2(b) to ΔE as

$$(\Delta E)_b = -\frac{i\hbar c}{16\pi^2 \epsilon_0} \sum_{i,j,k,l} \sum_{r,s} \sum_{m',m''} E_{lj} \mu_l^{fs} \theta_{ij}^{sr} \mu_k^{rf} \eta_i \eta_j \eta_k \frac{\partial}{\partial x_i} \int_0^\infty dk_0 \frac{1}{E_{fs} + i\eta} \left[\frac{1}{E_{fr} - \hbar c k_{00} + i\eta} \right.$$

$$\left. + \frac{1}{E_{fr} + \hbar c k_0 + i\eta} \right] \eta_j g_{jk}^F(|k_0|, \widetilde{R}) \ . \tag{27}$$

In a similar way, the contribution of 2(c) can be written as

$$(\Delta E)_c = -\frac{i\hbar c}{16\pi^2 \epsilon_0} \sum_{i,j,k,l} \sum_{r,s} \sum_{m',m''} E_{lj} \mu_k^{fr} \mu_l^{rs} \theta_{ij}^{sf} \frac{\partial}{\partial x_i} \int_0^\infty dk_0 \left[\frac{1}{(E_{fr} - \hbar c k_0 + i\eta)(E_{fs} - \hbar c k_0 + i\eta)} \right.$$

$$\left. + \frac{1}{(E_{fr} + \hbar c k_0 + i\eta)(E_{fs} + \hbar c k_0 + i\eta)} \right] \eta_j g_{jk}^F(|k_0|, \widetilde{R}) \ . \tag{28}$$

Because of Eq. (26), $(\Delta E)_d$ is given by (28) after changing $\eta_j g_{jk}^F$ into $\eta_i \eta_j \eta_k (\eta_j g_{jk}^F)$, $(\Delta E)_e$ is given by (27) after changing $\eta_i \eta_j \eta_k (\eta_j g_{jk}^F)$ into $\eta_j g_{jk}^F$, and $(\Delta E)_f$ is given by (25) with $\eta_i \eta_i \eta_k (\eta_j g_{jh}^F)$ at the place of $\eta_j g_{jk}^F$ (Fig. 2).

ΔE is obtained by summing all these contributions. To perform integration on k_0 in ΔE, we can note by looking at Eqs. (24)–(26) that the integrand has poles at $\hbar c k_0 = \pm(E_{fr} + i\eta)$ and $\hbar c k_0 = \pm(E_{fs} + i\eta)$, that is to say, under the positive part of the real axis and above its negative part. We may thus consider the contour presented in Fig. 4. with the use of

$$\chi_{lkij}(0, -\hbar c k) = \frac{1}{8\pi\epsilon_0} \sum_{r,s} \sum_{m',m''} \left\{ \theta_{ij}^{fs} \mu_k^{sr} \mu_l^{rf} \left[\frac{1}{E_{fr}} \left[\frac{1}{E_{fs} - \hbar c k_0} + \frac{1}{E_{fs} + \hbar c k_0} \right] \right] \right.$$

$$+ \theta_{ij}^{fs} \mu_l^{sr} \mu_k^{rf} \left[\frac{1}{(E_{fr} - \hbar c k_0)(E_{fs} - \hbar c k_0)} + \frac{1}{(E_{fr} + \hbar c k_0)(E_{fs} + \hbar c k_0)} \right]$$

$$+ \mu_l^{fs} \theta_{ij}^{sr} \mu_k^{rf} \left[\frac{1}{E_{fs}} \left[\frac{1}{E_{fr} - \hbar c k_0} + \frac{1}{E_{fr} + \hbar c k_0} \right] \right] \right\} \ , \tag{29}$$

FIG. 3. Graph corresponding to the energy shift: In a free field, this graph only represents the self-energy of the system. Because the Feynman's propagator of the mode contains two terms, this diagram contains in the present case the interaction energy with the mirror in addition to the usual self-energy term.
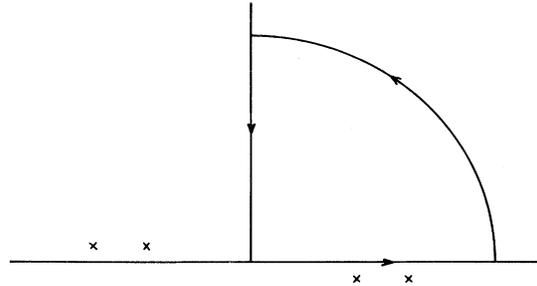
FIG. 4. Integration path in the complex plane. Crosses are the poles of the integrand.

the dynamical hyperpolarizability of the system,[27,28] and noting $k_0 = iu$, ΔE becomes

$$\Delta E = \frac{\hbar c}{2\pi} \sum_{i,j,k,l} \frac{\partial}{\partial x_i} \int_0^\infty du \, e^{-u\widetilde{R}} u^3 \eta_j h_{ijk}(iu,\widetilde{R}) E_l (1 + \eta_i \eta_j \eta_k) \chi_{lkij}(0, -iu) \ . \tag{30}$$

The static dipole moment of the coupled system is then obtained by using Eq. (16):

$$\mu_l = -\frac{\hbar c}{2\pi} \sum_{i,j,l} \frac{\partial}{\partial x_i} \int_0^\infty du \, e^{-u\widetilde{R}} u^3 \eta_j \eta h_{ijk}(iu,\widetilde{R}) E_l (1 + \eta_i \eta_j \eta_k) \chi_{lkij}(0, -iu) \ . \tag{31}$$

These two above results are quite general. We want to give now their expression in the near-zone (London) and in the far-zone (Casimir) limits.

A. Near-zone limit

Denoting E_I as the characteristic energy of transitions in the coupled system, the near-zone limit is usually defined by the condition $k_I \widetilde{R} \ll 1$. In this case, we can thus take $e^{-u\widetilde{R}} \sim 1$ and only consider in (13) or (14) the last terms which vary as $1/\widetilde{R}^3$ and $1/\widetilde{R}^4$, respectively. Equation (30) can thus be expressed as follows:

$$\Delta E = \frac{\hbar c}{2\pi} \frac{3}{\widetilde{R}^4} \sum_{i,j,k,l} E_l \eta_i \eta_j \left[\frac{\widetilde{R}_i \delta_{jk} + \widetilde{R}_j \delta_{ki} + \widetilde{R}_k \delta_{ij}}{\widetilde{R}} - \frac{5\widetilde{R}_i \widetilde{R}_j \widetilde{R}_k}{\widetilde{R}^3} \right] (1 + \eta_i \eta_j \eta_k) \int_0^\infty du \, \chi_{lkij}(0, -iu) \ . \tag{32}$$

Using (29) and

$$\int_0^\infty \frac{dx}{\alpha^2 + x^2} = \frac{\pi}{2\alpha} \ , \tag{33}$$

we obtain

$$\Delta E = \frac{-3}{16\pi\epsilon_0} \frac{1}{\widetilde{R}^4} \sum_{i,j,k,l} E_l \eta_i \eta_j (1 + \eta_i \eta_j \eta_k) \left[\frac{\widetilde{R}_i \delta_{jk} + \widetilde{R}_j \delta_{ki} + \widetilde{R}_k \delta_{ij}}{\widetilde{R}} - \frac{5\widetilde{R}_i \widetilde{R}_j \widetilde{R}_k}{\widetilde{R}^3} \right] \sum_{r,s} \left[\frac{\theta_{ij}^{fs} \mu_k^{sr} \mu_l^{rf}}{E_{fr}} + \frac{\mu_l^{fs} \theta_{ij}^{sr} \mu_k^{rf}}{E_{fs}} \right] \ . \tag{34}$$

Because of the definitions $E_{fr} = E_f - E_r < 0$ and $E_{fs} - E_f - E_s < 0$, we easily see that ΔE is negative and consequently corresponds to an attractive potential between the atom (or centrosymmetric molecule) and the surface. μ_l is easily deduced from (34) by using (16); its varies as $1/\widetilde{R}^4$.

B. Far-zone limit

This zone is defined by $k_I R \gg 1$. Because of the quickly decreasing factor $\exp(-u\widetilde{R})$ when u is greater than some $1/\widetilde{R}$, the integrand of (30) quickly decreases outside the interval 0 less than u less than some $1/\widetilde{R}$. In this interval, χ is practically constant: Looking in fact at (29) we see that when $u \ll k_I$, $\hbar c k_0$ can be neglected with regard to E_{fr} or E_{fs}. The corresponding expression of ΔE in the far-zone limit may thus be obtained by taking $u = 0$ in the atomic term. Therefore, it is clear that we have

$$\Delta E = \frac{\hbar c}{2\pi} \sum_{i,j,k,l} \eta_j E_l (1 + \eta_i \eta_j \eta_k) \chi_{lkij}(0,0) \frac{\partial}{\partial x_i} \int_0^\infty du \, e^{-u\widetilde{R}} u^3 h_{ijk}(iu,\widetilde{R}) \ . \tag{35}$$

Integration on u can be performed as follows: Using (14), we get an expression which can easily be written in the form

$$\int_0^\infty du \, e^{-u\widetilde{R}} (\alpha + \beta u + \gamma u^2 + \delta u^3) \ . \tag{36}$$

Then taking $x = u\widetilde{R}$ and using

$$I_n = \int_0^\infty dx \, x^n e^{-x} = nI_{n-1} = n! \tag{37}$$

we obtain

$$\Delta E = \frac{4}{\widetilde{R}^5} \frac{\hbar c}{\pi} \sum_{i,j,k,l} \eta_i \eta_j E_l (1 + \eta_i \eta_j \eta_k) \chi_{lkij}(0,0) \left[\frac{2\widetilde{R}_i \delta_{jk} + \widetilde{R}_j \delta_{ki} + \widetilde{R}_k \delta_{ij}}{\widetilde{R}} - \frac{6\widetilde{R}_i \widetilde{R}_j \widetilde{R}_k}{\widetilde{R}^3} \right] \ . \tag{38}$$

In the far-zone limit the shift ΔE varies as $1/\widetilde{R}^5$. The expression of the static dipole moment of the coupled system is obtained by using (16). It is clear it varies as $1/\widetilde{R}^5$.

IV. CASE OF TWO SPHERICAL SYSTEMS

If the species is spherically symmetric the polarizability tensor is isotropic and, summations on magnetic quantum numbers lead to

$$\chi_{\alpha\beta\gamma\delta}(0, -\omega) = \chi_{xxxx}(0, -\omega) [\tfrac{3}{4} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) - \tfrac{1}{2} \delta_{\alpha\beta} \delta_{\gamma\delta}] \ . \tag{39}$$

It must be noted that according to Refs. 27 and 28, we have

$$\chi_{xxxx}(0,-\omega)=\tfrac{2}{15}\chi_{\alpha\beta\alpha\beta}(0,-\omega)\ ,\tag{40}$$

where the convention in which a repeated greek subscript denotes a summation over all three Cartesian components has been used.

Equation (30) can be written

$$\Delta E=\frac{\hbar c}{2\pi}\sum_{i,j}\int_0^\infty du\ e^{-u\widetilde{R}}u^4(1+\eta_j)E_j\chi_{xxxx}(0,-iu)[\tfrac{3}{4}\eta_i\eta_j(h_{iji}+h_{jii})-\tfrac{1}{2}h_{iij}]\ .\tag{41}$$

Noting that $h_{ijk}=h_{ikj}$ and using Eq. (8), (42) reduces to

$$\Delta E=-\frac{3\hbar c}{2\pi}E_z\int_0^\infty du\ e^{-u\widetilde{R}}u^4\chi_{xxxx}(0,-iu)\left[\frac{1}{u\widetilde{R}}+\frac{5}{u^2\widetilde{R}^2}+\frac{12}{u^3\widetilde{R}^3}+\frac{12}{u^4\widetilde{R}^4}\right]\ .\tag{42}$$

The dipole moment is easily obtained by using (42) and (16).

A. Near-zone limit

In this zone, we may only take into account the last term in (43) and write $\exp(-u\widetilde{R})\sim 1$. We thus obtain

$$\Delta E=-\frac{36\hbar c}{2\pi}\frac{E_z}{\widetilde{R}^4}\int_0^\infty du\ \chi_{xxxx}(0,-iu)\tag{43}$$

integration can be performed as in Sec. III A. We get [according to (12) and (9), $\widetilde{R}=2z$]

$$\Delta E=-\frac{9}{4\pi\epsilon_0}\frac{E_z}{16z^4}\sum_{r,s}\left[\frac{\theta_{xx}^{fs}\mu_x^{sr}\mu_x^{rf}}{E_{fr}}+\frac{\mu_x^{fs}\theta_{xx}^{sr}\mu_x^{rf}}{E_{fs}}\right]\tag{44}$$

and (noting $\vec{u}$ a unitary vector in the z direction)

$$\vec{\mu}=\mu_z\vec{u}=+\frac{9}{4\pi\epsilon_0}\frac{1}{16z^4}\sum_{r,s}\left[\frac{\theta_{xx}^{fs}\mu_x^{sr}\mu_x^{rf}}{E_{fr}}+\frac{\mu_x^{fr}\theta_{xx}^{sr}\mu_x^{rf}}{E_{fs}}\right]\vec{u}\ .\tag{45}$$

We note that, because of the definition $E_{fr}=E_f-E_r<0$, the shift ΔE is negative and thus corresponds to an attractive potential between the atom and the surface, and the dipole moment is directed in the positive direction of the z axis.

B. Far-zone limit

As explained above, the atomic term in this case has no time to evaluate and we may approximate (30) and (31) by considering that $\chi(0,iu)$ always keeps its initial value $\chi(0,0)$. Calculations are then similar to calculations presented in Sec. III B:

$$\Delta E=-\frac{3\hbar_c}{2\pi}\frac{E_z}{\widetilde{R}^5}\chi_{xxxx}(0,0)$$

$$\times\int_0^\infty dx\ e^{-x}(x^3+5x^2+12x+12)\ .\tag{46}$$

Using then (37) we obtain ($\widetilde{R}=2z$)

$$\Delta E=-\frac{15}{8\pi}\frac{\hbar c}{z^5}\chi_{xxxx}(0,0)E_z\tag{47}$$

and

$$\vec{\mu}\equiv\mu_z\vec{u}=\frac{15}{8\pi}\frac{\hbar c}{z^5}\chi_{xxxx}(0,0)\vec{u}\tag{48}$$

or

$$\vec{\mu}=\frac{15\hbar c}{32\pi^2\epsilon_0}\frac{\vec{u}}{z^5}\sum_{r,s}\frac{\theta_{xx}^{fs}\mu_x^{sr}\mu_x^{rf}+\theta_{xx}^{fs}\mu_x^{sr}\mu_x^{rf}+\mu_x^{fs}\theta_{xx}^{sr}\mu_x^{rf}}{E_{fs}E_{fr}}\ .\tag{49}$$

As in the near zone, the shift ΔE (negative) corresponds to an attractive potential between the atom and the surface and the dipole moment (positive) is directed in the positive direction of the z axis.

V. CONCLUSION

The interaction of an atom or of a molecule with the electromagnetic field near a surface gives rise to an electric polarization of the system. In the long-range approximation (near-zone limit) the dipole moment varies as z^{-4}; in the very-long-range approximation (far-zone limit) because of retardation effects, it only varies as z^{-5}. In all cases, it is obviously directed in the direction perpendicular to the surface.

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