Quantum size and nonlocal effects in the electromagnetic properties of small metallic spheres

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The electromagnetic properties of small spheres are analyzed by including quantum size effects and nonlocal properties of the response function. Our model neglects the diffuseness of the surface electron charge but includes effects associated with the surface roughness, which is assumed to randomize the electrons scattering off the surface. Quantum size and roughness effects are discussed and we analyze under what specific conditions they can appear.

I. INTRODUCTION

The electromagnetic properties of inhomogeneous systems is a fashionable topic. Thus, the response of a metallic inhomogeneous surface has been the subject of many different publications.[1–4] In this case, the role of the change in the metal electron density across the surface on the optical reflectivity and the surface photoeffect,[2,5] as well as the effect of the surface roughness on the electromagnetic properties[4,6] of the sample have received a great attention. Similarly, a lot of work has been done on films[7,8] by considering the effect of interference between the em waves reflected from the two planar surfaces. A new effect may appear for very thin films: this is related to the quantization of the electronic wave functions in the direction perpendicular to the surface. A theoretical analysis[9] based on a random-phase-approximation method shows that a new structure may appear in the optical absorption of the film due to the electronic levels quantization.

Recently, many different works have appeared on the optical properties of small spheres. This has been partly promoted by the good control achieved in the preparation of samples with uniform size. Very small particles, around 20 Å in size, present, like thin films, the specific effects associated with the quantization of the electronic levels inside the sample.[10–13] Most of the work on small spheres have been addressed, however, to understand the effect of the abrupt change in the electron density across the surface on their optical properties.[14–16] On small spheres, only Wood and Ashcroft,[17] and Gor'kov and Eliashberg,[10] up to our knowledge, have analyzed the effect of the discrete quantum levels on the optical properties of the sample. The interest of this analysis for spheres is related not only to the interpretation of photoyield experiments,[16] but to specific optical effects like the blue shift[17] in the absorption peak associated with the excitation of surface plasmons and the enhancement for the absorption energy in the far infrared.[10,17] Very recently, Ekardt[18] has calculated the dynamical polarizability of small spheres; this analysis, however, does not include the effects associated with the coupling between the electromagnetic field and different surface modes and, accordingly, some specific optical effects cannot be surmised from it.

In this paper, we present a calculation of the electromagnetic response of small spheres, by introducing the effect of the quantization of the electronic energy levels inside the sample. In our analysis, instead of using a dipole approximation in order to calculate the dielectric function inside the sphere,[17] we have attempted to include the electronic excitation up to any multipole order by introducing an appropriate k-dependent dielectric function. Our model neglects some specific effects related to the diffuseness of the surface-electron-charge,[18,19] effects that must appear in a complete self-consistent calculation,[18] and tries to focus on the important effects associated with the quantization of the electronic levels. For very small spheres these levels are very far apart in energy and we do not expect that surface roughness can introduce any important electron surface scattering modifying the results obtained for an ideal surface.[4,6] One output of our calculation for complete specular surfaces is the minimum radius of a metallic sphere for which the different electronic excitations start to overlap, allowing the electrons to scatter from one level to another. For greater radii, most sphere surfaces can be expected to behave with a high degree of roughness, and to modify accordingly the optical properties of the sphere. In this paper, we also present calculations for the case of a complete rough surface: a case for which electrons are assumed to scatter at random from the sphere surface.

In Sec. II we present the model and introduce the dielectric functions defining the sphere polarizability. In Sec. III we present the method used to calculate the optical properties of the sphere, and finally, in Sec. IV we present our results and their discussion.

II. THE MODEL

The model we follow to analyze the optical properties of the metallic sphere is equivalent to the semiclassical infinite-barrier (SCIB) model that people have been using for the planar surface.[1,4] In this model a step function is assumed for the metallic electron density, and the electronic polarizability is calculated by neglecting the interference quantum terms appearing near the surface. This approximation has been shown[20,21] to be more appropriate for calculating the optical properties at frequencies higher than the plasmon frequency; at lower frequencies, the optical properties seem to depend crucially on the smooth electronic profile existing at the interface.[22] These effects can be introduced[19] in an *ad hoc* way by means of two effective lengths associated with the variation of the electric field across that interface. For the purposes of the present paper, however, these effects are not so important[18] as we are more interested in analyzing (i) the quantum effects associated with the sphere size, and (ii) the effect of the surface roughness on the optical absorption.

Following the SCIB model we assume the sphere embedded in an infinite metallic medium (see Fig. 1), and calculate the electromagnetic field *inside* the sphere by introducing (i) external stimuli in the region $r>R$, and by defining (ii) a dielectric function $\epsilon(k,\omega)$ associated with the infinite metal.

As regards the external stimuli, we determine them by imposing certain conditions on the field *outside* the sphere. To be specific, consider the case of a surface with such strong roughness that it randomizes all the electrons coming from it. For this case, the induced dipole inside the sphere can be written as follows:[4]

$$\mathbf{P}(\mathbf{r})=\int_{r'<R}\boldsymbol{\chi}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{E}(\mathbf{r}')d\mathbf{r}' , \tag{1}$$

where $\boldsymbol{\chi}$ is the electronic polarizability of the metal, and the integral *only* extends to the region inside the sphere. Then, we can simulate Eq. (1) by means of the infinite extended medium *if* we impose on the electric field the following condition:

$$\mathbf{E}(\mathbf{r})=0 \quad \text{for } r>R . \tag{2}$$

From a physical point of view this means that the induced dipole at $\mathbf{r}$ is only due to direct effects between $\mathbf{r}$ and $\mathbf{r}'$ (see Fig. 1), with no contribution coming from trajectories reflecting specularly at the surface.

Equation (2) is the condition we have to impose on the field to simulate the polarizability of the sphere by an infinite metal, when we have a complete randomizing surface. Similar arguments can be given for a specular surface, but a complete discussion of this case will be deferred up to Sec. III.

As regards the dielectric function we introduce to analyze the optical properties of the sphere, assumed to be embedded in the infinite medium, we follow the work of Apell and Ahlqvist[9] for thin films. In this work, the dielectric response of a metal layer has been obtained within a random-phase approximation by including the electronic quantum levels associated with the direction perpendicular to the surface, and by approximating the surface response by a SCIB scheme. The important result coming out from this calculation is that the metal layer can be simulated by embedding it in an infinite medium *if* we introduce for this infinite system an adequate dielectric function which includes properly the quantum size effects. Accordingly, we assume that the sphere response is defined by a longitudinal, $\epsilon_L(k,\omega)$, and a transverse part, $\epsilon_T(k,\omega)$; as regards $\epsilon_T(k,\omega)$, in this paper we follow the usual simplification and take $\epsilon_T(k,\omega)=1-(\omega_p^2/\omega^2)\equiv\epsilon_T(\omega)$, while the quantum size effects are introduced in $\epsilon_L(k,\omega)$. At this point, we introduce a further simplification and follow Wood and Ashcroft[17] by assuming that $\epsilon_L(k,\omega)$ for the sphere is well approximated by the longitudinal dielectric function of an equivalent cube as *calculated along the direction of its principal axis.* This dielectric function can be straightforwardly calculated by using a SCIB model for a cube of side L (see Fig. 2). For this case, we follow the discussion given by Apell and Ahlqvist[9] for thin films, embed the cube in an infinite medium with appropriate symmetry conditions, and obtain the following result:

$$\epsilon_L(k,\omega)=1-A(k)\sum_i\frac{f_i(k)}{\omega^2-\omega_i^2(k)} , \tag{3}$$

where ω_i is the excitation energy defined by the initial state $\mathbf{k}_i$ of the quantized cube, and $\mathbf{k}$ is the momentum transfer along a principal axis: $\frac{1}{2}(\mathbf{k}_i+\mathbf{k})^2-\frac{1}{2}k_i^2$ (we use atomic units). $f(k)$ is the oscillator strength related to the number of initial states having the same excitation energy $\omega_i(k)$ (see Fig. 2). Note that $\mathbf{k}$ is taken along the principal axis of the cube, this being the reason for writing a scalar dependence on k for ω_i and A; moreover, $A(k)=\omega_p^2/\sum_i f_i$, in such a way that

$$\epsilon_L(k,\omega)\rightarrow 1-\frac{\omega_p^2}{\omega^2} \quad \text{as } \omega\rightarrow\infty .$$

For a cube and the SCIB model, the dielectronic function given by Eq. (3) is only defined for $k=(2\pi/L)m$ (m being an integer). In our approximation for the sphere, we extend *formally* Eq. (3) to any value of k such that the final state $\mathbf{k}_i+\mathbf{k}$ is above the Fermi level. For a spherical specular surface, this means that the final states are *quan-*

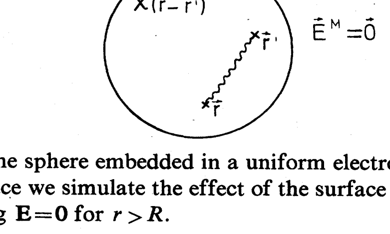

FIG. 1. The sphere embedded in a uniform electron gas. For a rough surface we simulate the effect of the surface on the electron by taking $\mathbf{E}=0$ for $r>R$.

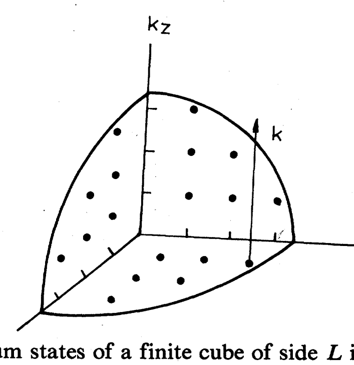

FIG. 2. Quantum states of a finite cube of side L in momentum space. k is the transfer of momentum associated with the dielectric function $\epsilon_L(k,\omega)$. States having the same initial z-component momentum have the same excitation energy $\omega_i(k)$.

tized according to the allowed values of k as determined by the conditions associated with the spherical symmetry [see Eq. (28)]. Quantum size effects appear in Eq. (3) through the number of zeros and poles for ϵ_L. Figure 3 shows the dispersion relation for the six zeros and six poles of a case for which $L = 15.3$ Å and $r_s = 4.86$. These results are similar to the ones found by Apell and Ahlqvist[9] for a thin film; it is of interest to notice that the number of poles is related to N bare electron-hole modes, while the zeros give the plasmon and $N-1$ dressed electron-hole pairs. The number of bare modes N changes with the cube size in such a way that for $L \to \infty$ there appear infinite bare modes and we recover the Lindhard dielectric function (see Ref. 9 for more details).

In the calculations presented in this paper for a nonspecular surface, it is convenient to use, instead of Eq. (3), a different dielectric function having a simpler dependence on k. To this end we have approximated Eq. (3) by the following expression:

$$\epsilon_L(k,\omega) = \frac{\omega^2 - \omega_p^2 - \beta^2 k^2 - \frac{1}{4}k^4}{\omega^2 - (\beta')^2 k^2 - \frac{1}{4}k^4} \prod_{i=1}^{N-1} \frac{\omega^2 - \gamma_i k^2 - \frac{1}{4}k^4}{\omega^2 - \gamma_i' k^2 - \frac{1}{4}k^4} , \tag{4}$$

where the number of poles is directly related to the bare electron-hole pairs, and the zeros to the plasmon dispersion relation $\omega^2 = \omega_p^2 + \beta^2 k^2 + \frac{1}{4}k^4$, and to the dressed electron-hole modes. Note that in all the modes of Eq. (4) we have included a term behaving as $\frac{1}{4}k^4$: this yields the correct limiting behavior, $\omega \to \frac{1}{2}k^2$, for ω and $k \to \infty$. On the other hand, in Eq. (4) we assume the coefficients β^2, $(\beta')^2$, γ_i, and γ_i' to be ω dependent; $(\beta')^2$, γ_i, and γ_i' have been adjusted to yielding, at each frequency, the same pairs modes (zeros and poles) as Eq. (3), while β^2 has been chosen to verify the following relation:

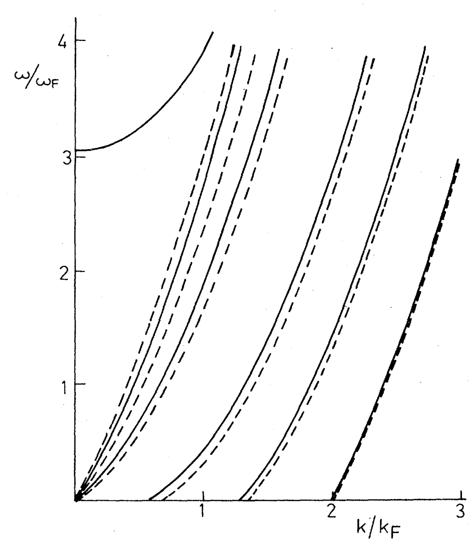

FIG. 3. Dispersion relation for the zeros (——) and poles (— — —) of $\epsilon_L(q,\omega)$ for a cube of side $L = 15.3$ Å and $r_s = 4.86$. ω and k are given in units of ω_F and k_F, respectively [$k_F = n_F(\pi/L)$ and $\omega_F = \frac{1}{2}k_F^2$; in the case shown, $n_F = 3$].

$$\beta^2 + \sum_{i=1}^{N-1} \gamma_i = (\beta')^2 + \sum_{i=1}^{N-1} \gamma_i' , \tag{5}$$

this ensures that the f-sum rule is automatically satisfied.

The dielectric function given by Eq. (3) will be used to analyze small-size spheres, a case for which we can assume that electrons in the metal scatter off specularly at the surface. Equation (4) will be used, however, to analyze the effect of a strong roughness that randomizes electrons at the surface on the optical properties of the sphere.

III. THE THEORY

In our method of calculation we follow Penn and Rendell[16] and develop the electric field in the extended metallic medium in a set of basis states, $\mathbf{l}_i$, $\mathbf{m}_i$, and $\mathbf{n}_i$, verifying the wave equation:

$$\nabla^2 \mathbf{C} + k^2 \mathbf{C} = 0 . \tag{6}$$

$\mathbf{l}_i$, $\mathbf{m}_i$, and $\mathbf{n}_i$ are the spherical vector functions[23]

$$\mathbf{l}_{ilm}(k,\mathbf{r}),\quad \mathbf{m}_{ilm}(k,\mathbf{r}),\quad \mathbf{n}_{ilm}(k,\mathbf{r}) ,\quad \text{with } i = e \text{ or } o$$

where the three modes are represented by their quantum numbers l and m, and by their parity (even or odd) with respect to the azimuthal angle variable (m takes only positive values).

We shall discuss the case of an em plane wave being diffracted by the metallic sphere. It is well known that the plane wave $\mathbf{E}(\mathbf{r}) = E_0 \exp(ik_0 z)\mathbf{x}$, where $k_0 = \omega/c$, with its polarization along x, can be written as follows:[23]

$$\mathbf{E}(\mathbf{r}) = \sum_{l=1}^{\infty} i^l \frac{2l+1}{l(l+1)} [\mathbf{m}_{ol1}(k_0,\mathbf{r}) - i\mathbf{n}_{el1}(k_0,\mathbf{r})] . \tag{7}$$

This equation suggests that only the modes with $m = 1$ must be considered in our problem. The functions $\mathbf{m}_{ol1}(k,\mathbf{r})$ and $\mathbf{n}_{el1}(k,\mathbf{r})$ are given by[23]

$$\mathbf{m}_{ol1}(k,\mathbf{r}) = j_l(kr)\frac{1}{\sin\theta}P_l^1(\cos\theta)(\cos\phi)\mathbf{i}_2 - j_l(kr)\frac{dP_l^1(\cos\theta)}{d\theta}(\sin\phi)\mathbf{i}_3 , \tag{8a}$$

$$\mathbf{n}_{el1}(k,\mathbf{r}) = \frac{l(l+1)}{kr} j_l(kr) P_l^1(\cos\theta)(\cos\phi)\mathbf{i}_1 + \frac{1}{kr}\frac{d}{dr}[rj_l(kr)]\frac{dP_l^1(\cos\theta)}{d\theta}(\cos\phi)\mathbf{i}_2 - \frac{1}{kr}\frac{d}{dr}[rj_l(kr)]P_l^1(\cos\theta)(\sin\phi)\mathbf{i}_3 , \tag{8b}$$

where j_l are the Bessel spherical functions, P_l^1 the usual Legendre functions, and $\mathbf{i}_1$, $\mathbf{i}_2$, and $\mathbf{i}_3$ the unit vectors associated with the spherical coordinates.

The refraction of the em plane wave at the sphere mixes the $\mathbf{n}_{el1}$ mode with the longitudinal mode $\mathbf{l}_{el1}$. This mode is given by[23]

$$\mathbf{l}_{el1}(k,\mathbf{r})=\frac{d}{dr}[j_l(kr)]P_l^1(\cos\theta)(\cos\phi)\mathbf{i}_1+\frac{j_l(kr)}{r}\frac{dP_l^1(\cos\theta)}{d\theta}(\cos\phi)\mathbf{i}_2-\frac{j_l(kr)}{r}P_l^1(\cos\theta)(\sin\phi)\mathbf{i}_3\ . \tag{8c}$$

In general, the field in the extended metallic medium can be written as a combination of the different modes $\mathbf{l}_{el1}$, $\mathbf{n}_{el1}$, and $\mathbf{m}_{ol1}$ as follows:

$$\mathbf{E}(\mathbf{r})=\sum_{l=1}^{\infty} i^l\frac{2l+1}{l(l+1)}\mathbf{E}_l(\mathbf{r})\ , \tag{9}$$

where

$$\mathbf{E}_l(\mathbf{r})=\int_0^\infty k^2[E_l^{(l)}(k)\mathbf{l}_{el1}(k,\mathbf{r})+E_l^{(n)}(k)\mathbf{n}_{el1}(k,\mathbf{r})+E_l^{(m)}(k)\mathbf{m}_{ol1}(k,\mathbf{r})]dk\ . \tag{10}$$

It is convenient to introduce, at this point, the functions $\phi_l(r)$, $E_l^{(n)}(r)$, and $E_l^{(m)}(r)$, which are defined by means of the following Bessel transform:

$$\phi_l(r)=\int_0^\infty k^2E_l^{(l)}(k)j_l(kr)dk\ , \tag{11a}$$

$$E_l^{(n)}(r)=\int_0^\infty k^2E_l^{(n)}(k)j_l(kr)dk\ , \tag{11b}$$

$$E_l^{(m)}(r)=\int_0^\infty k^2E_l^{(m)}(k)j_l(kr)dk\ . \tag{11c}$$

The factor $i^l[(2l+1)/l(l+1)]$ in Eq. (9) is introduced by convenience, while the coefficients $E_l^{(l)}(k)$, $E_l^{(n)}(k)$, and $E_l^{(m)}(k)$ [or $\phi_l(r)$, $E_l^{(n)}(r)$, and $E_l^{(m)}(r)$] measure the amplitude of the different modes being excited in the metallic medium. In order to determine completely the field inside the sphere we have to calculate those coefficients. This is accomplished by solving the wave equation and by imposing the adequate conditions on the field for $r>R$ (see Sec. II).

A. Rough surface

Let us first consider the case of complete nonspecular scattering at the sphere surface. According to the discussion of Sec. II, this means that we must take $\mathbf{E}=0$ for $r>R$ in the extended medium; this can be accomplished with adequate external stimuli at $r\geq R$. These stimuli, however, create a field inside the sphere $r<R$; we expect this field to be a combination of the different normal modes excited in the infinite metal and be defined by the following equations. For longitudinal modes,

$$\epsilon_L(L_i,\omega)=0\ , \tag{12a}$$

for transverse modes,

$$T_i^2-\frac{\omega^2}{c^2}\epsilon_T(T_i,\omega)=0\ . \tag{12b}$$

Equations (12a) and (12b) define the different longitudinal and transverse modes in the extended medium for a given frequency ω. Due to the local approximation we are using for ϵ_T, $\epsilon_T(\omega)=1-(\omega_p^2/\omega^2)$, Eq. (12b) only yields one solution for the transverse modes:

$$T^2=\frac{\omega^2}{c^2}\epsilon_T(\omega)\ . \tag{12c}$$

The field inside the sphere can be expected to be a combination of the normal modes associated with Eqs. (12). Since the normal modes are the eigenfunctions of the operator $-\nabla^2\equiv k^2$, we can write for the l component of that field:

$$\mathbf{E}_l(\mathbf{r})=\sum_{L_i}E_l^{(L_i)}\mathbf{l}_{el1}(L_i,\mathbf{r})+E_l^{(n)}\mathbf{n}_{el1}(T,\mathbf{r})+E_l^{(m)}\mathbf{m}_{ol1}(T,\mathbf{r}),\quad r<R \tag{13}$$

where $E_l^{(L_i)}$, $E_l^{(n)}$, and $E_l^{(m)}$ are constants to be determined later on.

On the other hand, we need to introduce a singular term in $\mathbf{E}$ at $r=R$.[4,8,16] The reason is that we have to impose a condition associated with the induced current at $r=R$, namely, the normal component of the current must be zero:

$$J_r(r=R)=0\ . \tag{14}$$

This condition can be achieved by introducing a singular stimulus at $r=R$, or equivalently, a singular field at the sphere surface. The l component of this singular term takes the following form:

$$\mathscr{D}_l\delta(r-R)P_l^1(\cos\theta)(\cos\phi)\mathbf{i}_1\ , \tag{15}$$

where $\mathscr{D}_l$ is a constant to be determined later on.

Putting together the different pieces of the field, we have the following expression in the extended metal medium:

$$\mathbf{E}_l(\mathbf{r})=\theta(R-r)\left[\sum_{L_i}E_l^{(L_i)}\mathbf{l}_{el1}(L_i,\mathbf{r})+E_l^{(n)}\mathbf{n}_{el1}(T,\mathbf{r})+E_l^{(m)}\mathbf{m}_{ol1}(T,\mathbf{r})\right]+\mathscr{D}_l\delta(r-R)P_l^1(\cos\theta)(\cos\phi)\mathbf{i}_1\equiv\mathbf{E}_l^R(\mathbf{r})+\mathbf{E}_l^S(\mathbf{r})\ , \tag{16}$$

where $\mathbf{E}_l^R$ and $\mathbf{E}_l^S$ are the regular and singular parts of $\mathbf{E}_l(\mathbf{r})$ ($\mathbf{E}_l^S$ is associated with $\mathscr{D}_l$).

It is convenient to express $\mathbf{E}_l(\mathbf{r})$ in the general form given by Eq. (10) and to look for the different coefficients appearing in that equation. Details of this calculation are given in the Appendix. Here we collect the main results; for the regular part of the field given by Eq. (16) we obtain the following result:

$$\phi_l^R(r)=\begin{cases}\sum_{L_i} E_l^{(L_i)} j_l(L_i r)-A^{<}(l+1)r^l, & r<R\\ A^{>}\dfrac{l}{r^{l+1}}, & r>R\end{cases} \tag{17a}$$

$$E_l^{R(n)}(r)=\begin{cases}E_l^{(n)}\dfrac{j_l(Tr)}{T}+A^{<}r^l, & r<R\\ A^{>}/r^{l+1}, & r>R\end{cases} \tag{17b}$$

$$E_l^{R(m)}(r)=\begin{cases}E_l^{(m)}j_l(Tr), & r<R\\ 0, & r>R\end{cases} \tag{17c}$$

where

$$A^{<}=\frac{R^{l+1}}{2l+1}\left[\sum_{L_i}E_l^{(L_i)}j_l(L_iR)+\frac{l+1}{T}E_l^{(n)}j_l(TR)\right], \tag{17d}$$

$$A^{>}=\frac{1}{(2l+1)R^l}\left[\sum_{L_i}E_l^{(L_i)}j_l(L_iR)-\frac{l}{T}E_l^{(n)}j_l(TR)\right], \tag{17e}$$

while the singular part associated with $\mathscr{D}_l$ is given by

$$E_l^{S(l)}(k)=\frac{2}{\pi}\frac{R^2}{k}\mathscr{D}_l j_l'(kR), \tag{18a}$$

$$E_l^{S(n)}(k)=\frac{2}{\pi}\frac{R}{k}\mathscr{D}_l j_l(kR), \tag{18b}$$

$$E_l^{S(m)}(k)=0, \tag{18c}$$

j_l' being $(d/dx)[j_l(x)]$.

The different constants $E_l^{(L_i)}$, $E_l^{(n)}$, $E_l^{(m)}$, and $\mathscr{D}_l$ appearing in the total field are not independent. Indeed, they have to verify certain relations that can be determined by analyzing the field equation:

$$\nabla\times(\nabla\times\mathbf{E})-\frac{\omega^2}{c^2}\mathbf{E}=4\pi\omega^2\mathbf{P}/c^2, \tag{19}$$

where $\mathbf{P}$ is the polarization field in the metal. Equation (19) only holds for $r<R$; for $r>R$, external currents must be included in the right-hand side. The l components of $\mathbf{P}$ for $r<R$ can be obtained from the general equation

$$4\pi\mathbf{P}_l(\mathbf{r})=\int[\underline{\boldsymbol{\epsilon}}(\mathbf{r}-\mathbf{r}',\omega)-\underline{\mathbf{I}}\delta(\mathbf{r}-\mathbf{r}')]\cdot\mathbf{E}_l(\mathbf{r}')d\mathbf{r}', \tag{20}$$

where $\underline{\boldsymbol{\epsilon}}$ is a tensor having longitudinal and transverse components and $\underline{\mathbf{I}}$ is the unit tensor. Equation (20) can be easily worked out if we use for the field the general expression (10), since we have the following relations:[16]

$$\int\underline{\boldsymbol{\epsilon}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{l}_{el1}(k,\mathbf{r}')d\mathbf{r}'=\epsilon_L(k,\omega)\mathbf{l}_{el1}(k,\mathbf{r}), \tag{21a}$$

$$\int\underline{\boldsymbol{\epsilon}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{m}_{ol1}(k,\mathbf{r}')d\mathbf{r}'=\epsilon_T(k,\omega)\mathbf{m}_{ol1}(k,\mathbf{r}), \tag{21b}$$

and

$$\int\underline{\boldsymbol{\epsilon}}(\mathbf{r}-\mathbf{r}')\cdot\mathbf{n}_{el1}(k,\mathbf{r}')d\mathbf{r}'=\epsilon_T(k,\omega)\mathbf{n}_{el1}(k,\mathbf{r}). \tag{21c}$$

Substituting Eqs. (17), (18), and (21) into Eq. (20), we obtain the following even part of $\mathbf{P}_l(\mathbf{r})$:

$$\begin{aligned}4\pi\mathbf{P}_{e,l}(\mathbf{r})\cdot\mathbf{i}_1&\equiv4\pi P_{e,l}(r)P_l^1(\cos\theta)\cos\phi\\&=P_l^1(\cos\theta)(\cos\phi)\frac{2}{\pi}\\&\quad\times\left[\int_0^\infty k^3[\epsilon_L(k,\omega)-1]j_l'(kr)dk\int_0^\infty(r')^2j_l(kr')\phi_l(r')dr'+[\epsilon_T(\omega)-1]\frac{l(l+1)}{r}E_l^{(n)}(r)\right.\\&\quad\left.+\mathscr{D}_l\left[\int_0^\infty k^2[\epsilon_L(k,\omega)-1]R^2j_l'(kR)j_l'(kr)dk+[\epsilon_T(\omega)-1]\frac{\pi}{2}\frac{l(l+1)}{2l+1}\frac{r^{l-1}}{R^l}\right]\right].\end{aligned} \tag{22}$$

There is also an odd part for $\mathbf{P}_l(\mathbf{r})$, $\mathbf{P}_{o,l}$. As it leads to no relevant result, it is not given here.

Let us now assume that $\epsilon_L(k,\omega)$ is given by Eq. (4). For this case, the dielectric function takes the following form:

$$\epsilon_L(k,\omega)=\prod_{i=1}^{2N}(k^2-L_i^2)\Big/\prod_{i=1}^{2N}(k^2-l_i^2). \tag{23}$$

From Eqs. (22) and (23) we get the following result:

$$4\pi P_{e,l}(r) = -\sum_{i=1}^{2N} E_l^{(L_i)} L_i j_l'(L_i r) + (\epsilon_T(\omega)-1) E_l^{(n)} \frac{l(l+1)}{Tr} j_l(Tr) + i \sum_{i=1}^{2N} l_i j_l'(l_i r) \frac{\prod_{j=1}^{2N}(l_i^2 - L_j^2)}{\prod_{j\neq i}^{2N}(l_i^2 - l_j^2)} \left[\sum_{j=1}^{2N} E_l^{(L_j)} \frac{L_j}{L_j^2 - l_i^2} [L_j j_l(L_j R) h_l'(l_i R) - l_i j_l'(L_j R) h_l(l_i R)] + E_l^{(n)} \frac{l(l+1)}{TR} j_l(TR) \frac{h_l(l_i R)}{l_i} + \mathscr{D}_l h_l'(l_i R) \right], \tag{24}$$

where h_l is the spherical Bessel function $j_l + i n_l$. Equation (24) gives for $P_{e,l}(r)$ several pieces. (i) The first two terms represent the polarization associated with the even modes $\mathbf{l}_{el1}$ and $\mathbf{n}_{el1}$. When Eqs. (24) and (16) are substituted into Eq. (19), these two terms lead to identities, related to the fact that the field is correctly constructed and satisfies the field equation. (ii) The other terms of Eq. (24) do not have equivalent terms coming from the field in Eq. (16). They must vanish, giving the following $2N$ conditions:

$$\sum_{j=1}^{2N} E_l^{(L_j)} \frac{L_j}{L_j^2 - l_i^2} [L_j j_l(L_j R) h_l'(l_i R) - l_i j_l'(L_j R) h_l(l_i R)] + E_l^{(n)} \frac{l(l+1)}{TR} j_l(TR) \frac{h_l(l_i R)}{l_i} + \mathscr{D}_l h_l'(l_i R) = 0 \tag{25}$$

for the $(2N+2)$ unknowns, $E_l^{(L_i)}$, $E_l^{(n)}$, and $\mathscr{D}_l$.

As regards the odd part of P_l, $P_{o,l}$, when its general expression is worked out by using Eq. (23), we only obtain terms verifying identically Eq. (19). Thus, for the odd part, no new condition equivalent to (25) is found.

One more condition for the unknowns $E_l^{(L_i)}$, $E_l^{(n)}$ and $\mathscr{D}_l$ can be obtained by imposing the condition that the current (or the polarizability) at $r=R$ be zero. This condition yields

$$\sum_{L_i} E_l^{(L_i)} L_i j_l'(L_i R) = [\epsilon_T(\omega) - 1] E_l^{(n)} \frac{l(l+1)}{TR} j_l(TR) . \tag{26}$$

Equations (25) and (26) allow us to express the even l component of the field in the extended metallic medium as a function of only one constant. Similarly, the odd l component of the field can also be written in the extended medium as a function of only one constant. In the two cases, the field inside the metal sphere, for $r<R$, is known up to a normalizing factor which has to be determined by matching the field to the even and odd parts of the vacuum field. For completeness, let us write the even and odd components of this field:

$$\mathbf{E}_{e,l}^V(\mathbf{r}) = i^l \frac{2l+1}{l(l+1)} [-i\mathbf{n}_{el1}(k_0,\mathbf{r}) + b_l \mathbf{n}_{el1}^r(k_0,\mathbf{r})] , \tag{27a}$$

$$\mathbf{E}_{o,l}^V(\mathbf{r}) = i^l \frac{2l+1}{l(l+1)} [\mathbf{m}_{ol1}(k_0,\mathbf{r}) + a_l \mathbf{m}_{ol1}^r(k_0,\mathbf{r})] , \tag{27b}$$

where $\mathbf{n}_{el1}^r$ and $\mathbf{m}_{ol1}^r$ are given by Eqs. (8) with the spherical Bessel functions $h_l(k_0 r)$ substituting for $j_l(k_0 r)$. The coefficients a_l and b_l and the normalizing factors for the field inside the sphere are determined by means of the usual matching equations at the sphere surface. Having found the field, we can proceed and calculate all the optical properties of the sphere, surface impedance, reflectivity, absorption, etc.

B. Specular surface

We argued in Sec. II that, for a completely rough surface, the sphere could be embedded in an infinite metal if we imposed the condition that the field be zero at $r>R$. Specular surfaces do not reflect the electrons at random, and we have to look for different conditions for the field at $r>R$, conditions which must take into account adequately the effects associated with the specular surface. At this point we are guided by the work of Apell and Ahlqvist for thin films,[9] and instead of using the complete basis defined by the continuous values of k in Eq. (6), we only use those basis states defined by the wave vector k, verifying the conditions appropriate for a specular surface. These conditions are the following:

$$E_r(R) = 0 , \tag{28a}$$

$$\left.\frac{dE_\theta(r)}{dr}\right|_{r=R} = 0 , \tag{28b}$$

$$\left.\frac{dE_\phi(r)}{dr}\right|_{r=R} = 0 , \tag{28c}$$

E_r, E_θ, and E_ϕ being the radial and angular components of the field, respectively.

With this choice, we define a complete set of vector states for the region $r<R$. Thus, we can develop the field inside the sphere in these vector states. Now, our main assumption about the infinite extended metallic medium is that, in analogy to the work of Apell and Ahlqvist,[9] *we extend the series obtained for the field inside the sphere* ($r<R$) *to the whole space.* Conditions (28) guarantee that the extended field for $r>R$ near the sphere surface is appropriate for a specular surface.

According to this discussion, we substitute Eq. (10) for the following equation:

$$\mathbf{E}_l(\mathbf{r})=\sum_i C_{li}^{(l)}\mathbf{l}_{el\,1}(k_i\mathbf{r})+\sum_j C_{lj}^{(n)}\mathbf{n}_{el\,1}(k_j,\mathbf{r})+\sum_s C_{ls}^{(m)}\mathbf{m}_{ol\,1}(k_s,\mathbf{r})\ , \tag{29}$$

where the eigenvectors l, $\mathbf{n}$, and $\mathbf{m}$ verify the boundary conditions (28), and have the corresponding eigenmomenta k_i, k_j, and k_s. Comparing with Eq. (16), it is worthwhile noticing that, in Eq. (29), the longitudinal and transverse modes extend to the whole space, while in Eq. (16) the field at $r>R$ is zero; in this last case, a singular term has been also added at the surface.

Our problem is to calculate the coefficients $C_{li}^{(l)}$, $C_{lj}^{(n)}$, and $C_{ls}^{(m)}$, that is, the field inside the sphere created by the incident em plane wave. As regards the transverse components, since we are using a local approximation for ϵ_T, we can easily obtain $\sum_j C_{lj}^{(n)}\mathbf{n}_{el\,1}(k_j,\mathbf{r})$ and $\sum_s C_{ls}^{(m)}\mathbf{m}_{ol\,1}(k_s,\mathbf{r})$, the two transverse polariton waves for an l component, except for a constant factor. Indeed, the two fields, say $\mathbf{E}_{T,el}$ and $\mathbf{E}_{T,ol}$, are the transverse fields calculated in any standard text book for a local dielectric function.[23]

Thus, our problem reduces to obtaining the longitudinal part of Eq. (29). Details of this calculation are published elsewhere.[24] Let us only mention here that the longitudinal mode is defined by an electrostatic potential ϕ_l, given, up to a normalization factor ρ_l, by the following equation:

$$\phi_l(r)=\sum_n B_{l,n}j_l\left[x'_{ln}\frac{r}{R}\right]\ , \tag{30}$$

with

$$B_{l,n}=-4\pi\frac{R\rho_l}{j_l(x'_{ln})[(x'_{ln})^2-l(l+1)]}\times\left[\frac{1}{\epsilon_L\left[\dfrac{x'_{ln}}{R},\omega\right]}-\frac{1}{\epsilon_L(0,\omega)}\right]\ , \tag{31}$$

where x'_{ln} defines the different eigenmomenta, $k_{ln}=x'_{ln}/R$, associated with the condition $dj_l(kR)/dr=0$ [see condition (28a)]. Then the whole field inside the sphere is a linear combination of the longitudinal mode $\nabla[\phi_l(r)P_l^1(\cos\theta)\cos\phi]$ and the two usual transverse polariton modes. Note that the longitudinal mode is only coupled to the even transverse mode (see above), giving a mixed mode which corresponds to the p-like em wave of planar surface. The odd mode is decoupled from longitudinal modes and corresponds to the s-like em wave of planar surfaces.

The mixed mode for the longitudinal and transverse even modes can be obtained by imposing the condition of zero value for the normal component of the induced current at the sphere surface. This condition gives the right combination of the above-mentioned modes, and determines completely the field inside the sphere except for a normalization constant which will be finally calculated by matching the em fields inside the sphere and the vacuum field at $r=R$. This is equivalent to the discussion given above at the end of the "diffuse-surface" case.

C. Optical absorption

Once the electromagnetic field has been obtained, we can calculate the optical absorption for a sphere by means of the following equation:

$$\sigma=-\frac{\dfrac{c}{8\pi}\displaystyle\int_S(\mathbf{E}\times\mathbf{H}^*)\cdot\mathbf{n}\,dS}{\dfrac{c}{8\pi}|E_0|^2}\ , \tag{32}$$

where $\mathbf{E}$ and $\mathbf{H}$ are the electric and magnetic fields, respectively, and $\mathbf{n}$ is the unit vector perpendicular to the sphere surface S of radius R. The numerator in Eq. (32) gives the rate of flow of energy across the sphere, and the denominator the same rate per unit area for the incident field. Therefore, Eq. (32) yields the sphere cross section to the optical absorption of the incident field.

Equations (27) and (32) yield the following result:

$$\sigma=-2\pi R^2\sum_{l=1}^{\infty}(2l+1)[\,|a_l|^2+|b_l|^2+\mathrm{Re}(a_l+b_l)]\ . \tag{33}$$

Coefficients b_l and a_l are associated with the l-electric and l-magnetic multipoles. In our actual calculations, for small spheres, only a_1 and b_1 give relevant contributions.

In order to calculate the optical absorption of an ensemble of small spheres filling the whole space with a given filling factor η we take into account[23] that the em field induces electric, p, and magnetic, m, dipoles in each sphere, which are related to the coefficients b_1 and a_1 by means of the following equations:

$$p=\frac{3}{2}(-ib_1)\frac{1}{k_0^3}\ , \tag{34a}$$

$$m=\frac{3}{2}(-ia_1)\frac{1}{k_0^3}\ . \tag{34b}$$

Now, by means of a Maxwell-Garnett[25] theory we can define an effective dielectric function ϵ_c given by the following Claussius-Mossotti-like equation:

$$\epsilon_c=\frac{1+2\eta p/R^3}{1-\eta p/R^3}=\frac{1+3\eta\dfrac{(-ib_1)}{(k_0R)^3}}{1-\dfrac{3\eta}{2}\dfrac{(-ib_1)}{(k_0R)^3}}\ . \tag{35a}$$

In a similar way we define an effective magnetic susceptibility μ_c:

$$\mu_c=\frac{1+3\eta\dfrac{(-ia_1)}{(k_0R)^3}}{1-\dfrac{3\eta}{2}\dfrac{(-ia_1)}{(k_0R)^3}}\ . \tag{35b}$$

From Eqs. (35) we define the effective absorption coefficient $\alpha(\omega)$ of the whole medium by means of the following equation:

$$\alpha(\omega)=2\frac{\omega}{c}\mathrm{Im}[(\epsilon_c\mu_c)^{1/2}]\ . \tag{36}$$

IV. RESULTS AND DISCUSSION

We have calculated the optical absorption for spheres of different radii and different electronic densities. Figures 4 and 5 show the results for the following conditions: $r_s = 4.86$ (potassium), the filling factor $\eta = 0.1$, $R = 18$, and 36 Å (corresponding to the following numbers of atoms: 343 and 2748) and specular surface. In these calculations we have introduced broadening effects in the dielectric function given by Eq. (3) by means of an imaginary component of ω, $\omega + i\gamma$, and by defining new real and imaginary dielectric components according to Mermin's prescription[17,26] (we have taken $\gamma = 5.3 \times 10^{-3}\omega_p$). In Figs. 6–8 we show the results for the optical absorption of the following spheres: $r_s = 2.07$ (aluminum), $\eta = 0.1$, $R = 7.5$, 15, and 36 Å (corresponding to the following numbers of atoms: 105, 845, and 11 864), and specular surface. Broadening effects are taken into account with the same Mermin prescription, and taking also $\gamma = 5.3 \times 10^{-3}\omega_p$. In all the figures we show Mie's results,[14] and in Fig. 8 we have also drawn Wood and Ashcroft's results[17] for comparison.

The most interesting results coming out of our calculations for the optical absorption of small spheres and specular surface is the resonant structure associated with the quantum size effects of the small particle (electron-hole pairs excitations). For potassium this structure appears clearly for $R = 18$ Å, while for Al we find similar results for $R = 7.5$ Å; in both metals, for much greater radii, the structure associated with the quantum size effects has many small peaks and all these contributions tend to overlap and give a smoother pattern. For $R = 36$ Å in K and $R = 15$ Å in Al, this effect has evolved partially, while for the case $R = 36$ Å in Al the process has evolved completely and the absorption spectrum becomes quite smooth. Our results show that quantum size effects can be only

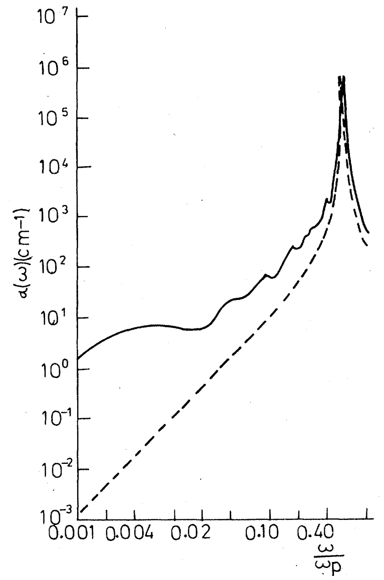

FIG. 5. As Fig. 4, for $R = 36$ Å.

observed for $R \lesssim 10$ Å in Al and for $R \lesssim 25$ Å in K. The difference in the results for the two metals is related to their different electron densities: for greater metallic densities and the same radii, there appear more electron-hole pairs excited in the sphere and the optical absorption spectrum becomes smoother.

It is interesting to compare our results with other calculations. Comparing with Wood and Ashcroft,[17] our results show a smoother structure (see Fig. 8); again, this effect is associated with the number of electron-hole excitations, much greater in our calculation than in Wood and Ashcroft's paper where a dipole approximation is used for $\epsilon(\omega)$. The "multipole" electron-hole pairs introduced in

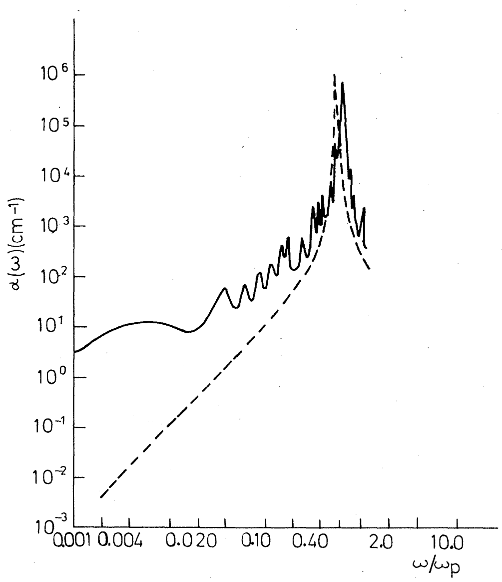

FIG. 4. Optical absorption for spheres of radii 18 Å, $r_s = 4.86$, $\gamma = 5.3 \times 10^{-3}\omega_p$, and $\eta = 0.1$ with specular surface conditions. Mie's results are also shown (dashed line).

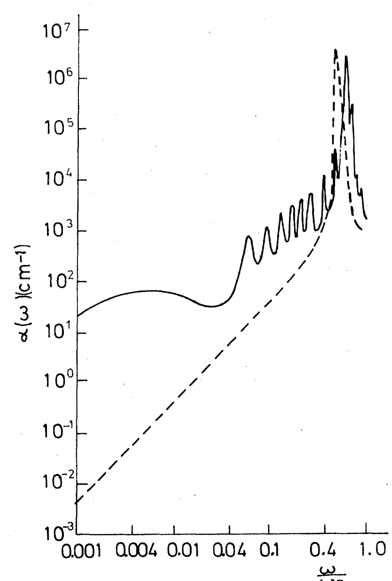

FIG. 6. As Fig. 4, for $R = 7.5$ Å, $r_s = 2.07$, and $\eta = 0.1$.

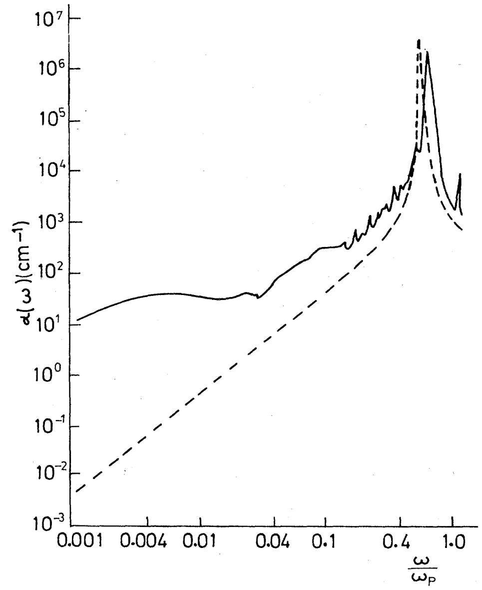

FIG. 7. As Fig. 4, for $R=15$ Å, $r_s=2.07$, and $\eta=0.1$.

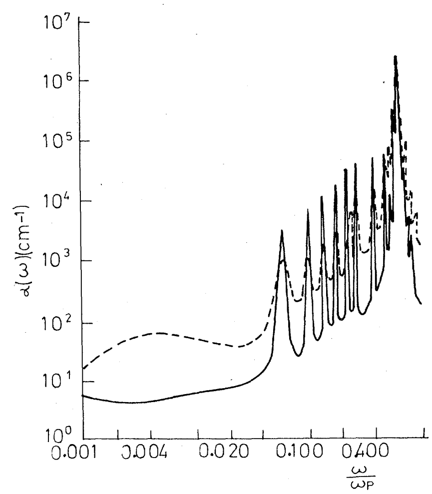

FIG. 9. Optical absorption for spheres of radii 7.5 Å, $r_s=2.07$, and $\eta=0.1$. Solid line: $\gamma=5.3\times10^{-4}\omega_p$. Dashed line: $\gamma=5.3\times10^{-3}\omega_p$.

our calculation are also responsible for the general increase of the optical absorption that we find for frequencies lower than the plasmon peak, with respect to Wood and Ashcroft's. Comparing now with Ekardt,[18] it is worth noticing the similarity between our results for K and $R=18$ Å, and Ekardt's results for Na and $R=23$ Å; both cases show quite clearly the structure associated with the pairs excitations. Let us comment, at this point, that in our calculations this structure is broadened by the coupling between the longitudinal (pairs or plasmon) modes and the transverse electromagnetic field. In order to show how the broadening of the different pairs modes depends on that coupling, we have also calculated the optical absorption spectrum for Al, with $R=7.5$ Å, but reducing by 1 order of magnitude γ, which now has been taken as $5.3\times10^{-4}\omega_p$. Figure 9 shows the new results; we find the same kind of spectrum than in Fig. 6 with somewhat deeper "pairs" peaks but having widths similar to the ones of Fig. 6. These widths are mainly controlled by the pairs—electromagnetic-field coupling.

All our calculations for K and Al present a blue shift for the frequency of the plasmon peak with respect to the classical Drude result and an important enhancement of the optical absorption at low frequencies. The blue shift is a consequence of the model used in this work, where the diffuseness of the surface electron density has been neglected. It is well known that a realistic surface-

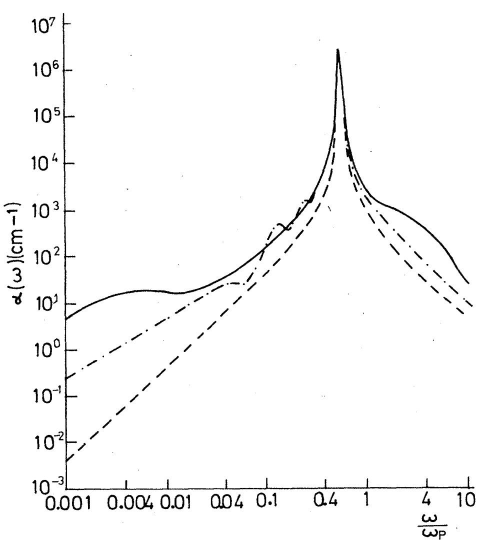

FIG. 8. As Fig. 4, for $R=36$ Å, $r_s=2.07$, and $\eta=0.1$. Dot-dashed line: Wood and Ashcroft's results.

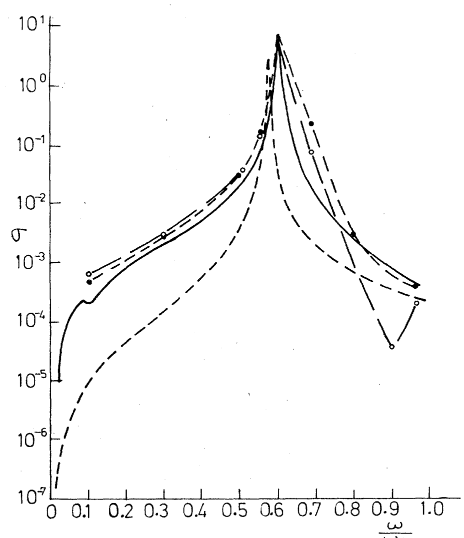

FIG. 10. Cross section (in units of πR^2) to the optical absorption for a sphere of radius 25 Å, $r_s=4$, $\gamma=10^{-3}\omega_p$ and specular surface. ○ and ●: Penn and Rendell's results. Dashed line: Mie's results. Solid line: our results.

electron-density profile produces a red shift in the plasmon peak;[27] this is clearly seen by comparing our Fig. 4 and Ekardt's results: the red shift found in the latter paper is a consequence of the self-consistency introduced in the electronic charge. Notice that this self-consistency can be expected to introduce little effects, however, on the pair structure discussed above, since the pairs extend to the whole sphere. On the other hand, the enhancement of the optical absorption at low frequencies is a result of the electronic pair structure; this point has been stressed previously by Penn and Rendell[16] and is in good agreement with our calculations. It is worth commenting that at variance with Penn and Rendell we have introduced specific quantum size effects in the calculations for the sphere; however, for great radii, this structure disappears and the effect of the pairs is only to enhance the optical absorption at low frequencies. To see how our model reproduces Penn and Rendell's results, we have calculated the optical absorption of a sphere with the same parameters of Ref. 16: $r_s=4$, $R=25$ Å, $\gamma=10^{-3}\omega_p$, *but* we have used a Lindhard-Mermin dielectric function instead of the one introduced in Sec. II [Eq. (3)]. Figure 10 shows our results, Penn and Rendell's calculations, and the ones given by Mie's theory. This figure shows that our model yields values quite close to the ones given by Penn and Rendell when the *same* dielectric function is used in both cases.

When the structure of the electron-hole pairs tends to overlap in the optical spectrum, there is a finite probability for the excited pairs of being mixed among them. This means that electrons reflected from the surface can be scattered off into many different final states; for this case, surface irregularities are important since electrons can be randomized at the surface. Then, the analysis presented in this paper for rough surfaces comes in. According to the results obtained for specular surfaces, that case appears for K and Al when the sphere radii are greater than 40 and 20 Å, respectively.

Before discussing our results for spheres with rough surfaces, it is convenient to present calculations showing the good approximation that the dielectric function of Eq. (4) is to the more exact dielectric function given in Eq. (3), in order to calculate optical properties. This has been checked by calculating the optical absorption of Al spheres ($r_s=2.07$) having $R=36$ Å, $\eta=0.1$, and $\gamma=5.3\times10^{-3}\omega_p$, with the two dielectric functions (3) and (4). Figure 11 shows the results of our calculations for the two cases. Notice that both calculations yield practically the same optical absorption; in the same figure we have drawn the classical results for comparison. It is convenient to comment that in the approximated dielectric function given by Eq. (4), we have introduced broadening effects by substituting $\omega(\omega+i\gamma)$ for ω^2 in each factor of $[\omega^2-\omega^2(k)]$.

Let us now move on to presenting the results of our calculations for rough surfaces. Figure 12 shows the optical absorption of Al spheres for $R=36$ Å, $\eta=0.1$, and $\gamma=5.3\times10^{-3}\omega_p$. In the same figure, we have drawn the results of our calculation for a specular surface. The main result arising from the comparison between our two calculations is that *rough surfaces introduce little effects, if any, on the optical properties of spheres.* This result can be more deeply understood if we compare it with similar results for planar surfaces. For this case, it has been shown[8] that rough surfaces introduce no change on the optical properties of surfaces if a model is used of a nonlocal longitudinal dielectric function and a local transverse dielectric function. Roughness only introduces new effects on the optical properties of metal spheres *if a nonlocal transverse dielectric function is used in the calculation;* the physical reason is that transverse modes can be excited in such a way that they dissipate the energy brought by the longitudinal modes to the surface.[28] In light of this result for planar surfaces the results found in this work

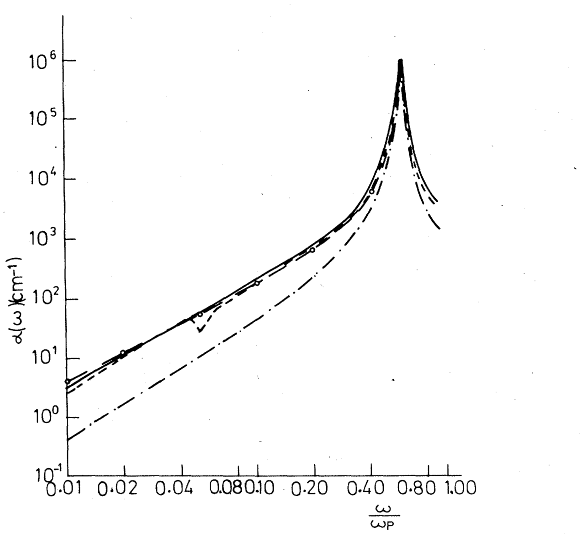

FIG. 11. Optical absorption for $R=36$ Å, $\eta=0.1$, $r_s=2.07$, and $\gamma=5.3\times10^{-3}\omega_p$. ——, results using the dielectric function of Eq. (3). o——o, results using the dielectric function of Eq. (4). — — —, results using the Lindhard dielectric function. ·—·—·, Mie's results.

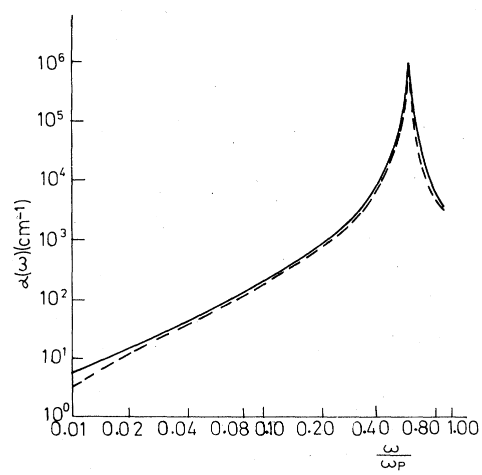

FIG. 12. Optical absorption for spheres of rough surfaces. $R=36$ Å, $r_s=2.06$, $\eta=0.1$, and $\gamma=5.3\times10^{-3}\omega_p$. Dashed line: results for spheres of specular surfaces.

are not surprising at all. On the contrary, by analogy with the planar case, we conclude that surface roughness can only introduce effects on the optical properties of spheres if a transverse nonlocal dielectric function is introduced. For this case we expect to find some increase in the optical absorption for low frequencies.[8] Work along this line is in progress in our laboratory.

ACKNOWLEDGMENTS

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APPENDIX A

In this appendix we calculate the coefficients of the expansion given by Eq. (10) for the field of Eq. (16). As regards the singular part $\mathscr{D}_l\delta(r-R)P_l^1(\cos\theta)(\cos\phi)\mathbf{i}_1$, it is quite straightforward to find the coefficients given by Eqs. (18) using the inverse relations:

$$k^2E_1^{(l)}(k)=\frac{1}{\pi^2}\frac{l(l+1)}{2l+1}\int \mathbf{E}_l(\mathbf{r})\cdot\mathbf{l}_{el1}(k,\mathbf{r})d^3r\ , \quad (A1)$$

$$E_l^{(n)}(k)=\frac{1}{\pi^2}\frac{l^2(l+1)^2}{2l+1}\int \mathbf{E}_l(\mathbf{r})\cdot\mathbf{n}_{el1}(k,\mathbf{r})d^3\mathbf{r}\ , \quad (A2)$$

$$E_l^{(m)}(k)=\frac{1}{\pi^2}\frac{l^2(l+1)^2}{2l+1}\int \mathbf{E}_l(\mathbf{r})\cdot\mathbf{m}_{ol1}(k,\mathbf{r})d^3r\ . \quad (A3)$$

For the regular part

$$\mathbf{E}_l^R(\mathbf{r})=\theta(R-r)\left[\sum_{L_i}E_l^{(L_i)}\mathbf{l}_{el1}(L_i,\mathbf{r})+E_l^{(n)}\mathbf{n}_{ol1}(T,\mathbf{r})+E_l^{(m)}\mathbf{m}_{ol1}(T,\mathbf{r})\right]\ , \quad (A4)$$

we proceed as follows.

First of all, equate the $\mathbf{i}_1$ components of Eqs. (10) and (16). This yields

$$\frac{d}{dr}\int_0^\infty k^2E_l^{(l)}(k)j_l(kr)dk+\frac{l(l+1)}{r}\int_0^\infty k^2\frac{E_l^{(n)}(k)}{k}j_l(kr)dk=\Theta(R-r)\left[\sum_{L_i}E_l^{(L_i)}\frac{d}{dr}j_l(L_ir)+E_l^{(n)}\frac{l(l+1)}{Tr}j_l(Tr)\right]\ . \quad (A5)$$

Using the Bessel-transform definitions given by Eqs. (11), we can write

$$\frac{d}{dr}\phi_l(r)+\frac{l(l+1)}{r}E_l^{(n)}(r)=\Theta(R-r)\left[\sum_{L_i}E_l^{(L_i)}\frac{d}{dr}j_r(L_ir)+E_l^{(n)}\frac{l(l+1)}{Tr}j_l(Tr)\right]\ . \quad (A6)$$

By equating the $\mathbf{i}_2$ and $\mathbf{i}_3$ components of Eqs. (10) and (16), we obtain the following equations:

$$\frac{1}{r}\phi_l(r)+\frac{1}{r}\frac{\partial}{\partial r}[rE_l^{(n)}(r)]+E_l^{(m)}(r)=\Theta(R-r)\left[\sum_{L_i}E_l^{(L_i)}\frac{1}{r}j_l(L_ir)+E_l^{(n)}\frac{1}{Tr}\frac{\partial}{\partial r}[rj_l(Tr)]+E_l^{(m)}j_l(Tr)\right]\ . \quad (A7)$$

Equations (A6) and (A7) have the following solutions:

$$\phi_l(r)=\Theta(R-r)\left[\sum_{L_i}E_l^{(L_i)}j_l(L_ir)+f_l^<(r)\right]+\Theta(r-R)f_l^>(r)\ , \quad (A8)$$

$$E_l^{(n)}(r)=\Theta(R-r)\left[\frac{E_l^{(n)}}{T}j_l(Tr)+f_n^<(r)\right]+\Theta(r-R)f_n^>(r)\ , \quad (A9)$$

$$E_l^{(m)}(r)=\Theta(R-r)E_l^{(m)}j_l(Tr)\ , \quad (A10)$$

with $f_l^<(r)$, $f_l^>(r)$, $f_n^<(r)$, and $f_n^>(r)$ verifying the equations

$$\frac{df_l^{\lessgtr}}{dr}+\frac{l(l+1)}{r}f_n^{\lessgtr}=0 \quad (A11)$$

and

$$f_l^{\gtrless}+\frac{d}{dr}(rf_n^{\gtrless})=0\ , \quad (A12)$$

and the continuity conditions

$$\phi_l(R^-)=\phi_l(R^+)\ , \quad (A13)$$

$$E_l^{(n)}(R^-)=E_l^{(n)}(R^+)\ . \quad (A14)$$

Equations (A11) and (A12) yield

$$f_l^<(R)=-A^<(1+l)r^l\ , \quad (A15)$$

$$f_l^>(r)=A^>\frac{l}{r^{l+1}}\ , \quad (A16)$$

$$f_n^<(r)=A^<r^l\ , \quad (A17)$$

$$f_n^>(r)=\frac{A^>}{r^{l+1}}\ , \quad (A18)$$

while conditions (A13) and (A14) yield Eqs. (17b) and (17e) for $A^<$ and $A^>$.

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