Optical nonlinear response of small metal particles: A self-consistent calculation

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We report a self-consistent calculation of the optical nonlinear response of the electrons of a small metal spherical particle. We use the jellium model to describe the metal sphere and work within the random-phase approximation. This calculation allows us to obtain general expressions of the linear polarizability and of the third-order nonlinear source polarization, in a form very similar to those calculated in the local approximation. This model has been applied numerically to the case of a homogeneous response of the electrons and it is shown that screening effects may be important in the nonlinear response of spheres with radii in the range of a few nanometers.

I. INTRODUCTION

In the last decade, much attention has been paid to the study of optical properties of small metallic particles.[1] The mechanisms of the surface plasma resonance[2,3] and of the broadening of the absorption band[4,5] in small spherical particles have been investigated in a large number of papers. The calculations were first performed assuming independent electrons in the local approximation[1,6,7] and improvements were then brought by introducing the nonlocal character of the response of electrons.[8–11] A more general situation, including exchange and correlation effects in the quantum treatment of the dynamical polarizability has also been proposed by Ekardt.[12]

More recently, Ricard *et al.*[13,14] have studied nonlinear optical phenomena in such particles by means of optical phase conjugation in gold and silver colloids. The surface plasma resonance occurs for this nonlinear process[14] in the same way as for linear properties. Indeed, a first approach using an effective dielectric constant model,[3] shows that the resonant local field factor f_1, defined by the ratio between the field inside and outside the sphere, enters to the fourth power in the third-order Kerr nonlinear source polarization $P^{(3)}_{\mathrm{NLS}}(\omega)$. In this treatment,[13,14] a separation occurs between the electronic response of the metal characterized by the nonlinear third-order susceptibility $\chi^{(3)}_m(\omega_1,\omega_2,\omega_3)$ and the local-field factor $f_1(\omega)$:

$$P^{(3)}_{\mathrm{NLS}}(\omega)=3p\,|\,f_1(\omega)\,|^2 f_1^2(\omega)\chi^{(3)}_m(\omega,-\omega,\omega)\times|\,E_0(\omega)\,|^2 E_0(\omega)\ , \quad (1)$$

where p is the volume fraction occupied by the metal particles and $E_0(\omega)$ is the external field.

A calculation of the Kerr-type polarizability $\chi^{(3)}_m$ for small metal spheres, using the quantum-mechanical description of a gas of free electrons in a three-dimensional spherical well is described in Ref. 14. The first model accounts for the observed anisotropy of this polarizability and provides an estimate of its magnitude. Nevertheless, the nonlinear source polarization given in Eq. (1) is obtained from a local response theory of the metal for which the dielectric constant $\epsilon(\omega)$ is assumed to be homogeneous overall in the sphere.

Our purpose in this paper is to perform a calculation of a general self-consistent form for $P^{(3)}_{\mathrm{NLS}}(\omega)$, for the same system, i.e., small metallic spheres embedded in a dielectric medium. In this approach, the charge-density susceptibility formalism is applied within the random-phase approximation (RPA). A jellium model with infinite barrier[9,10,15] is used to describe the electronic properties of the metal. It is well understood that this approximation can be crude, but it seems to us a necessary condition to perform tractable analytical calculations, more specially in the expression of the boundary condition at the sphere surface.

In Sec. II, the main aspects of the linear response of a spherical particle are recovered within the framework of Newns's method.[15] The same formalism is used to determine the third-order nonlinear source polarization in Sec. III. It is shown that a local-field factor still occurs and enters again to the fourth power as in Refs. 13 and 14. In Sec. V the values of the factor $\tilde{f}_1$ evaluated for a complete local treatment are compared with those issued from a nonlocal one based on the hydrodynamical model.[9]

II. LINEAR RESPONSE

We first calculate, in a self-consistent way, the linear response of the electrons confined in a metallic sphere of radius a, embedded in a dielectric medium with real dielectric constant $\epsilon_2(\omega)$. The sphere is submitted to an external electric field **E** given by [cf. Fig. (1)]

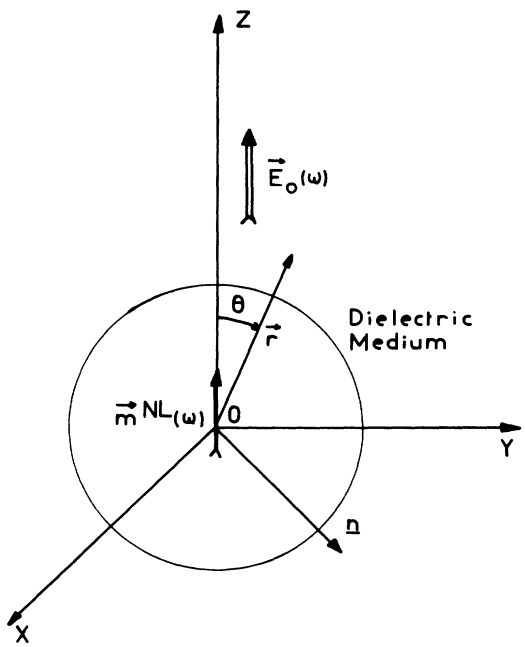

FIG. 1. Geometry of a spherical metal particle embedded in a dielectric medium. $\mathbf{m}^{NL}(\omega)$ at the center of the sphere represents the equivalent nonlinear dipole moment induced in the metal [Eq. (33)].

$$\mathbf{E}=[\mathbf{E}_0(\omega)e^{i\omega t}+\text{c.c.}]\mathbf{U}_z \ , \tag{2}$$

where $\mathbf{U}_z$ is a unit vector parallel to the $0z$ axis. The wavelength λ of this field is assumed to be very large with respect to the sphere radius a, so that retardation effects can be neglected. As a consequence, the external field appears as the gradient of the electric potential $\phi_0(\mathbf{r})$ defined by

$$\phi_0(\mathbf{r})=-E_0(\omega)r\cos\theta \ , \tag{3}$$

where $\theta=(\mathbf{U}_z,\mathbf{r})$.

Since in this paper all the functions $g(\mathbf{r})$ describing a physical quantity inside the sphere ($|\mathbf{r}|<a$) are separable like

$$g(\mathbf{r})=g(r)Y_1^0(\theta,\psi) \ , \tag{4}$$

we can expand them in a similar way as in Ref. 16:

$$g(\mathbf{r})=g(r,\theta,\psi)=\sum_k \left[\frac{2}{A_k a^3}\right]^{1/2} j_1(kr)Y_1^0(\theta,\psi)g(k) \ , \tag{5}$$

where j_1 is the spherical Bessel function of first order and the wave numbers k are chosen so that[16]

$$\left[\frac{dj_1(x)}{dx}\right]_{x=ka}=0 \tag{6}$$

and

$$A_k=j_1^2(ka)-j_0(ka)j_2(ka) \ . \tag{6'}$$

The inverse transform is given by

$$g(k)=\left[\frac{2}{A_k a^3}\right]^{1/2}\int_V d\mathbf{r}\, j_1(kr)Y_1^0(\theta,\psi)g(\mathbf{r}) \ , \tag{7}$$

where V is the volume of the sphere.

A. Potential inside the sphere

To derive a self-consistent expression of the linear polarizability of the metallic sphere, we first have to calculate the electric potential inside the particle. In the framework of the RPA, we can write the induced electronic charge density $\delta\rho(\mathbf{r},\omega)$ as

$$\delta\rho(\mathbf{r},\omega)=\int_V d\mathbf{r}'\, \chi_S(\mathbf{r},\mathbf{r}',\omega)\phi_1(\mathbf{r}',\omega) \ , \tag{8}$$

where χ_S represents the linear density-density response function[15] and $\phi_1(\mathbf{r}',\omega)$ is the potential inside the metal. The transformation of Eq. (8) in the (k,ω) representation leads to

$$\delta\rho(k,\omega)=\sum_{k'}\chi_S(k,k',\omega)\phi_1(k',\omega) \ , \tag{9}$$

with

$$\chi_S(k,k',\omega)=\frac{2}{a^3(A_k A_{k'})^{1/2}} \times\int\int d\mathbf{r}\,d\mathbf{r}' j_1(kr)j_1(k'r')Y_1^0(\theta,\psi) \times Y_1^0(\theta',\psi')\chi_S(\mathbf{r},\mathbf{r}',\omega) \ . \tag{10}$$

The self-consistency of the problem is obtained after writing the Poisson equation,

$$\Delta\phi_1(\mathbf{r},\omega)=-4\pi\delta\rho(\mathbf{r},\omega) \ , \tag{11}$$

which becomes in the (k,ω) representation

$$\left[\frac{2}{A_k a^3}\right]^{1/2}\int d\mathbf{r}\, j_1(kr)Y_1^0(\theta,\psi)\Delta_{\mathbf{r}}\phi_1(\mathbf{r},\omega) =-4\pi\sum_{k,k'}\chi_S(k,k',\omega)\phi_1(k',\omega) \ . \tag{12}$$

We now apply the second Green identity on the left-hand side to solve Eq. (12):

$$\int_V d\mathbf{r}\, j_1(kr)Y_1^0(\theta,\psi)\Delta_{\mathbf{r}}\phi_1(\mathbf{r},\omega)=\int_V d\mathbf{r}\,\phi_1(\mathbf{r},\omega)\Delta_{\mathbf{r}}[j_1(kr)Y_1^0(\theta,\psi)]+\int_S a^2 d\Omega\{j_1(kr)Y_1^0(\theta,\psi)\mathbf{n}\cdot\nabla_{\mathbf{r}}\phi_1(\mathbf{r},\omega) -\phi_1(\mathbf{r},\omega)\mathbf{n}\cdot\nabla_{\mathbf{r}}[j_1(kr)Y_1^0(\theta,\psi)]\} \ , \tag{13}$$

where $\int_S$ indicates an integration over the surface of the sphere, $d\Omega$ represents the elementary solid angle, and $\mathbf{n}$ is the normal unit vector (cf. Fig. 1). Equation (13), calculated by introducing the condition (6), reduces to

$$\sum_{k'}\mathcal{E}(k,k',\omega)\phi_1(k',\omega)=\left[\frac{2a}{A_k}\right]^{1/2}\phi_1'(a,\omega)j_1(ka) , \quad (14)$$

where

$$\phi_1'(a,\omega)=\left.\frac{\partial\phi_1(\mathbf{r},\omega)}{\partial r}\right|_{r=a} \quad (15)$$

and, as in the theory of Newns,[15] we introduce the following notation:

$$\mathcal{E}(k,k',\omega)=k^2\delta_{k,k'}-4\pi\chi_S(k,k',\omega) . \quad (16)$$

Note that the function $k^{-2}\mathcal{E}(k,k',\omega)$ is the RPA dielectric constant appropriate to this problem.[16] All the physical information about the metal particle is contained in this quantity. Returning now to the $(\mathbf{r},\omega)$ representation leads to

$$\phi_1(\mathbf{r},\omega)=\frac{2}{a}\phi_1'(a,\omega)Y_1^0(\theta,\psi)\sum_{k,k'}\frac{j_1(kr)j_1(k'a)}{(A_k A_{k'})^{1/2}}\mathcal{E}^{-1}(k,k',\omega) . \quad (17)$$

This latter relation connects the potential at any point of the metal with its normal derivative at the surface of the metal particle.

B. Potential outside the sphere

The electric potential in the dielectric medium is written as

$$\phi_2(\mathbf{r},\omega)=\phi_0(\mathbf{r},\omega)+\phi_{2r}(\mathbf{r},\omega) , \quad (18)$$

where $\phi_0(\mathbf{r},\omega)$ is given by Eq. (3). $\phi_{2r}(r,\omega)$ represents the response potential to $\phi_0(\mathbf{r},\omega)$ and obeys the Laplace equation in the dielectric

$$\Delta\phi_{2r}(\mathbf{r},\omega)=0, \quad |\mathbf{r}|>a . \quad (19)$$

In the present problem, we look for solutions of the form

$$\phi_{2r}(\mathbf{r},\omega)=\frac{A(\omega)Y_1^0(\theta,\psi)}{r^2} , \quad (20)$$

where $A(\omega)$ is a quantity to be determined. The boundary conditions at $r=a$ for the electric potentials [Eqs. (17) and (18)] lead to the following system of equations:

$$\begin{aligned}\phi_1'(a,\omega)+\frac{2A(\omega)}{a^3}\epsilon_2(\omega)&=-\epsilon_2(\omega)E_0(\omega)\sqrt{4\pi/3} ,\\ \phi_1'(a,\omega)\mathcal{F}(a,\omega)-\frac{A(\omega)}{a^2}&=-E_0(\omega)a\sqrt{4\pi/3} ,\end{aligned} \quad (21)$$

where

$$\mathcal{F}(\mathbf{r},\omega)=\frac{2}{a}\sum_{k,k'}\frac{j_1(kr)j_1(k'a)}{(A_k A_{k'})^{1/2}}\mathcal{E}^{-1}(k,k',\omega) . \quad (22)$$

These equations allow us to express the coefficients $A(\omega)$ and $\phi'(a,\omega)$ in terms of the dynamical properties of the electrons in the sphere. The electric potentials in each region of space are then given by

$$\phi_1(\mathbf{r},\omega)=-E_0(\omega)\cos\theta\frac{3\epsilon_2(\omega)a}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)}\mathcal{F}(r,\omega) , \quad (23)$$

$$\phi_2(\mathbf{r},\omega)=E_0(\omega)\cos\theta\frac{a^3}{r^2}\frac{a-\epsilon_2(\omega)\mathcal{F}(a,\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)} . \quad (24)$$

As an example, the induced electric dipole moment in the sphere can be obtained from these potentials. We have

$$P(\omega)\equiv P_z(\omega)=\int_V d\mathbf{r}\, r\cos\theta\delta\rho(\mathbf{r}) . \quad (25)$$

The substitution of Eq. (9) after integration leads to

$$P(\omega)=\sqrt{4\pi/3}a^2\sum_{k,k'}\left[\frac{2}{a^3A_k}\right]^{1/2}\frac{1}{k^2}j_1(ka)\times\chi_S(k,k',\omega)\phi_1(k',\omega) . \quad (26)$$

Now, by rewriting Eq. (14) as

$$\sum_{k'}\chi_S(k,k',\omega)\phi_1(k',\omega)=\frac{1}{4\pi}\left[k^2\phi_1(k,\omega)-\left[\frac{2a}{A_k}\right]^{1/2}\phi_1'(a,\omega)j_1(ka)\right] , \quad (27)$$

and by using the following identity

$$r=\frac{2}{a}\sum_k \frac{j_1(kr)j_1(ka)}{A_k k^2}\ , \tag{28}$$

we obtain finally

$$P(\omega)=a^3\epsilon_2(\omega)\frac{a-\mathcal{F}(a,\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)}E_0(\omega)\ . \tag{29}$$

This expression, which was calculated without any further approximation than the RPA, has a similar form to those obtained in Refs. (17) and (9) (cf. Sec. IV).

III. NONLINEAR RESPONSE

We now examine the nonlinear behavior of the electrons inside the metal particle. Due to the spherical symmetry of the problem, the nonlinear second-order contributions vanish. Moreover, among all the possible third-order effects, we will study the case of the degenerate four-wave mixing, with terms oscillating at the frequency ω only. In the framework of the charge-density susceptibility formalism,[18,19] the internal electric potential $\phi_1(\mathbf{r},\omega)$ induces a nonlinear variation of the electronic charge density defined by

$$\begin{aligned}\delta\rho^{(3)}(\mathbf{r},\omega)=\int\int\int {}^{\rho}\chi^{\rho+\rho+\rho}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\omega,-\omega,\omega)\\ \times\phi_1(\mathbf{r}_1,\omega)\phi_1^*(\mathbf{r}_2,\omega)\\ \times\phi_1(\mathbf{r}_3,\omega)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\ ,\end{aligned} \tag{30}$$

where ${}^{\rho}\chi^{\rho+\rho+\rho}$ represents the third-order nonlinear susceptibility of the metal sphere in absence of perturbation.[18,19]

A. The effective electric potential inside the sphere

The extra contribution $\delta\rho^{(3)}$ modifies the initial potential $\phi_1(\mathbf{r},\omega)$ calculated in the previous section. One therefore defines an effective potential $\tilde{\phi}_1(\mathbf{r},\omega)$ by

$$\tilde{\phi}_1(\mathbf{r},\omega)=\phi_1(\mathbf{r},\omega)+\delta\phi(\mathbf{r},\omega) \tag{31}$$

which must verify the Poisson equation with a nonlinear source term:

$$\Delta_r\tilde{\phi}_1(\mathbf{r},\omega)=-4\pi\delta\rho(\mathbf{r},\omega)-4\pi\delta\rho^{(3)}(\mathbf{r},\omega)\ . \tag{32}$$

The introduction of Eq. (30) in Eq. (32) would lead to an untractable problem. So we replace $\delta\rho^{(3)}(\mathbf{r},\omega)$ by an equivalent nonlinear dipole moment $\mathbf{m}^{\mathrm{NL}}(\omega)$ placed at the center of the sphere and directed along the z axis (cf. Fig. 1).

$$\mathbf{m}^{\mathrm{NL}}(\omega)=\int_V \delta\rho^{(3)}(\mathbf{r},\omega)\mathbf{r}\,d\mathbf{r}\ . \tag{33}$$

Thus, the Poisson equation becomes

$$\Delta_r\tilde{\phi}_1(\mathbf{r},\omega)=-4\pi\delta\rho(\mathbf{r},\omega)+4\pi\mathbf{m}^{\mathrm{NL}}(\omega)\cdot\nabla_r\delta(\mathbf{r})\ , \tag{34}$$

where it may be noted that now the linear induced charge density is defined by

$$\delta\rho(\mathbf{r},\omega)=\int_V \chi_S(\mathbf{r},\mathbf{r}',\omega)\tilde{\phi}_1(\mathbf{r}',\omega)d\mathbf{r}'\ . \tag{35}$$

After expressing Eq. (34) in the (k,ω) representation and using the notation of Sec. II, we can write

$$\begin{aligned}\sum_{k'}\mathcal{E}(k,k',\omega)\tilde{\phi}_1(k',\omega)\\ =\left[\frac{2a}{A_k}\right]^{1/2}\tilde{\phi}'_1(a,\omega)j_1(ka)\\ +\left[\frac{4\pi}{3}\right]^{1/2}\left[\frac{2}{a^3A_k}\right]^{1/2}km^{\mathrm{NL}}(\omega)\end{aligned} \tag{36}$$

with

$$\tilde{\phi}'_1(a,\omega)=\frac{\partial\tilde{\phi}_1}{\partial r}(\mathbf{r},\omega)\Bigg|_{r=a}\ . \tag{36$'$}$$

The effective potential $\tilde{\phi}_1(\mathbf{r},\omega)$ inside the sphere is obtained from the same algebra developed in Sec. II:

$$\begin{aligned}\tilde{\phi}_1(\mathbf{r},\omega)=[\tilde{\phi}'_1(a,\omega)\mathcal{F}(r,\omega)\\ +(4\pi/3)^{1/2}m^{\mathrm{NL}}(\omega)\mathcal{N}(r,\omega)]Y_1^0(\theta,\psi)\ ,\end{aligned} \tag{37}$$

where the additional source term is defined by

$$\mathcal{N}(r,\omega)=\frac{2}{a^3}\sum_{k,k'}\frac{k'j_1(kr)}{(A_kA_{k'})^{1/2}}\mathcal{E}^{-1}(k,k',\omega)\ . \tag{37$'$}$$

B. The nonlinear source polarization

The nonlinear dipole moment $m^{\mathrm{NL}}(\omega)$ generates an extra potential $\phi_{2m}(\mathbf{r},\omega)$, *outside* the sphere, having the following form:

$$\phi_{2m}(\mathbf{r},\omega)=\frac{1}{\epsilon_2(\omega)}B(\omega)\frac{m^{\mathrm{NL}}(\omega)\cos\theta}{r^2}\ . \tag{38}$$

The factor $B(\omega)$ can be determined by applying again the boundary conditions. We have then

$$\phi_{2m}(\mathbf{r},\omega)=\frac{m^{\mathrm{NL}}(\omega)\mathcal{N}(a,\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)}\frac{a^3}{r^2}\cos\theta\ . \tag{39}$$

Since the potential generated by a dipole moment $m^{\mathrm{NLS}}(\omega)$ seen by an observer lying outside the sphere, may be defined by the equation[17]

$$\phi_{2m}(\mathbf{r},\omega)=\frac{1}{\epsilon_2(\omega)}\frac{m^{\mathrm{NLS}}(\omega)\cos\theta}{r^2}\ ; \tag{40}$$

then from Eqs. (39) and (40), the source dipole moment is given by

$$m^{\mathrm{NLS}}(\omega)=m^{\mathrm{NL}}(\omega)\frac{a^3\mathcal{N}(a,\omega)\epsilon_2(\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)}\ . \tag{41}$$

Now, in order to obtain the expression of the nonlinear source polarization of a composite medium containing N spheres per unit volume, one writes

$$P^{(3)}_{\mathrm{NLS}}(\omega)=Nm^{\mathrm{NLS}}(\omega) \tag{42}$$

or, from Eqs. (23), (30), (33), and (41),

$$P^{(3)}_{\rm NLS}(\omega)=\left[\frac{27N\mathcal{N}(a,\omega)\epsilon_2^4(\omega)a^6}{|a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)|^2[a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)]^2}\right.$$
$$\times\int\int\int {}^{\rho}\chi^{\rho+\rho+\rho}(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\omega,-\omega,\omega)\mathcal{F}(\mathbf{r}_1,\omega)\mathcal{F}^*(\mathbf{r}_2,\omega)\mathcal{F}(\mathbf{r}_3,\omega)$$
$$\left.\times r\cos\theta\cos\theta_1\cos\theta_2\cos\theta_3 d\mathbf{r}\,d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3\right]|E_0(\omega)|^2E_0(\omega)\ . \tag{43}$$

Up to now, the only approximations done are the RPA, the infinite barrier and, in the case of the nonlinear response, the replacement of the actual $\delta\rho^{(3)}$ by a dipole located at the center of the sphere. So, Eq. (43) is very general and is the central result of this paper. But, as it stands, it is of limited practical use unless one knows an expression for ${}^{\rho}\chi^{\rho+\rho+\rho}$.

One possible way would be to calculate this nonlinear susceptibility applying the density-functional formalism proposed by Senatore and Subbaswamy[19] to study the nonlinear response of closed-shell atoms. Given that the direct transposition of this nonlocal treatment to a metal sphere is not presently possible, we limit the numerical study to a simplified model which uses the dipolar approximation for the evaluation of ${}^{\rho}\chi^{\rho+\rho+\rho}$:[20]

$$\begin{aligned}{}^{\rho}\chi^{\rho+\rho+\rho}&(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\omega,-\omega,\omega)\\ &=3V\chi_m^{(3)}(\omega,-\omega,\omega)\\ &\quad\times \mathrm{T}_4\nabla_{\mathbf{r}}\delta(\mathbf{r})\nabla_{\mathbf{r}_1}\delta(\mathbf{r}_1)\nabla_{\mathbf{r}_2}\delta(\mathbf{r}_2)\nabla_{\mathbf{r}_3}\delta(\mathbf{r}_3)\ .\end{aligned} \tag{44}$$

where they symbol T_4 indicates the contraction of two fourth-rank tensors and $\chi_m^{(3)}$ represents the third-order local dipolar susceptibility of the metal particle. A model calculation of this quantity was performed in Ref. 14.

The substitution of Eq. (44) in Eq. (43) leads to

$$\begin{aligned}P^{(3)}_{\rm NLS}(\omega)&=3p\,|\tilde f_1(\omega)|^2\tilde f_1^{\,2}(\omega)\chi_m^{(3)}(\omega,-\omega,\omega)\\ &\quad\times|E_0(\omega)|^2E_0(\omega)\ ,\end{aligned} \tag{45}$$

where $\chi_m^{(3)}\equiv\chi^{(3)}_{m\,zzzz}$ and the factor $\tilde f_1(\omega)$ is defined by

$$\tilde f_1(\omega)=a^3\frac{\mathcal{N}(a,\omega)\epsilon_2(\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)}\ . \tag{46}$$

Equation (45) has a similar form to that obtained from the local treatment [cf. Eq. (1)]. Thus $\tilde f_1(\omega)$ appears as a new local field factor which, for the non linear process studied here, takes into accout the spatial dispersion effect in the sphere. Moreover, by applying the following identity

$$\mathcal{N}(a,\omega)=\frac{3}{a^2}\left.\frac{\partial\mathcal{F}(r,\omega)}{\partial r}\right|_{r=0} \tag{47}$$

it is possible to establish that

$$E_1(r=0,\omega)=\tilde f_1(\omega)E_0(\omega)\ . \tag{48}$$

The factor $\tilde f_1$ thus connects the electric field at the center of the sphere to the applied one. This simple expression [Eq. (48)] is a consequence of the dipolar approximation used to determine the nonlinear response of the electrons.

We remark also that the factor $\tilde f_1(\omega)$ occurs four times in the nonlinear source polarization given by the Eq. (45) in a similar way as for the local treatment.[13] However, our present calculation, based on the RPA response functions of the electrons, is more rigorous since it does not introduce any effective dielectric constant. Such an approach allows us to understand the physical origin of the fourth power of the factor $\tilde f_1(\omega)$. Three factors are due to the third-order nonlinear process in the sphere and the fourth occurs when one examines, outside the sphere, the field generated by this nonlinear polarization.

The calculation of $\chi_m^{(3)}$ reported in Ref. (14) assumes an electric field uniform over the metal sphere, which is the case in the local approximation. One may then wonder whether the mean field $\langle E_1(\omega)\rangle$ inside the sphere is not a more physically relevant quantity than the field at the center of the sphere. These considerations, leading to another local field factor $\bar f_1(\omega)$, are detailed in the Appendix. The two quantities differ because of the nonuniformity of the electric field inside the sphere when nonlocality is taken into account. However, even in this case, the field is uniform over the major part of the sphere and starts decreasing 5–6 Å from the surface where it almost vanishes. At present, it is not clear which of these two quantities (mean field or field at center) is the most relevant. We recall anyway that the correct result is Eq. (43).

IV. CONNECTION WITH OTHER APPROACHES

If we neglect the nonlocal behavior of the response of the electrons, the linear susceptibility $\chi_S(\mathbf{r},\mathbf{r}',\omega)$ becomes independent of the position $\mathbf{r}$ and $\mathbf{r}'$ in the metal. Then, Eq. (16) reads

$$\mathcal{E}(k,k',\omega)=k^2\delta_{k,k'}\epsilon(\omega)\ , \tag{49}$$

where $\epsilon(\omega)$ is the local dielectric constant of the metal sphere. In this case, we have very simple relations for $\mathcal{F}$ and $\mathcal{N}$:

$$\mathcal{F}(r,\omega)=r/\epsilon(\omega),\quad \mathcal{N}(a,\omega)=3/[a^2\epsilon(\omega)] \tag{50}$$

and known results of electrostatics[17] are recovered after introducing these relations in Eqs. (29) and (46). The linear polarization $P(\omega)$ and the local field factor $\tilde f_1(\omega)$ are simplified as

$$P(\omega)=a^3\frac{\epsilon_2(\omega)[\epsilon(\omega)-1]}{\epsilon(\omega)+2\epsilon_2(\omega)}E_0(\omega) \tag{51}$$

and

$$f_1(\omega)=\frac{3\epsilon_2(\omega)}{\epsilon(\omega)+2\epsilon_2(\omega)} . \quad (52)$$

Another interesting approximation is the specular reflection model (SRM) for electrons at the bounding surface.[9,10] In this case, the response of the free electrons in the sphere is assumed to be homogeneous. We have then, between the function $\mathcal{E}(k,k',\omega)$ and the Lindhard bulk dielectric constant[21] $\epsilon(k,\omega)$, the following relation:

$$\mathcal{E}(k,k',\omega)=k^2\delta_{k,k'}\epsilon(k,\omega) . \quad (53)$$

Moreover, when we replace the discrete sum on the wave number k in Eq. (22) by an integral,[16] we obtain

$$\mathcal{F}(r,\omega)=3a^2F(r,\omega) , \quad (54)$$

where, we define, as Dasgupta and Fuchs,[9]

$$F(r,\omega)=\frac{2}{\pi}\int_0^{+\infty}\frac{j_1(kr)j_1(ka)}{\epsilon(k,\omega)}dk . \quad (55)$$

Within this approximation, the linear polarization $P(\omega)$ becomes

$$P(\omega)=a^3\epsilon_2(\omega)\frac{1-3aF(a,\omega)}{1+6a\epsilon_2(\omega)F(a,\omega)}E_0(\omega) , \quad (56)$$

which is in agreement with the result of Ref. 9.

V. NUMERICAL RESULTS

Equation (45) can be used to estimate the nonlinear polarization $P^{(3)}_{\rm NLS}(\omega)$. In this equation two quantities must be calculated: the dipolar susceptibility $\chi^{(3)}_m(\omega,-\omega,\omega)$ of the sphere and the local-field factor $\tilde{f}_1(\omega)$. A calculation of $\chi^{(3)}_m(\omega,-\omega,\omega)$ is performed in Ref. 14 from standard perturbation theory applied to independent electrons in an infinite spherical potential well. To evaluate numerically the factor f_1, we consider the Eqs. (52), (46), and (A3).

Within the local approximation [i.e., Eq. (52)], a Drude dielectric function is used:

$$\epsilon(\omega)=\epsilon_0(\omega)-\frac{\omega_p^2}{\omega(\omega+i\gamma)} , \quad (57)$$

where the complex constant $\epsilon_0(\omega)$ is calculated from the data of Ref. 22 and

$$\gamma=1/\tau+v_F/a . \quad (58)$$

v_F labels the Fermi velocity and τ is a phenomenological relaxation time. It will be chosen about 10^{-14} s for a gold sphere.[22]

The *nonlocal calculation* [Eqs. (46) and (A3) are performed in the framework of the specular reflection theory (cf. Eqs. (53)–(56)]. In fact, within this approximation, we neglect the nondiagonal terms in the matrix $\mathcal{E}(k,k',\omega)$.[9,15] The improved numerical study is left for a forthcoming paper. Moreover, to describe the spatial dispersion effect, we use the hydrodynamic model to express the dielectric constant $\epsilon(k,\omega)$ of the metal:

$$\epsilon(k,\omega)=\epsilon_0(\omega)-\frac{\omega_p^2}{\omega(\omega+i\gamma)-\delta^2k^2} , \quad (59)$$

where $\delta^2=3/5v_F^2$. This equation allows us to evaluate the factor $\mathcal{F}(a,\omega)$ [Eq. (54)] analytically.[9,16] We have then

$$\mathcal{F}(r,\omega=r\left[\frac{1}{\epsilon_0}-\frac{\omega_p^2}{\epsilon_0^2\delta^2\eta^2}\right]+\frac{3a^2\omega_p^2}{\epsilon_0\delta^2\eta^2\sqrt{ar}}I_{3/2}(\eta r)K_{3/2}(\eta a) , \quad (60)$$

where $I_{3/2}$ and $K_{3/2}$ are modified Bessel functions of half-integer order and

$$\eta=\left[\frac{\omega_p^2/\epsilon_0-\omega^2-i\omega/\gamma}{\delta^2}\right]^{1/2} . \quad (61)$$

The above relations (57) to (61) are used to draw the factors f_1, $\tilde{f}_1$ and $\bar{f}_1$ defined by Eqs. (52), (46), and (A3), respectively as a function of the radius for a gold sphere. We have chosen two typical frequencies ω_1 and ω_2 and a surrounding dielectric of index equal to 1.5 (glass).

For the frequency $\omega_1=3.55\times10^{15}$ s^{-1}, we are very close to the surface plasma resonance [when $\mathrm{Re}(\epsilon)\cong-2\epsilon_2$] and $\epsilon_0=10.3+i1.87$.[21]

For the second value $\omega_2=3.37\times10^{15}$ s^{-1}, we have $\epsilon_0=9.93+i1.33$.

Figures 2(a) and 2(b) present the real and the imaginary

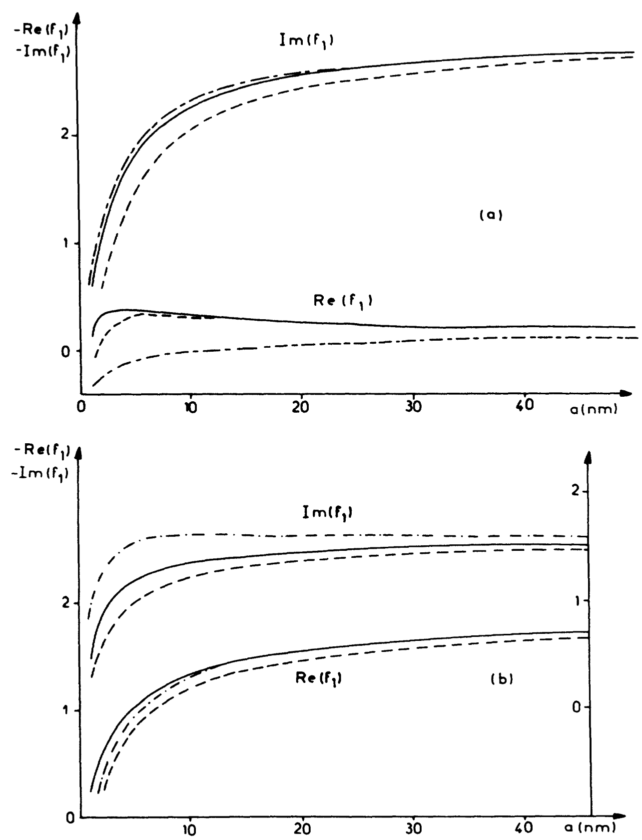

FIG. 2. (a) Real and imaginary parts of the local-field factor calculated for the frequency $\omega_1=3.55\times10^{15}$ s^{-1}. The dot-dashed line corresponds to the local calculations [Eq. (52)], the solid and dotted lines correspond to the nonlocal calculation performed from Eqs. (46) and (A3), respectively. (b) same as (a) for $\omega_2=3.37\times10^{15}$ s^{-1}.

part of the local field factors f_1, $\tilde{f}_1$, and $\bar{f}_1$ calculated for ω_1 and ω_2, respectively. We can observe that the non local character of the response of the metal tends to modify the magnitude of both real and imaginary parts of the local field factors. We remark that the modifications of the real part of f_1 become more important when we are close to the surface plasma resonance [Fig. 2(a)]. This effect corresponds to the blue shift already discussed in hydrodynamical calculations.[23,24] Moreover, the nonlocal corrections in factor f_1 increase for spheres of small size. Thus, the modifications introduced by the screening effects may become important in the magnitude of the intensity of the conjugate signal measured in experiments.[13] Indeed the factor f_1 appears to the eighth power in the expression of this quantity.

VI. CONCLUSION

A general self-consistent treatment of the optical nonlinear response of the electrons confined in a small metallic sphere has been presented here. The screening effect in these metal particles has been introduced within the framework of the RPA theory and the nonlinear response calculation has been performed by using the charge-density susceptibility formalism. Thus, we have expressed the linear polarizability and the third-order nonlinear source polarization $P_{\mathrm{NLS}}^{(3)}$ of the sphere with similar equations to that obtained in recent local calculations. More precisely, we have verified from a microscopic point of view, the validity of the effective dielectric constant model (EDC) introduced recently to calculate $P_{\mathrm{NLS}}^{(3)}$. Moreover, we show as in the EDC approach that the local-field factor f_1 occurs again to the fourth power. The numerical estimates of f_1 have been performed by neglecting the nondiagonal contributions in the generalized dielectric constant $k^{-2}\mathcal{E}(k,k',\omega)$ (SRM approximation). They show that the dispersion spatial effect may become important for spheres of radii lower than 10 nm. We believe that the present approach, under the above restrictive hypothesis, provides a good basis for a simple and comprehensive formulation of the nonlinear processes in the metal colloids. Furthermore, the numerical estimations may be improved by taking into account the nonhomogeneous character of the electronic response contained in the formalism of Secs. II and III.

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APPENDIX

We present in this Appendix an alternative method to define the local-field factor. We first calculate the mean field induced inside the sphere by the external field $E_0(\omega)$:

$$\langle \mathbf{E}_1(\omega)\rangle = -\frac{1}{V}\int_V \nabla\phi_1(\mathbf{r},\omega)d\mathbf{r} \; . \tag{A1}$$

The substitution of Eq. (23) into Eq. (A1), after integration, leads to

$$\langle E_1(\omega)\rangle = \frac{3\epsilon_2(\omega)\mathcal{F}(a,\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)}E_0(\omega) \tag{A2}$$

which corresponds to a local-field factor equal to

$$\bar{f}_1(\omega) = \frac{3\epsilon_2(\omega)\mathcal{F}(a,\omega)}{a+2\epsilon_2(\omega)\mathcal{F}(a,\omega)} \; . \tag{A3}$$

Note that a slightly different definition of the mean field has been proposed in a similar problem by Wiser.[25] In our case, it may be easily verified that, for very small radii a of the sphere, the nonlocal expressions (46) and (A3) become identical:

$$\bar{f}_1(\omega) = \tilde{f}_1(\omega) \quad \text{when } a \to 0 \; . \tag{A4}$$

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