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Quantum electrodynamics near an interface: Polarizability of a pair of adsorbed molecules

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The expression for the polarizability of a pair of centrosymmetric systems adsorbed on a dielectric or a metallic surface is given for the first time to our knowledge. Of course, if no surface is present our results can also be applied to the case of interactions between colliding molecules in vacuum. The use of the multipolar Hamiltonian leads to a complete expression of the hyperpolarizability which contains at the same time dispersive and inductive effects. This makes it possible to write down calculations in a very compact and simple form.

I. INTRODUCTION

It is well known that an important consequence of the interaction between an atom and a surface, or between two atoms in a pair, is the modification of the intrinsic polarizability; adsorption or interactions between colliding molecules cause a change in the polarizability which affects both dielectric[1–4] and optical properties[5] of a microscopic sample. A good knowledge of such effects is important in surface physics, in spectroscopy, and in optics.

The study of the polarizability of a *single* atom (or molecule) near a surface has been previously considered by Antoniewicz,[6,7] Galatry and Girard,[8] Grossel,[9] Girard and Galatry,[10] and Van Labeke, Grossel, and Vigoureux.[11] Efrima and Metiu[12] have also defined an effective dynamical polarizability of an adsorbed molecule in their study of the Raman scattering near surfaces. Later, Korzeniewski, Maniv, and Metiu[13] introduced a more general situation where the description of the surface is improved in order to take into account the continuous change of the dielectric constant across the surface. Long-range situations have been introduced in that context by Feilbelman.[14]

The polarizability of *interacting atoms* (or molecules) in the free space (that is to say without surface) has first been studied by Silberstein,[15] Kirkwood,[16] and Brown.[17] More recently, Jansen and Mazur,[18] Buckingham,[19] Certain and Fortune,[20] Buckingham, Martin, and Watts,[21] MacKrodt,[22] and Buckingham and Clarke[23] have given a quantum-mechanical treatment of the polarizability of a pair of like atoms separated by a large distance. Hunt, Zilles, and Bohr[24] have presented a complete study of these effects by incorporating the frequency dependence of the molecular response to the fluctuating fields. In a study of discriminating interactions between chiral molecules, Taylor and Thirunamachandran[25] have also published interesting results on this subject. Pearson, Waldman, and Gordon[26] have also given some estimations of these effects.

Our aim in this paper is to combine the two cases above and to present a general study of the polarizability of two atoms (or centrosymmetric molecules) interacting both with each other and with a metallic or dielectric surface. Such a problem, taking into account *cooperative effects between adatoms,* is quite important to understand experiments in surface science, spectroscopy, or surface optics. As far as we know it has never been studied up to now. We study successively the alteration of the intrinsic polarizability of a given adatom by its neighbor and the polarizability of the pair. All calculations are given to order R^{-6}.

In this paper we use the quantum electrodynamic formalism as extended in previous works to study interactions between the electromagnetic field and matter near a surface.[11,27–35] Although its use in molecular physics has been clearly presented by Craig and Thirunamachandran,[36] this method is not used in surface science. As a rule, in quantum electrodynamics, interactions are mediated by exchanges of virtual quanta of the electromagnetic field. In a free field these quanta are ordinary photons; near a surface, they are "surface modes." In the present study, a first advantage of this formalism is that it reduces a three-body problem (molecule-molecule-surface) to the usual two-body one (molecule-molecule). To be clearer let us compare the case of two interacting molecules in a free field with the one of two interacting molecules near a surface. In the field of quantum electrodynamics the only difference between these two cases is that, in the first one, molecules only exchange usual photons whereas in the second one the interaction is mediated by specific surface modes. In other words, the presence of the surface (with characteristics of the solid half space) is included in the definition of the field. Because of this, we may calculate interactions near the surface exactly as we do in a free field in vacuum. The two cases can then be compared stage by stage. This helps to foresee and to interpret surface effects.

To use this method the problem is, of course, to define these specific surface modes which mediate interactions. As explained in Refs. 31 and 32 the usual method of doing this involves quantifying the radiation field through a mode expansion appropriated to a half space of vacuum bounded by the medium. This has been performed for dielectrics[37,38] and perfect metallic surfaces (including plasmons).[9,39–42] Following McLachlan,[43–45] Agarwal[46–48] has shown that for more realistic surfaces quantum electrodynamics can be used by introducing correlation functions that appear in linear-response theory. The analytic form of the propagator of the electromagnetic field near the surface then depends on the model of the dielectric function $\epsilon(\mathbf{k},\omega)$ chosen for describing the medium, on the geometry of the surface, and on the assumed boundary conditions. Although in such general cases a number of theoretical problems have not been solved and although, as shown by Barton,[49] one must be very cautious when using such "realistic" responses, they can, of course, be useful in quantitative studies. However, in those cases, calculations take a very complicated form and integrations, which then have to be performed numerically, make results difficult to interpret. Because of this, in this paper we shall deal only with the case of a local theory when retardation effects can be ignored. We also only consider the case of atoms or centrosymmetric molecules. We think that this model remains useful in that it allows us to examine the situation in the simplest possible way. It will be possible to adapt our results to more sophisticated cases by modifying the field propagator appearing in calculations.

The organization of the paper is as follows. In Sec. II we present the formalism that we use. The propagator of the field near the surface is given in the local limit. We next briefly discuss its form in general cases. In Sec. III we study the *polarizability of a single atom near a surface.* This polarizability, which is noted α^{surf}, can be obtained from the interaction energy ΔU of the system when a fictitious external static field is applied. Results in this part are not new[6–14] but we choose to present them here because we need them in following discussions and especially because they permit us to illustrate our method and to compare it with the usual ones. Two differences have thus to be underlined. The first one, as explained above, is that, in this case, our calculations reduce the usual two-body problem (molecule-surface) to the one-body problem (molecule in a field). The second one is that the hyperpolarizability which directly appears in our *ab initio* calculations takes into account at the same time inductive and dispersive effects which are to be considered separately in all usual treatments. The use of such a "generalized hyperpolarizability," which constitutes a first result of this paper, gives thus a direct route to study surface effects. In Secs. IV and V we calculate the polarizability of a pair of molecules near the surface. This polarizability results from two different processes which are considered separately. The first one, which we shall call the intrinsic polarizability of the pair near the surface can be obtained from the interaction energy ΔU of the total system when the fictitious static field is applied on each atom. This term, which is noted $\alpha_{AB}^{\text{surf}}$, is presented in Sec. IV. The second one leads to the alteration of the intrinsic polarizability of one adsorbed molecule A due to the interaction with the neighbor B. It can be obtained by differentiating ΔU with respect to the external static field only applied on the molecule A. This term, which is noted $\alpha_{A\leftarrow B}^{\text{surf}}$, is presented in Sec. V. Some general remarks are then given. Our chief aim in this paper being to expose the above major results about the use of electrodynamics near a surface and to prevent only general results on the polarizability of adsorbed systems, we neglect overlap in calculations.

II. GENERAL PRESENTATION OF THE FORMALISM

In vacuum, calculations involving interacting atoms or molecules are generally simpler with the multipolar Hamiltonian than with the minimal-coupling one. The connection between these two Hamiltonians can be performed by using a Power-Zienau transformation which may be used near a surface as recently shown by Power and Thirunamachandran.[33] With the multipolar Hamiltonian that we use, interactions between two systems A and B are only mediated by transverse modes of the field. Consequently, instantaneous Coulombic interactions do not explicitly appear, provided we consider neutral systems.

We consider two atoms (or centrosymmetric molecules) located at points $\mathbf{R}_A$ and $\mathbf{R}_B$ near a surface. We take the origin of our reference frame on the surface, its z axis being directed from medium toward the vacuum and its xz plane containing AB.

Interactions between A and B are mediated by the Feynman's propagator of the field between the two space-time points $(\mathbf{R}_A,\tau_A)$ and $(\mathbf{R}_B,\tau_B)$. Its physical meaning corresponds to the usual process of an emission (absorption) of a virtual quantum of the field at point $(\mathbf{R}_A,\tau_A)$ followed by its absorption (emission) at $(\mathbf{R}_B,\tau_B)$. For the case near a perfect metallic surface this propagator has been defined in Ref. 27. In the presence of a dielectric interface it can, for example, be deduced from the response function given by Agarwal[48] or from the expression calculated by Carniglia and Mandel[37] for the electric field commutators in the half space.

In the field of a local theory, and when retardation effects can be neglected, this propagator can be written

$$D_{ij}(R_A\tau_A,R_B\tau_B) = -\frac{i\hbar}{2\pi}\int_{-\infty}^{+\infty} d\omega\, e^{-i\omega(\tau_B-\tau_A)} g_{ij}^{T}(\omega;R_A,R_B)\ . \tag{1}$$

Noting $\mathbf{R}_A=(x_B,y_A,z_A)$ and $\widetilde{\mathbf{R}}_A=(x_A,y_A,-z_A)$ (in the particular case of a perfect mirror, A would thus be the image of the point A) and writing

$$\begin{aligned}&\mathbf{R}_{AB}=\mathbf{R}_B-\mathbf{R}_A,\quad R_{AB}=|\mathbf{R}_{AB}|\\&\widetilde{\mathbf{R}}_{AB}\equiv\mathbf{R}_{\widetilde{A}B}=\mathbf{R}_B-\mathbf{R}_{\widetilde{A}},\quad \widetilde{R}_{AB}=|\widetilde{\mathbf{R}}_{AB}|\end{aligned} \tag{2}$$

we have, when the two above restrictions are satisfied,

$$g_{ij}^{T}(\omega;R_A,R_B)=g_{ij}(\omega,\mathbf{R}_{AB})+\theta_i\Delta(\omega)g_{ij}(\omega,\widetilde{\mathbf{R}}_{AB})\ . \tag{3}$$

In order to simplify notations, g_{ij}^{0} and g_{ij}^{S} will be written instead of $g_{ij}(R_{AB})$ and $g_{ij}(\widetilde{R}_{AB})$, respectively, in each case when this change will be clear.

In this expression, where θ_i and $\Delta(\omega)$ are defined by

$$\begin{aligned}\theta_i &= -1 \quad \text{for } i \equiv x,y \ ,\\ \theta_i &= +1 \quad \text{for } i \equiv z \ ,\end{aligned} \tag{4}$$

and

$$\Delta(\omega) = \frac{\epsilon(\omega)-1}{\epsilon(\omega)+1} \ , \tag{5}$$

g_{ij} is the Feynman's propagator in vacuum limited to its short-range term,

$$g_{ij}(\omega,R) = \frac{e^{i\omega R}}{R^3}\left[3\frac{R_iR_j}{R^2} - \delta_{ij}\right] . \tag{6}$$

It is important to note that, following Eqs. (1) and (3), D_{ij} is the sum of two independent terms. The first one describes the direct propagation between A and B; it will thus lead to usual interactions when no surface is present. The second one describes the interaction arising through the mediation of the surface; it will lead to specific surface interactions.

Some properties of $g_{ij}(\omega,R)$ will be useful in calculations. From Eq.(6) we have

$$g_{ij}(R_{AB}) = g_{ji}(R_{AB}) = g_{ij}(R_{BA}) = g_{ji}(R_{BA}) \ . \tag{7}$$

By using (2) and (4) we also have

$$\begin{aligned}\theta_i g_{ij}(\tilde{R}_{AB}) &= \theta_j g_{ji}(\tilde{R}_{BA}) = \theta_i g_{ji}(\tilde{R}_{AB})\\ &= \theta_j g_{ij}(\tilde{R}_{BA}) \ .\end{aligned} \tag{8}$$

Let us emphasize that Eqs. (3) and (6) are only valid within the quasistatic limit.

In general cases it can be possible to write down expressions corresponding to Eqs. (3) and (6) by using the linear-response theory. When bodies are separated by a distance d at which retardation effects can be ignored, we can give to g_{ij} the following form:[46–48]

$$\begin{aligned}g_{ij} = \frac{i}{2\pi}\frac{\partial^2}{\partial x_{Ai}\partial x_{Bj}} \int\int \frac{du\,dv}{w} e^{iu(x_A-x_B)+iv(y_A-y_B)}\\ \times\left(e^{iw|z-z_0|} + a e^{iw(z+z_0)}\right) .\end{aligned} \tag{9}$$

As also shown in Refs. 31 and 46—48 the multiplicative factor a can be given the interpretation of a "generalized" reflection coefficient. Its form contains a resonant denominator the vanishing of which gives the polariton dispersion relations, in the case of a dielectric, and the plasmon dispersion ones in the case of a metal. The analytic form of a depends on the model of the dielectric function $\epsilon(\mathbf{k},\omega)$, on the geometry of the surface and on the assumed behavior of the system at $z=0$.

III. POLARIZABILITY OF ONE ADATOM

In a quite general way the polarizability of a system can be obtained by differentiating its interaction energy ΔU when a fictitious external static field E is applied,

$$\Delta U = -\tfrac{1}{2}\sum_{i,j}\alpha^0_{ij}E_iE_j \ . \tag{10}$$

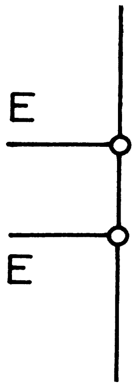

FIG. 1. Graph illustrating the static polarizability of a quantum system. ○ indicates a dipolar interaction. Horizontal lines correspond to a static electric field.

To the lowest order this energy shift is represented by the graph in Fig. 1. The process is thus characterized by two dipolar interactions (dipole vertices ○) between the atom (the vertical line) and the external static field (horizontal lines). This graph leads to the well-known static polarizability of the ground state,

$$\alpha^0_{ij} = 2e^2\sum_e \frac{\langle f\,|\,r_j\,|\,e\rangle\langle e\,|\,r_i\,|\,f\rangle}{E_e-E_f} \ . \tag{11}$$

Of course, at this order, there are no contributions due to the presence of a surface. As explained in Sec. I such a contribution is in fact included in the definition (3) of the propagator of the field, and, consequently, only appears in diagrams in which this propagator is explicitly used. When considering an atom or a centrosymmetric molecule, the parity-selection rules show that in such diagrams (and, in the lowest order), four dipolar vertices are to be used. The contribution to the polarizability due to the presence of the interface thus appears as a correction of

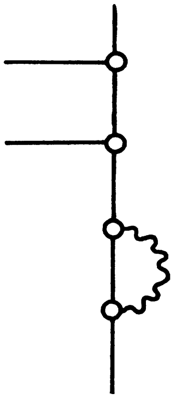

FIG. 2. Graph illustrating the polarizability of a quantum system in the presence of a surface. The wavy line corresponds to a virtual mode of the electromagnetic field near the surface.

order e^4 to the leading term (11). It is illustrated by the graph of Fig. 2 where the field propagator (3) is represented by a wavy line.

The energy shift ΔU near the surface can be found by adding contributions of this graph and of the ones obtained by permuting vertices. By using elementary calculation rules presented in Refs. 27 and 50 we obtain (the superscript S indicates the presence of the surface)

$$\Delta U_A^S = -\frac{i\hbar}{2\pi} \sum_{i,j,k,l} \int_{-\infty}^{+\infty} d\omega \tfrac{1}{4} \chi_{ijkl}^G(\omega) \times g_{kl}^T(\omega, R_A, R_{\tilde{A}}) E_i E_j \tag{12}$$

with

$$\begin{aligned}
\chi_{ijkl}^G(\omega) = 4e^4 \sum_{e,e',e''} \Bigg[& \frac{\langle f | r_k | e'' \rangle \langle e'' | r_j | e' \rangle \langle e' | r_i | e \rangle \langle e | r_l | f \rangle}{(E_e - E_f - i\eta)(E_{e'} - E_f + \hbar\omega - i\eta')(E_{e''} - E_f - i\eta'')} \\
& + \frac{\langle f | r_j | e'' \rangle \langle e'' | r_l | e' \rangle \langle e' | r_k | e \rangle \langle e | r_i | f \rangle}{(E_e - E_f + \hbar\omega - i\eta)(E_{e'} - E_f + \hbar\omega - i\eta')(E_{e''} - E_f + \hbar\omega - i\eta'')} \\
& + \frac{2\langle f | r_j | e'' \rangle \langle e'' | r_l | e' \rangle \langle e' | r_i | e \rangle \langle e | r_k | f \rangle}{(E_e - E_f - i\eta)(E_{e'} - E_f + \hbar\omega - i\eta')(E_{e''} - E_f + \hbar\omega - i\eta'')} \Bigg] \\
+ 2e^4 \sum_{\substack{e,e,e'' \\ (e' \neq f)}} & \frac{\langle f | r_l | e'' \rangle \langle e'' | r_k | e' \rangle \langle e' | r_j | e \rangle \langle e | r_i | f \rangle}{(E_e - E_f + i\eta)(E_{e'} - E_f - i\eta')(E_{e''} - E_f + \hbar\omega - i\eta'')} \\
- e^4 \sum_{e,e''} & \frac{\langle f | r_l | e'' \rangle \langle e'' | r_k | f \rangle \langle f | r_j | e \rangle \langle e | r_i | f \rangle}{(E_e - E_f)^2 (E_{e''} - E_f + \hbar\omega - i\eta'')} \\
- e^4 \sum_{e,e''} & \frac{\langle f | r_l | e'' \rangle \langle e'' | r_k | f \rangle \langle f | r_j | e \rangle \langle e | r_i | f \rangle}{(E_e - E_f)(E_{e''} - E_f + \hbar\omega - i\eta'')^2} .
\end{aligned} \tag{13}$$

As in the present case there are two static fields and two virtual processes, this coefficient is slightly different from the one usually found in literature. Let us emphasize that in Eq. (13) the ground state $|f\rangle$ is included in summations and that the two last terms correspond to regularized diagrams.

Result (12) is quite general. The total propagator g^T includes a free part and a surface one. By using Eq. (3) we thus obtain two terms. The first one does not depend on the distance d between the atom and the surface; it only describes the dressing of the atom by the free field and corresponds to a renormalization of its intrinsic polarizability. The second one characterizes surface effects. It can be written ($\omega = iu$),

$$\alpha_{ij}^S = \frac{\hbar}{4\pi} \sum_{k,l} \int_{-\infty}^{+\infty} du \chi_{ijkl}^G(iu) \times \theta_k g_{kl}^S(iu, R_A, R_{\tilde{A}}) \Delta(iu) . \tag{14}$$

This result is quite compact since it includes both inductive and dispersive terms. These two independent effects can be separated by making explicit the pole which appears for $w = 0$ in the first three terms of Eq. (13) when $|e'\rangle = |f\rangle$. As shown in Ref. 11 we obtain

$$\chi_{ijkl}^G(\omega) = 4 \frac{\alpha_{kj}(0) \alpha_{il}(0)}{\hbar\omega} + \chi_{ijkl}(\omega) . \tag{15}$$

It is to be emphasized that in the expression of $\chi_{ijkl}(\omega)$ the ground state $|f\rangle$ is now excluded from summation. As we shall see, the above separation of $\chi_{ijkl}^G(\omega)$ into two terms leads to inductive and dispersive terms which are thus all included in χ_{ijkl}^G. That is the meaning of superscript G, which characterizes this general hyperpolarizability and which indicates that dispersive and inductive terms are both taken into account. By putting (15) and (6) into Eq. (14) we find an expression for α_{ij}^S in which the purely classical contribution and the van der Waals contribution are separated [noting $R = (0,0,2d)$, and $\beta_i = 2$ for $i \equiv z$ and $\beta_i = 1$ for $i \equiv x$ or y] we have

$$\alpha_{ij}^S = \frac{\alpha_A^2(0)}{(2d)^3} \beta_i \delta_{ij} \Delta(0) + \frac{\hbar}{4\pi} \sum_l \int_{-\infty}^{+\infty} du\, \gamma_{ijll}(0, -iu, iu) \times \theta_l g_{ll}^S(R_A, R_{\tilde{A}}) \Delta(iu) . \tag{16}$$

Let us emphasize that, for a metal and in the local limit, $\Delta(0) = 1$ whatever the model chosen for describing the surface (perfect metallic surface or more realistic models including surface plasmons) may be.

In this result, γ_{ijkl} is the even part of χ_{ijkl},

$$\gamma_{ijkl}(0, -iu, iu) = \tfrac{1}{2} [\chi_{ijkl}(iu) + \chi_{ijkl}(-iu)] , \tag{17}$$

and the notation $\gamma(\omega_1,\omega_2,\omega_3)$ has been used instead of $\gamma(-\omega';\omega_1,\omega_2,\omega_3)$, dropping the index ω' which is constrained to have values $\omega'=\omega_1+\omega_2+\omega_3$. This symmetrical second hyperpolarizability γ_{ijkl} corresponds to the one of Ref. 24.

Equation (16) describes the alteration by the surface of the intrinsic polarizability of A. The first term is connected to the field of the image dipole moment as studied by Antoniewicz.[7] It coincides with the second term of the expansion of the classical effective polarizability of Refs. 6 and 8. Let us emphasize that this classical contribution is never retarded and varies as d^{-3} whatever the distance d may be. The second term is essentially a quantum one and corresponds to a nonlinear effect caused by vacuum fluctuations of the field near the surface.

Noting that for isotropic systems ($\alpha_{ij}=\alpha\delta_{ij}$) the hyperpolarizability has only three independent elements (see, for example, Ref. 51). We obtain for such systems

$$\alpha^S_{xx}=\alpha^S_{yy}=\frac{\alpha^2(0)\Delta(0)}{8d^3}+\frac{\hbar}{4\pi}\frac{1}{8d^3}\int_{-\infty}^{+\infty}du\,\Delta(iu)[\gamma_{xxxx}(0,-iu,iu)+3\gamma_{xxzz}(0,-iu,iu)]\ , \tag{18}$$

$$\alpha^S_{zz}=\frac{\alpha^2(0)\Delta(0)}{4d^3}+\frac{\hbar}{4\pi}\frac{1}{8d^3}\int_{-\infty}^{+\infty}du\,\Delta(iu)[2\gamma_{xxxx}(0,-iu,iu)+2\gamma_{xxzz}(0,-iu,iu)]\ . \tag{19}$$

These results agree with those of Refs. 8–11.

The total effective polarizability of the atom A near the surface is obtained by summing Eqs. (11), (18), and (19),

$$\alpha_A^{\mathrm{surf}}=\alpha_A^0+\alpha_A^S\ . \tag{20}$$

IV. POLARIZABILITY OF A PAIR OF INTERACTING ATOMS IN THE PRESENCE OF A SURFACE. INTRINSIC POLARIZABILITY OF THE PAIR

The polarizability α^0_{AB} of two atoms interacting in the free space has been presented in Refs. 16–26. As far as we know no paper has been concerned with the alteration of this polarizability of the pair by the presence of a neighboring interface. Let us now consider this effect.

As in the previous part the polarizability of the system can be obtained by differentiating the interaction energy ΔU [Eq. (10)] with respect to a fictitious external static field. The system being now a pair of molecules, two different processes are to be considered. The first one corresponds to the case when the static field is applied on each molecule [Fig. 3(a) or 3(b)]. We call the corresponding polarizability the polarizability of the pair and we note it $\alpha^{\mathrm{surf}}_{AB}$. The second one corresponds to the case when the static field acts two times on the same molecule A. We call it the polarizability of the molecule A in the presence of its neighbor B and we note it $\alpha^{\mathrm{surf}}_{A\leftarrow B}$. In this section we only calculate the first of these processes.

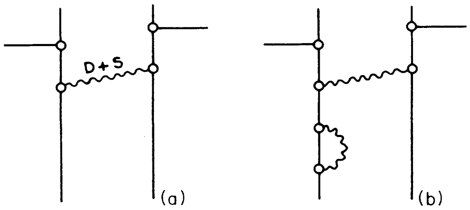

FIG. 3. Graphs illustrating the intrinsic polarizability of the pair: the static field acts on each atom (or molecule). The lowest order in power of e^2 is given by (a), the following one by (b).

A. Calculation in the lowest order in powers of e^2

In the lowest order this process can be illustrated by Fig. 3(a) (and all other graphs obtained by permuting vertices). It is important to underline that in Fig. 3(a) the static field (horizontal lines) is applied on the atom A *and* on the atom B. This clearly defines the polarizability α_{AB} of the pair. The wavy line in Fig. 3 corresponds to the propagator of the field which can be separated into two parts: a direct part (D) will lead to the "intrinsic" polarizability α^0_{AB} of the pair (that is to say its polarizability in the absence of surface); a surface part (S) will lead to the correction α^S_{AB} of this pair polarizability due to the presence of the neighboring surface.

In order to calculate ΔU we proceed as explained in Refs. 27 and 50. The essential feature in these calculations is that when integrating on all possible electromagnetic modes $(\mathbf{k},\omega)$ exchanged between A and B only the zero-frequency one contributes to ΔU. Let us note that because of this the propagator given in Eq. (6) and consequently all results obtained in this case are valid not only in the near zone but in the whole space. The static polarizability of the pair thus varies as R^{-3} whatever the distance R between A and B may be.

Making use of this remark calculation becomes straightforward and we obtain

$$\Delta U=-\sum_{i,j,\alpha,\beta}[\alpha^0_A(0)]_{i\alpha}g^T_{\alpha\beta}(0,R_A,R_B)\times[\alpha^0_B(0)]_{\beta j}E_iE_j\ . \tag{21}$$

This result was expected since it corresponds to the direct algebraic transcription of Fig. 3(a); the two vertical lines with their two dipole vertices (○) represent the polarizabilities α_A and α_B of each atom (as in Fig. 1). The two horizontal lines correspond to the static fields E_i and E_j (as in Figs. 1 and 2). The wavy line reduced to its only zero frequency as explained above is the term g^T.

By using Eqs. (21) and (10) we obtain the polarizability ($\alpha^{\mathrm{surf}}_{AB}$) of the pair in the vicinity of the surface; as expected this polarizability is the sum of a free space contribution α^0_{AB} and of a surface one α^S_{AB},

$$(\alpha_{AB}^{\mathrm{surf}})_{ij}=(\alpha_{AB}^{0})_{ij}+(\alpha_{AB}^{S})_{ij} \tag{22}$$

with

$$(\alpha_{AB}^{0})_{ij}=\sum_{\alpha,\beta}(\alpha_{Ai\alpha}^{0}\alpha_{B\beta j}^{0}+\alpha_{Aj\alpha}^{0}\alpha_{B\beta i}^{0})g_{\alpha\beta}^{0}(0,R_A,R_B)\ , \tag{23}$$

$$(\alpha_{AB}^{S})_{ij}=\sum_{\alpha,\beta}(\alpha_{Ai\alpha}^{0}\alpha_{B\beta j}^{0}+\alpha_{Aj\alpha}^{0}\alpha_{B\beta i}^{0})\theta_{\alpha}g_{\alpha\beta}^{S}(0,R_A,R_B)\Delta(0)\ . \tag{24}$$

For spherical systems, summations over α and β can be carried out by using $\alpha_{ij}=\alpha_{ii}\delta_{ij}$. We thus obtain

$$(\alpha_{AB}^{\mathrm{surf}})_{ij}=[\alpha_A^0(0)]_{ii}[\alpha_B^0(0)]_{jj}\times[2g_{ij}^0(0)+(\theta_i+\theta_j)\Delta(0)g_{ij}^S(0)]\ . \tag{25}$$

Let us note that in this above relation, indices ii and jj could have been omitted in α_A and α_B. We have, however, conserved them to simplify further remarks.

In the particular case when the two atoms are located at the same distance d from the surface we have [noting $\mathbf{R}=(R,0,0)$ and $\tilde{\mathbf{R}}\equiv(R,0,2d)$]

$$(\alpha_{AB}^{\mathrm{surf}})_{xx}=\frac{4\alpha_A(0)\alpha_B(0)}{R^3}-2\alpha_A(0)\alpha_B(0)\Delta(0)\frac{2R^2-4d^2}{(R^2+4d^2)^{5/2}}\ , \tag{26}$$

$$(\alpha_{AB}^{\mathrm{surf}})_{yy}=-\frac{2\alpha_A(0)\alpha_B(0)}{R^3}+2\alpha_A(0)\alpha_B(0)\Delta(0)\frac{1}{(R^2+4d^2)^{3/2}}\ , \tag{27}$$

$$(\alpha_{AB}^{\mathrm{surf}})_{zz}=-\frac{2\alpha_A(0)\alpha_B(0)}{R^3}+2\alpha_A(0)\alpha_B(0)\Delta(0)\frac{8d^2-R^2}{(R^2+4d^2)^{5/2}}\ . \tag{28}$$

These results represent the polarizability of the pair. As noted in other processes (for example, Refs. 11 and 30) it is to be emphasized that, since the interaction between A and B is only mediated by the zero-frequency mode, the propagators g^0 and g^S reduce to their static term (6) not only in the short range but in the all half space. In other words, above results are never retarded, and are valid for any separation R, d between A and B or between A (B) and the surface (provided A and B are at the same distance d from the medium). The first term in Eqs. (26)—(28) corresponds to the direct interaction between the two atoms. It represents the well-known polarizability α_{AB}^0 of the pair in the free space previously studied in Refs. 15—25. To it, our present calculation, however, brings a new precision since it shows that it is valid in the entire half space. The second term α_{AB}^S in Eqs. (26)—(28) shows the alteration of the polarizability of the pair by the neighboring surface. It can be useful to evaluate this correction; in the particular case of two adatoms in contact both with each other and with a metallic surface ($R=2d=2r_0$, r_0 being the radius of the adatom) we obtain, by using Eqs. (26) and (28),

$$\begin{aligned}(\alpha_{AB}^{\mathrm{surf}})_{xx}&=0.91(\alpha_{AB}^0)_{xx}\ ,\\ (\alpha_{AB}^{\mathrm{surf}})_{yy}&=0.65(\alpha_{AB}^0)_{yy}\ ,\\ (\alpha_{AB}^{\mathrm{surf}})_{zz}&=0.83(\alpha_{AB}^0)_{zz}\ .\end{aligned} \tag{29}$$

The relative alteration of the polarizability of the pair in the presence of the interface is then (we note $\delta\alpha_{AB}=\alpha_{AB}^{\mathrm{surf}}-\alpha_{AB}^0=\alpha_{AB}^S$).

$$\begin{aligned}\frac{\delta(\alpha_{AB})_{xx}}{(\alpha_{AB}^0)_{xx}}&=-0.09\ ,\\ \frac{\delta(\alpha_{AB})_{yy}}{(\alpha_{AB}^0)_{yy}}&=-0.35\ ,\\ \frac{\delta(\alpha_{AB})_{zz}}{(\alpha_{AB}^0)_{zz}}&=-0.17\ .\end{aligned} \tag{30}$$

As emphasized above, this result is valid whatever may be the model chosen for describing the metal in the local limit [$\Delta(0)=1$].

B. Next term in the expansion of $\alpha_{AB}^{\mathrm{surf}}$

In Sec. V we will calculate the alteration of the intrinsic polarizability of one atom in the presence of the surface and of the neighboring atom. This effect will correspond to a term in e^6. To be coherent with Sec. V we have thus to calculate $\alpha_{AB}^{\mathrm{surf}}$ to the same order. This term can be illustrated by Fig. 3(b) in which now appear six dipolar vertices (e^6). As in the above case the essential feature when integrating on all possible electromagnetic modes $(\mathbf{k},\omega)$ exchanged between A and B is that only the static one $(\mathbf{k}=\mathbf{0})$ contributes to ΔU. This simplifies calculation, which becomes very direct. We find

$$\Delta U=-\frac{\hbar}{4\pi}(1+\mathscr{P}_{AB})\times\sum_{i,j,\alpha,\beta}\left[\sum_{k,l}\int_{-\infty}^{+\infty}du\,\chi_{i\alpha kl}^{G,A}(iu)g_{k,l}^{T}(iu)\right]\times g_{\alpha\beta}^{T}(0)\alpha_{Bj\beta}^{0}E_iE_j\ , \tag{31}$$

where $\mathscr{P}_{AB}$ permutes the indices A and B. In this expression $\chi_{i\alpha kl}^{G}(iu)$ is defined in Eq. (13). As explained above it contains both dispersive and inductive effects.

We can identify in Eq. (31) the expression found in Eq. (14) for the surface polarizability α_A^S of atom A. This was expected since the graph in Fig. 2 appears to be a part of the one of Fig. 3(b). Because of this, we can write

$$\Delta U=-(1+\mathscr{P}_{AB})\sum_{i,j,\alpha,\beta}\alpha_{Ai\alpha}^{S}g_{\alpha\beta}^{T}(0,R_A,R_B)\alpha_{B\beta j}^{0}E_iE_j\ . \tag{32}$$

In general cases this leads to results similar to Eqs. (22)–(24). We directly consider the case of isotropic systems. Noting that because of Eqs. (18) and (19) we may write

$$(\alpha_A^S)_{ij}=(\alpha_A^S)_{ii}\delta_{ij}\ . \qquad (33)$$

We obtain

$$(\alpha_{AB}^{\text{surf}})_{ij}=(1+\mathscr{P}_{AB})\alpha_{Aii}^S\alpha_{Bjj}^0 \times[2g_{ij}^0(0)+(\theta_i+\theta_j)g_{ij}^S(0)\Delta(0)]\ . \qquad (34)$$

This result is valid whatever may be the position of atoms A and B near the medium. In the particular case when they are at the same distance d from the surface, we obtain, by using Eqs. (18) and (19),

$$(\alpha_{AB}^{\text{surf}})_{xx}=2\alpha_B(0)\left[\frac{\alpha_A^2(0)\Delta(0)}{8d^3}+\frac{\hbar}{4\pi}\frac{1}{8d^3}\int_{-\infty}^{+\infty}du[\gamma_{xxxx}(0,-iu,iu)+3\gamma_{xxzz}(0,-iu,iu)]\Delta(iu)\right] \times\left[\frac{2}{R^3}-\Delta(0)\frac{2R^2-4d^2}{(R^2+4d^2)^{5/2}}\right](1+\mathscr{P}_{AB})\ , \qquad (35)$$

$$(\alpha_{AB}^{\text{surf}})_{yy}=2\alpha_B(0)\left[\frac{\alpha_A^2(0)\Delta(0)}{8d^3}+\frac{\hbar}{4\pi}\frac{1}{8d^3}\int_{-\infty}^{+\infty}du[\gamma_{xxxx}(0,-iu,iu)+3\gamma_{xxzz}(0,-iu,iu)]\Delta(iu)\right] \times\left[-\frac{1}{R^3}+\Delta(0)\frac{1}{(R^2+4d^2)^{3/2}}\right](1+\mathscr{P}_{AB})\ , \qquad (36)$$

$$(\alpha_{AB}^{\text{surf}})_{zz}=2\alpha_B(0)\left[\frac{\alpha_A^2(0)\Delta(0)}{4d^3}+\frac{\hbar}{4\pi}\frac{1}{8d^3}\int_{-\infty}^{+\infty}du\,[2\gamma_{xxxx}(0,iu,-iu)+2\gamma_{xxzz}(0,iu,-iu)]\Delta(iu)\right] \times\left[-\frac{1}{R^3}+\Delta(0)\frac{8d^2-R^2}{(R^2+4d^2)^{5/2}}\right](1+\mathscr{P}_{AB})\ . \qquad (37)$$

C. General expression for $\alpha_{AB}^{\text{surf}}$

The total expression for the polarizability of a pair of interacting atoms in the presence of the surface is obtained by summing results (25) and (34) [or, equivalently, by summing Eqs. (26), (27), and (28) and (35), (36), and (37)].

In all these above results, we choose to separate on the one hand the free-space contribution α_{AB}^0 and the surface contribution α_{AB}^S of the pair polarizability and, on the other hand, dispersive and inductive effects. This was done in order to present our results in the form usually used in surface physics.

However, we want now to point out that it is possible to write all these results in a single compact form. Equations (21) and (32) can in fact be unified by using Eq. (20). We obtain

$$\Delta U^{\text{tot}}=-\sum_{i,j,\alpha,\beta}(\alpha_A^{\text{surf}})_{i\alpha}g_{\alpha\beta}^T(0,R_A,R_B) \times(\alpha_B^{\text{surf}})_{\beta j}E_iE_j\ . \qquad (38)$$

Results (25) and (34) can also be unified in the same way,

$$(\alpha_{AB}^{\text{surf}})_{ij}=(\alpha_A^{\text{surf}})_{ii}(\alpha_B^{\text{surf}})_{jj} \times[2g_{ij}^0(0)+(\theta_i+\theta_j)\Delta(0)g_{ij}^S(0)]\ . \qquad (39)$$

This above expression corresponds to the interaction between two atoms "dressed" by surface modes (the free polarizability α^0 of each one being changed into α^{surf}).

V. POLARIZABILITY OF ONE ATOM IN THE PRESENCE OF A SURFACE AND OF A NEIGHBORING ATOM

As explained above the polarizability of a given system, which can be obtained from its interaction energy when an external static field is applied, is the sum of two different processes. The first one corresponds to the case when this field is applied on the total pair, that is to say on *each* atom. The second one, which we call the polarizability of one atom in the presence of the other, similarly corresponds to the case when the field acts *on the same given* atom. This process can be illustrated by the diagram in Fig. 4. It corresponds to corrections of higher order (e^6) to calculations given in Sec. III and describes

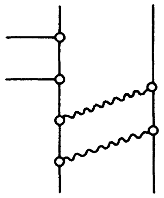

FIG. 4. Polarizability of one atom in the presence of another one. The static field acts on only *one* atom. The field propagator (illustrated by wavy lines) contains at the same time a "free" and a "surface" part.

contributions due to the presence of other molecules to the leading term (11) of the polarizability. On this diagram, the interaction between A and B is represented in the lowest order by the two propagators between A and B. Recalling that these latter have a direct (D) and a surface term (S) we can foresee that three different processes will appear which can be labeled by DD, DS (SD), and SS. The first one, in which the surface does not appear, will represent the alteration of the intrinsic polarizability of atom A by the presence of the only atom B (when no surface is present); it will be noted $\alpha^0_{A\leftarrow B}$. The energy shift of the system can be obtained by associating to each part of the diagram in Fig. 4 its algebraic expression as explained in Refs. 27 and 50. This immediately gives

$$\Delta U=\frac{i\hbar}{4\pi}\sum_{i,j,k,l}\sum_{\alpha,\beta}\int_{-\infty}^{+\infty}d\omega\,\chi^{G,A}_{ijkl}(\omega)\alpha^B_{\alpha\beta}(\omega)\times g^T_{k\alpha}(\omega,R_{AB})g^T_{l\beta}(\omega,R_{AB})E_iE_j\ , \tag{40}$$

where χ^G is given in Eq. (13) and where $\alpha^B(\omega)$ is the dynamical polarizability of B,

$$\alpha_{ij}(\omega)=e^2\sum_e\left[\frac{\langle f\,|\,r_j\,|\,e\rangle\langle e\,|\,r_i\,|\,f\rangle}{E_e-E_f-\hbar\omega}+\frac{\langle f\,|\,r_j\,|\,e\rangle\langle e\,|\,r_i\,|\,f\rangle}{E_e-E_f+\hbar\omega}\right]. \tag{41}$$

By using Eq. (1), Eq. (40) leads to the following polarizability of A in the presence of B and of the surface [we use Eqs. (7) and (8)]:

$$(\alpha^{\rm surf}_{A\leftarrow B})_{ij}=-\frac{i\hbar}{4\pi}\sum_{k,l,\alpha,\beta}\int_{-\infty}^{+\infty}d\omega\,\chi^{G,A}_{ijkl}(\omega)\alpha^B_{\alpha\beta}(\omega)\times g^T_{\alpha k}(\omega,R_{BA})g^T_{\beta l}(\omega,R_{BA})\ . \tag{42}$$

Calculation of g^Tg^T will give the different processes altering the intrinsic polarizability α_A of atom A. Using Eq. (3) it is clear that

$$g^T_{\alpha k}(R_{BA})g^T_{\beta l}(R_{BA})=g^0_{\alpha k}(R_{BA})g^0_{\beta l}(R_{BA})+\Delta(iu)[\theta_\alpha g^S_{\alpha k}(R_{BA})g^0_{\beta l}(R_{BA})+\theta_\beta g^0_{\alpha k}(R_{BA})g^S_{\beta l}(R_{BA})]+\Delta^2(iu)\theta_\alpha\theta_\beta g^S_{\alpha k}(R_{BA})g^S_{\beta l}(R_{BA})\ . \tag{43}$$

The first of these terms corresponds to the direct interaction (DD) between A and B, the second one corresponds to the case where the two atoms interact at the same time both directly and by the mediation of the surface (DS and SD). The last one corresponds to interaction completely mediated by the surface (SS). The use of Eq. (43) in Eq. (42) gives the polarizability in a quite general case. We only make this result explicit in the case of two spherical systems located at the same distance d from the surface.

Noting

$$h^s_1(iu)=\frac{4}{R^6}-\frac{4\Delta(iu)}{R^3\tilde R^3}\left[\frac{2R^2-4d^2}{\tilde R^2}\right]+\frac{\Delta^2(iu)}{\tilde R^6}\,\frac{4R^2+4d^2}{\tilde R^2}\ , \tag{44}$$

$$h^s_2(iu)=\frac{1}{R^6}-\frac{2\Delta(iu)}{R^3\tilde R^3}+\frac{\Delta^2(iu)}{\tilde R^6}\ , \tag{45}$$

$$h^s_3(iu)=\frac{1}{R^6}-\frac{2\Delta(iu)}{R^3\tilde R^3}\left[\frac{8d^2-R^2}{\tilde R^2}\right]+\frac{\Delta^2(iu)}{\tilde R^6}\,\frac{R^2+16d^2}{\tilde R^2}\ , \tag{46}$$

$$h^s_4(iu)=\frac{6Rd}{\tilde R^5}\left[\frac{3\Delta(iu)}{R^3}-\frac{\Delta^2(iu)}{\tilde R^3}\right], \tag{47}$$

we obtain in this case

$$(\alpha^{\rm surf}_{A\leftarrow B})_{ij}=\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\,\alpha_A(iu)\{h^s_1(iu)\chi^{G,A}_{ijxx}(iu)+h^s_2(iu)\chi^{G,A}_{ijyy}(iu)+h^s_3(iu)\chi^{G,A}_{ijzz}(iu)+h^s_4(iu)[\chi^{G,A}_{ijzx}(iu)+\chi^{G,A}_{ijxz}(iu)]\}\ . \tag{48}$$

Let us recall that the hyperpolarizability χ^G contains both the dispersive and the inductive part of the process. Using Eq. (15) we can separate these two parts,

$$(\alpha^{\rm surf}_{A\leftarrow B})_{xx}=\alpha^2_A\alpha_Bh^s_1(0)+\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\,\alpha_B(iu)\{\gamma_{xxxx}(0,-iu,iu)h^s_1(iu)+\gamma_{xxyy}(0,-iu,iu)[h^s_2(iu)+h^s_3(iu)]\}\ , \tag{49}$$

$$(\alpha^{\rm surf}_{A\leftarrow B})_{yy}=\alpha^2_A\alpha_Bh^s_2(0)+\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\,\alpha_B(iu)\{\gamma_{xxxx}(0,-iu,iu)h^s_2(iu)+\gamma_{xxyy}(0,-iu,iu)[h^s_3(iu+h^s_1(iu)]\}\ , \tag{50}$$

$$(\alpha^{\rm surf}_{A\leftarrow B})_{zz}=\alpha^2_A\alpha_Bh^s_3(0)+\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty}du\,\alpha_B(iu)\{\gamma_{xxxx}(0,-iu,iu)h^s_3(iu)+\gamma_{xxyy}(0,-iu,iu)[h^s_1(iu)+h^s_2(iu)]\}\ , \tag{51}$$

$$(\alpha^{\text{surf}}_{A\leftarrow B})_{xz}=(\alpha^{\text{surf}}_{A\leftarrow B})_{zx}=\alpha_A^2\alpha_B h_4^s(0)+\frac{\hbar}{4\pi}\int_{-\infty}^{+\infty} du\,\alpha_B(iu)[\gamma_{xzzx}(0,-iu,iu)+\gamma_{xzxz}(0,-iu,iu)]h_4^s(iu)\ . \tag{52}$$

Let us emphasize in these above results the appearance of the two components α_{xz} and α_{zx} of the polarizability which are zero when no surface is present. In the case of two identical atoms ($A\equiv B$) the summation of these terms for $\alpha_{A\leftarrow B}$ and $\alpha_{B\leftarrow A}$ will, of course, give zero.

When calculating the total polarizability of the pair, we have to consider (among other terms) the sum

$$(\alpha^{\text{surf}})_{ij}=(\alpha^{\text{surf}}_{A\leftarrow B})_{ij}+(\alpha^{\text{surf}}_{B\leftarrow A})_{ij}\ . \tag{53}$$

Because of the multiplicative factor $\theta_\alpha\theta_\beta$ in the last term of Eq. (43) we obtain

$$(\alpha^{\text{surf}})_{xz}=(\alpha^{\text{surf}}_{A\leftarrow B})_{xz}-(\alpha^{\text{surf}}_{B\leftarrow A})_{xz}\ . \tag{54}$$

This result will give zero in the particular case of two identical atoms. In other cases, it will correspond to a new induced surface part of the pair polarizability.

As a limit case of our results, it can be interesting to consider two interacting atoms in the free space (that is to say, when no surface is present). Making then $d\rightarrow\infty$ in Eqs. (44)–(47) and introducing these limit values of $h_i^s(iu)$ into Eqs. (49)–(52) we obtain

$$(\alpha_{A\leftarrow B})_{xx}=4\frac{\alpha_A^2\alpha_B}{R^6}+\frac{\hbar}{4\pi}\frac{1}{R^6}\int_{-\infty}^{+\infty} du\,\alpha_B(iu)[4\gamma_{xxxx}(0,-iu,iu)+2\gamma_{xxyy}(0,-iu,iu)]\ , \tag{55}$$

$$(\alpha_{A\leftarrow B})_{yy}=(\alpha_{A\leftarrow B})_{zz}=\frac{\alpha_A^2\alpha_B}{R^6}+\frac{\hbar}{4\pi}\frac{1}{R^6}\int_{-\infty}^{+\infty} du\,\alpha_B(iu)[5\gamma_{xxyy}(0,-iu,iu)+\gamma_{xxxx}(0,-iu,iu)]\ . \tag{56}$$

These two results correspond to the ones of Hunt *et al.*[24] The first term gives the contribution from classical dipolar coupling. The second term corresponds to the modification of the intrinsic polarizability of A associated with dispersion forces.

We have to emphasize that we would have to take twice these results in calculating the total polarizability of A and B. As shown in Ref. 24 these above results are identical to the quantum-mechanical sum-over-states expressions for the coefficients $A_{\parallel}^6$ and $A_{\perp}^6$ given by Jansen and Mazur,[18] Certain and Fortune,[20] and Buckingham, Martin, and Watts.[21]

As a last remark, let us note that these different terms can be evaluated and compared with the polarizability of the same pair in the absence of the surface given in Eqs. (53) and (54). For two adatoms in contact with each other and with a metallic surface we obtain, noting $h_i^0(R)$, the corresponding value of $h_i(R)$ in the case of two colliding atoms in vacuum,

$$\begin{aligned} &h_1^s(R)=3.60/R^6,\quad h_1^0(R)=4/R^6\ ,\\ &h_2^s(R)=0.42/R^6,\quad h_2^0(R)=1/R^6\ ,\\ &h_3^s(R)=0.95/R^6,\quad h_3^0(R)=1/R^6\ ,\\ &h_4^s(R)=1.40/R^6,\quad h_4^0(R)=0\ . \end{aligned} \tag{57}$$

VI. FINAL REMARKS

All these results are valid in the quasistatic limit when the medium can be described by a local dielectric function $\epsilon(\omega)$. In Sec. II, we have presented a way to extend the formalism in the more general case of a nonlocal response of the medium. One of us recently studied such effects[52] (forces, dipolar moment, polarizability, and nonlinear effects).

Now let us come back to some important remarks. The first one deals with the use of the hyperpolarizability (13). As explained above, our *ab initio* calculation shows that the hyperpolarizability which directly appears takes into account at the same time the classical inductive terms and the dispersive ones associated with van der Waals forces. This opens a direct route to calculate surface effects. Studying them separately as is usually done is in fact not necessary since these two processes cannot be experimentally separated. Let us add that, in other treatments for interaction between light and matter near the surface, the use of hyperpolarizabilities (because they are usually phenomenologically introduced in calculations) has never been discussed.

Some other remarks should also be made. For com-

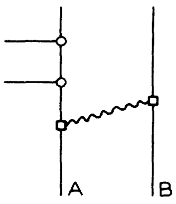

FIG. 5. Quadrupolar term of the polarizability.

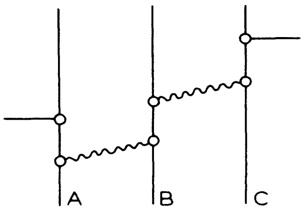

FIG. 6. Three-body terms in calculation of the polarizability.

pleteness, it should be noted that other processes should be taken into account in more general cases. For example, when the two interacting units are molecules with a center of symmetry but with permanent quadrupole moments (for example, nitrogen, hydrogen, carbon dioxide, etc.) diagrams such as the one of Fig. 5 would also have to be taken into account and would lead to a term varying as R^{-5}.

Our last remark concerns cooperative effects between three adatoms. In the lowest order in e^6, such effects can be illustrated by Fig. 6. Limiting ourselves to pairwise contributions we have not considered this process. It is, however, to be emphasized that the diagram in Fig. 6 leads to terms which contribute to α in the same order of magnitude. Such terms can, of course, be neglected in the free space since the probability of the collision of three atoms (or molecules) is negligible. It is no larger the case on a surface when coverage becomes important since the position of adsorbed systems is then fixed. Such a situation can greatly affect the polarizability α^{surf}. A similar effect exists for the permanent dipolar moment of three identical atoms.[53-56]

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