

Optical non-linear response of small metal particles: a complete self-consistent calculation including exchange and correlation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 8035

(<http://iopscience.iop.org/0953-8984/1/43/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 10/05/2010 at 20:40

Please note that [terms and conditions apply](#).

Optical non-linear response of small metal particles: a complete self-consistent calculation including exchange and correlation

F Hache and D Ricard

Laboratoire d'Optique Quantique du CNRS, Ecole Polytechnique, 91128 Palaiseau Cédex, France

Received 10 February 1989, in final form 12 May 1989

Abstract. We report a fully self-consistent calculation of the third-order Kerr polarisation in small metal spheres embedded in a dielectric medium. The random phase approximation with exchange is used leading to a fully symmetric expression accounting for the non-locality of the electronic response as well as exchange and correlation. This treatment generalises the results reported in a previous paper by Hache *et al.* The expression of the octupolar component of the charge density is also given.

1. Introduction

The linear optical properties of small metal particles have been extensively studied [1]. The connection between the absorption spectrum of a metal colloid and the surface plasma resonance [2–4], as well as the broadening of the absorption band when the size of the particles is reduced [5–7] have given rise to a large number of publications. The calculations were first performed assuming independent electrons in the local approximation [8–10] but later papers gave improved treatments taking into account the non-local character of the electronic response [11–13]. A more general situation, including exchange and correlation effects in the calculation of the dynamical polarisability, has also been considered [14].

On the other hand, and more recently, we have performed the first experimental studies of non-linear optical properties (the optical Kerr effect) of gold and silver colloids [15–17] using optical phase conjugation in the degenerate four-wave mixing configuration. A resonant enhancement of the non-linearity was observed in the vicinity of the surface plasma resonance. The enhancement was first interpreted as a local field effect [15], the local field correction being derived from an effective dielectric constant formalism [3] from which the four factors $f_i(\omega)$, where f_1 is the ratio between the field inside and outside the sphere, usually entering the expression of the third-order Kerr non-linear source polarisation $P_{\text{NLS}}^{(3)}(\omega)$ are easily recovered. Of course, such a treatment was obtained assuming a local response of the electrons, the metal sphere being characterised by a dielectric constant $\epsilon_1(\omega)$.

We have recently published [18] an improved treatment taking into account the non-locality of the electronic response, at least in its most important aspects, obtaining a self-consistent expression for $P_{\text{NLS}}^{(3)}(\omega)$. In the present paper, we will refer to [18] as paper I.

The central result, embodied in (43) of I, clearly shows how the externally applied potential is modified and how a fourth factor enters when one examines the field generated outside the sphere by the non-linear polarisation. A numerical comparison between this non-local and the local treatment shows that the consequences of non-locality may be important for very small metal particles [I]. Of course, the local treatment in which the local field factors and the non-linear susceptibility of the metal factorise provides a solid first approximation, especially in the case of intermediate-sized particles [17].

Nevertheless, a self-consistent treatment taking non-locality into account is preferable. From this viewpoint, I suffers from two shortcomings. First, the non-linear charge density $\delta\rho^{(3)}$ is replaced by an equivalent dipole located at the centre of the sphere. And secondly, exchange and correlation effects are not taken into account. The purpose of the present paper is to generalise the treatment given in I by treating the non-linear charge density as such and by taking into account exchange and correlation. As in I, the charge density susceptibility formalism is applied within the random phase approximation (RPA). A jellium model with infinite barriers will be used to describe the electronic properties of the metal [11, 19]. Furthermore, exchange and correlation will be introduced within the local density approximation (LDA) as proposed by Zangwill and Soven [20].

In § 2, the linear response of a spherical particle is treated using the same formalism as in I but with due account of exchange and correlation. In § 3, the dipolar part of the non-linear response is handled along the same lines, leading to a fully symmetric expression for $P_{\text{NLS}}^{(3)}(\omega)$, fully generalising the four local field factors of the local treatment. Section 4 is devoted to a numerical application exemplifying the role of exchange and correlation. The non-linear charge density is also comprised of an octupolar term whose contribution is utterly negligible but whose expression will be given for completeness in the appendix.

2. Linear response

We first consider the linear response of a metallic sphere of radius a embedded in a dielectric medium with real dielectric constant $\epsilon_2(\omega)$. An external electric field \mathbf{E} given by

$$\mathbf{E} = [\mathbf{E}_0(\omega) e^{i\omega t} + \text{cc}] \mathbf{e}_z \quad (1)$$

where \mathbf{e}_z is the unit vector of the Oz axis is applied to the system. The wavelength λ of this field is assumed to be large compared with the sphere radius a so that the electrostatic approximation is valid and the external field appears as the gradient of the potential $\phi_0(\mathbf{r})$

$$\phi_0(\mathbf{r}) = -E_0(\omega) r \cos \theta \quad (2)$$

where $\theta = (\mathbf{e}_z, \mathbf{r})$. We denote $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ the effective potentials inside and outside the sphere.

Following the LDA, ϕ_1 is written

$$\phi_1(\mathbf{r}) = \phi_0(\mathbf{r}) + \phi_c(\mathbf{r}) + \phi_{\text{xc}}(\mathbf{r}) \quad (3)$$

where ϕ_c is the coulombic potential due to the charge density $\delta\rho$

$$\phi_c(\mathbf{r}) = \int_V d\mathbf{r}' \frac{\delta\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (4)$$

V being the volume of the sphere. The sum of ϕ_0 and ϕ_c is the true electric potential $\bar{\phi}_1(\mathbf{r})$ whereas the last term in (3)

$$\phi_{xc}(\mathbf{r}) = \frac{\partial V_{xc}}{\partial \rho} \delta\rho(\mathbf{r}) \quad (5)$$

takes exchange and correlation into account [20]. We thus have

$$\phi_1(\mathbf{r}) = \bar{\phi}_1(\mathbf{r}) + \phi_{xc}(\mathbf{r}). \quad (6)$$

All functions $g(\mathbf{r})$ involved in this and the following section (dipolar terms) are of the form

$$g(\mathbf{r}) = g(r)Y_1^0(\theta, \varphi) \quad (7)$$

and for $r < a$, are then expanded [21] as in I

$$g(\mathbf{r}) = g(r, \theta, \varphi) = \sum_k B_k j_1(kr)Y_1^0(\theta, \varphi)g(k) \quad (8)$$

where j_1 is the spherical Bessel function of first order and the k are chosen so that

$$\left[\frac{dj_1(x)}{dx} \right]_{x=ka} = 0. \quad (9)$$

The constant B_k is given by

$$B_k = \{2a^{-3}[j_1^2(ka) - j_0(ka)j_2(ka)]^{-1}\}^{1/2} \quad (10)$$

and the inverse transform is

$$g(k) = B_k \int_V d\mathbf{r} j_1(kr)Y_1^0(\theta, \varphi)g(\mathbf{r}). \quad (11)$$

In the framework of the RPA with exchange, we can write the induced electric charge density $\delta\rho(\mathbf{r}, \omega)$ as

$$\delta\rho(\mathbf{r}, \omega) = \int_V d\mathbf{r}' \chi_s(\mathbf{r}, \mathbf{r}', \omega)\phi_1(\mathbf{r}', \omega) \quad (12)$$

where χ_s is the linear density-density response function. Transforming (12) in the k representation, we get

$$\delta\rho(k, \omega) = \sum_{k'} \chi_s(k, k', \omega)\phi_1(k', \omega) \quad (13)$$

where

$$\chi_s(k, k', \omega) = B_k B_{k'} \int \int d\mathbf{r} d\mathbf{r}' j_1(kr)j_1(k'r')Y_1^0(\theta, \varphi)Y_1^0(\theta', \varphi')\chi_s(\mathbf{r}, \mathbf{r}', \omega). \quad (14)$$

Using (5), (13) becomes

$$\delta\rho(k, \omega) = \sum_{k'} \chi_s(k, k', \omega) \left[\bar{\phi}_1(k', \omega) + \frac{\partial V_{xc}}{\partial \rho} \delta\rho(k', \omega) \right]. \quad (15)$$

Defining the matrix A

$$A(k, k', \omega) = \delta_{kk'} - \frac{\partial V_{xc}}{\partial \rho} \chi_s(k, k', \omega) \tag{16}$$

equation (15) reads

$$A \delta \rho = \chi_s \bar{\phi}_1 \tag{17}$$

leading to

$$\delta \rho(k, \omega) = \sum_{k'} \bar{\chi}_s(k, k', \omega) \bar{\phi}_1(k', \omega) \tag{18}$$

where the modified susceptibility $\bar{\chi}_s$ is defined as

$$\bar{\chi}_s(k, k', \omega) = \sum_{k''} A^{-1}(k, k'', \omega) \chi_s(k'', k', \omega). \tag{19}$$

We may note that the matrices χ_s and A are symmetric and commute, so that $\bar{\chi}_s$ is symmetric and it can easily be shown that

$$A^{-1} = I + \frac{\partial V_{xc}}{\partial \rho} \bar{\chi}_s \tag{20}$$

where I is the unit matrix.

The self-consistency of the problem is obtained from the Poisson equation

$$\Delta \bar{\phi}_1(r, \omega) = -4\pi \delta \rho(r, \omega) \tag{21}$$

which, in the k representation, reads

$$B_k \int_V d\mathbf{r} j_1(kr) Y_1^0(\theta, \varphi) \Delta_r \bar{\phi}_1(\mathbf{r}, \omega) = -4\pi \delta \rho(k, \omega). \tag{22}$$

The left-hand side is transformed using the second Green identity [I] and, using (18), (22), is solved for $\bar{\phi}_1(k, \omega)$.

$$\bar{\phi}_1(k, \omega) = \bar{\phi}'_1(a, \omega) \sum_{k'} B_{k'} a^2 j_1(k'a) \bar{\mathcal{E}}^{-1}(k, k', \omega) \tag{23}$$

where $\bar{\mathcal{E}}$ is the symmetric matrix

$$\bar{\mathcal{E}}(k, k', \omega) = k^2 \delta_{kk'} - 4\pi \bar{\chi}_s(k, k', \omega). \tag{24}$$

Returning now to the \mathbf{r} representation, we get

$$\bar{\phi}_1(\mathbf{r}, \omega) = \bar{\phi}'_1(a, \omega) Y_1^0(\theta, \varphi) \bar{\mathcal{F}}(\mathbf{r}, \omega) \tag{25}$$

with

$$\bar{\mathcal{F}}(\mathbf{r}, \omega) = a^2 \sum_{k, k'} B_k B_{k'} j_1(kr) j_1(k'a) \bar{\mathcal{E}}^{-1}(k, k', \omega). \tag{26}$$

The potential outside the sphere is

$$\phi_2(\mathbf{r}, \omega) = \phi_0(\mathbf{r}, \omega) + \phi_{2r}(\mathbf{r}, \omega) \tag{27}$$

where the response potential ϕ_{2r} can be written

$$\phi_{2r}(\mathbf{r}, \omega) = \frac{A_0(\omega)}{r^2} Y_1^0(\theta, \varphi). \tag{28}$$

The boundary conditions at $r = a$ apply to the electric part of the potentials, i.e. to $\bar{\phi}_1$ and ϕ_2 , leading to the solution

$$\bar{\phi}'_1(a, \omega) = -E_0 \sqrt{\frac{4\pi}{3}} \frac{3a\epsilon_2(\omega)}{a + 2\epsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)}. \tag{29}$$

We now derive the expressions for $\phi_1(\mathbf{r}, \omega)$ which acts as the effective potential in (12). From (6)

$$\phi_1(\mathbf{r}, \omega) = \bar{\phi}_1(\mathbf{r}, \omega) + \frac{\partial V_{xc}}{\partial \rho} \int_V d\mathbf{r}' \chi_s(\mathbf{r}, \mathbf{r}', \omega) \phi_1(\mathbf{r}', \omega) \tag{30}$$

or, in the k representation,

$$\phi_1(k, \omega) = \bar{\phi}_1(k, \omega) + \frac{\partial V_{xc}}{\partial \rho} \sum_{k'} \chi_s(k, k', \omega) \phi_1(k', \omega) \tag{31}$$

whose solution is

$$\phi_1(k, \omega) = \sum_{k'} A^{-1}(k, k', \omega) \bar{\phi}_1(k', \omega) \tag{32}$$

or

$$\phi_1(k, \omega) = a^2 \bar{\phi}'_1(a, \omega) \sum_{k'} B_{k'} j_1(k''a) \sum_{k''} A^{-1}(k, k', \omega) \bar{\mathcal{E}}^{-1}(k', k'', \omega). \tag{33}$$

Defining

$$\bar{\mathcal{E}}(k, k', \omega) = \sum_{k''} \bar{\mathcal{E}}(k, k'', \omega) A(k'', k', \omega) \tag{34}$$

and back in the \mathbf{r} representation, we get

$$\phi_1(\mathbf{r}, \omega) = \bar{\phi}'_1(a, \omega) \bar{\mathcal{F}}(\mathbf{r}, \omega) Y_1^0(\theta, \varphi) \tag{35}$$

with

$$\bar{\mathcal{F}}(\mathbf{r}, \omega) = a^2 \sum_{k, k'} B_k B_{k'} j_1(kr) j_1(k'a) \bar{\mathcal{E}}^{-1}(k, k', \omega). \tag{36}$$

3. Non-linear response

Among the third-order effects, we concentrate on the degenerate optical Kerr effect with terms oscillating at the frequency ω . In the framework of the charge density susceptibility formalism, the internal potential $\phi_1(\mathbf{r}, \omega)$ induces a non-linear variation of the electronic charge density

$$\begin{aligned} \delta\rho^{(3)}(\mathbf{r}, \omega) &= \iiint_V d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \rho \chi^{\rho+\rho+\rho}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \omega, -\omega, \omega) \\ &\times \phi_1(\mathbf{r}_1, \omega) \phi_1^*(\mathbf{r}_2, \omega) \phi_1(\mathbf{r}_3, \omega) \end{aligned} \tag{37}$$

where ${}^{\rho}\chi^{\rho+\rho+\rho}$ is the third-order density susceptibility. The angular dependence of $\delta\rho^{(3)}$ is $\cos^3\theta$ which, since

$$\cos^3\theta = \frac{3}{5}P_1(\cos\theta) + \frac{2}{5}P_3(\cos\theta)$$

where the P_n are the Legendre polynomials, means that $\delta\rho^{(3)}$ is comprised of a Y_1^0 (dipolar) term and a Y_3^0 (octupolar) one. In this section, we concentrate on the dominant dipolar term (the octupolar one is considered in the appendix) and use the same expansion as in § 2.

The presence of $\delta\rho^{(3)}$ slightly modifies the linear density to $\delta\tilde{\rho}$, the internal potential to $\tilde{\phi}_1$, with its pure electric part $\tilde{\phi}_1$. Equation (15) is modified to

$$\delta\tilde{\rho}(k, \omega) = \sum_{k'} \chi_s(k, k', \omega) \left(\tilde{\phi}_1(k', \omega) + \frac{\partial V_{xc}}{\partial \rho} [\delta\tilde{\rho}(k', \omega) + \delta\rho^{(3)}(k', \omega)] \right) \quad (38)$$

leading to

$$\delta\tilde{\rho}(k, \omega) = \sum_{k'} \tilde{\chi}_s(k, k', \omega) \tilde{\phi}_1(k', \omega) + \sum_{k'} \frac{\partial V_{xc}}{\partial \rho} \tilde{\chi}_s(k, k', \omega) \delta\rho^{(3)}(k', \omega). \quad (39)$$

Using Poisson's equation

$$\Delta \tilde{\phi}_1(\mathbf{r}, \omega) = -4\pi[\delta\tilde{\rho}(\mathbf{r}, \omega) + \delta\rho^{(3)}(\mathbf{r}, \omega)] \quad (40)$$

and proceeding as in § 2, we get

$$-k^2 \tilde{\phi}_1(k, \omega) + 4\pi[\delta\tilde{\rho}(k, \omega) + \delta\rho^{(3)}(k, \omega)] + B_k a^2 j_1(ka) \tilde{\phi}'_1(a, \omega) = 0 \quad (41)$$

whose solution is, using (39) and (20),

$$\begin{aligned} \tilde{\phi}_1(k, \omega) &= \sum_{k'} a^2 B_{k'} j_1(k'a) \tilde{\mathcal{E}}^{-1}(k, k', \omega) \tilde{\phi}'_1(a, \omega) \\ &+ 4\pi \sum_{k', k''} \tilde{\mathcal{E}}^{-1}(k, k', \omega) A^{-1}(k', k'', \omega) \delta\rho^{(3)}(k'', \omega) \end{aligned} \quad (42)$$

which may be rewritten, since $\tilde{\mathcal{E}}$ and A are symmetric, as

$$\begin{aligned} \tilde{\phi}_1(k, \omega) &= a^2 \tilde{\phi}'_1(a, \omega) \sum_{k'} B_{k'} j_1(k'a) \tilde{\mathcal{E}}^{-1}(k, k', \omega) \\ &+ 4\pi \sum_{k'} \delta\rho^{(3)}(k', \omega) \tilde{\mathcal{E}}^{-1}(k', k, \omega). \end{aligned} \quad (43)$$

Back in the \mathbf{r} representation, we get for $\phi_1(a, \omega)$ which is the quantity we need for the boundary conditions:

$$\tilde{\phi}_1(a, \omega) = \tilde{\phi}'_1(a, \omega) \tilde{\mathcal{F}}(a, \omega) + \frac{4\pi}{a^2} \int_V d\mathbf{r}' \delta\rho^{(3)}(\mathbf{r}', \omega) Y_1^0(\theta', \varphi') \tilde{\mathcal{F}}(\mathbf{r}', \omega). \quad (44)$$

The first term on the right hand side of (44) leads to the same response potential

ϕ_{2r} as previously (see (28)) whereas the non-linear charge density (the second term) generates an extra potential $\phi_{2m}(\mathbf{r}, \omega)$ outside the sphere of the following form:

$$\phi_{2m}(\mathbf{r}, \omega) = \frac{A_1}{r^2} Y_1^0(\theta, \varphi) \tag{45}$$

where A_1 is calculated using the boundary conditions

$$A_1 = \frac{4\pi a}{a + 2\varepsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)} \int_V d\mathbf{r}' \delta\rho^{(3)}(\mathbf{r}', \omega) Y_1^0(\theta', \varphi') \bar{\mathcal{F}}(\mathbf{r}', \omega). \tag{46}$$

ϕ_{2m} may be considered as being generated by a non-linear dipole moment $m^{\text{NLS}}(\omega)$

$$\phi_{2m}(\mathbf{r}, \omega) = \frac{1}{\varepsilon_2(\omega)} \frac{m^{\text{NLS}}(\omega) \cos \theta}{r^2}. \tag{47}$$

Now, the non-linear source polarisation $P_{\text{NLS}}^{(3)}(\omega)$ of a composite medium containing N spheres per unit volume is

$$P_{\text{NLS}}^{(3)}(\omega) = N m^{\text{NLS}}(\omega) \tag{48}$$

and using (46), (37), (35) and (29), we obtain the central result of this paper:

$$\begin{aligned} P_{\text{NLS}}^{(3)}(\omega) = & -N \left(\frac{3a\varepsilon_2(\omega)}{a + 2\varepsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)} \right)^2 \left| \frac{3a\varepsilon_2(\omega)}{a + 2\varepsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)} \right|^2 \iiint \iiint_V d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \\ & \times \rho\chi^{\rho+\rho+\rho}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \omega, -\omega, \omega) \bar{\mathcal{F}}(r, \omega) \bar{\mathcal{F}}(\mathbf{r}_1, \omega) \bar{\mathcal{F}}^*(\mathbf{r}_2, \omega) \bar{\mathcal{F}}(\mathbf{r}_3, \omega) \\ & \times \cos \theta \cos \theta_1 \cos \theta_2 \cos \theta_3 |E_0(\omega)|^2 E_0(\omega). \end{aligned} \tag{49}$$

This expression is completely self-consistent and takes exchange and correlation into account through the matrix A . It clearly shows how the applied potential is multiplied by the correction factor

$$\frac{3a\varepsilon_2(\omega)}{a + 2\varepsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)} \frac{\bar{\mathcal{F}}(r, \omega)}{r}$$

and how the fourth (identical) factor is introduced, leading to a fully symmetric result, which was not the case with (43) of I. The only approximations involved in the present calculation are the RPA, the LDA and the infinite barrier. Of course, to proceed further, a tractable expression for $\rho\chi^{\rho+\rho+\rho}$ is required. It could for example be calculated following the density-functional formalism proposed by Senatore and Subbaswamy [22]. Equation (49) contains as limiting cases: the treatment neglecting exchange and correlation, the homogeneous non-local (Lindhard [23]) case and the local case. In the local case for example, $\bar{\mathcal{F}}(r, \omega)$ and $\bar{\mathcal{F}}^*(r, \omega)$ are equal to $r/\varepsilon_1(\omega)$.

4. Numerical application

The linear response, as well as the non-linear response of a small metal particle, involves the ‘local field factor’ which connects the outer and the mean inner electric field. This factor is very important since it is at the origin of the surface plasmon resonance which gives rise to an absorption peak in metal colloids. Due to the occurrence of this factor at the fourth power in its expression, the non-linear response is also drastically increased

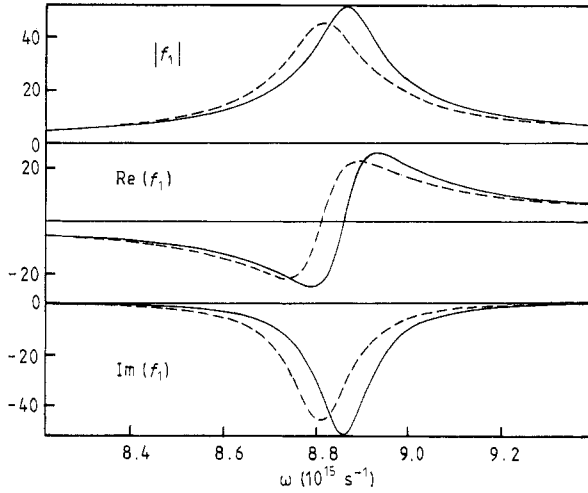


Figure 1. Modulus, real part and imaginary part of the 'local field factor' as a function of the frequency: non-local calculation with (f_{1xc} : full curves) and without (f_1 : broken curves) introduction of exchange correlation.

at this resonance frequency. In the case of very small spheres (a few tens of angströms), this resonance frequency is very sensitive to non-local effects and, in this section, we calculate numerically this factor as a function of the frequency of the electromagnetic field with and without introducing the exchange-correlation potential. In the first case, we have:

$$f_{1xc} = \frac{3\bar{\bar{\mathcal{F}}}(a, \omega)}{a + 2\bar{\bar{\mathcal{F}}}(a, \omega)}$$

and in the second case (I):

$$f_1 = \frac{3\mathcal{F}(a, \omega)}{a + 2\mathcal{F}(a, \omega)}$$

where

$$\mathcal{F}(r, \omega) = a^2 \sum_{k, k'} B_k B_{k'} j_1(kr) j_1(k'a) \mathcal{E}^{-1}(k, k', \omega).$$

To calculate \mathcal{F} , $\bar{\mathcal{F}}$, and $\bar{\bar{\mathcal{F}}}$, we use the non-local homogeneous approximation for which the matrix \mathcal{E} (equation (16) of I) reads:

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

We use for $\epsilon(k, \omega)$ the exact expression of the Lindhard dielectric constant [23] and perform the summation over 20 values of k . We have followed Zangwill and Soven [20] to introduce the exchange-correlation potential with, in the case of gold or silver, $r_s = 3$. Figure 1 shows the factors f_{1xc} (full curves) and f_1 (broken curves) as a function of the frequency ω for a 10 Å metal sphere. The surface plasmon resonance appears quite clearly. Before commenting on these curves, let us recall that the non-local calculation leads to a blue shift of this resonance: indeed, with a local calculation, the resonance occurs at $7.95 \times 10^{15} \text{ s}^{-1}$. The magnitude is also reduced (by nearly a factor of 2). We

can see in figure 1 that the introduction of an exchange-correlation potential slightly shifts the resonance towards the high frequencies, increasing the non-local blue shift, whereas the amplitude of the resonance is increased, reducing the decrease observed in non-local calculations. Though rather weak, the effect of exchange correlation should be taken into account in a careful analysis.

5. Conclusion

In summary, we have extended the previous results obtained in I by giving a complete, fully symmetric self-consistent expression for the third-order non-linear polarisation $P_{\text{NLS}}^{(3)}(\omega)$ of a metal colloid within the random phase approximation with exchange. We thus allow for the non-local response of the electrons in the metal sphere and also take exchange and correlation into account within the local density approximation framework. The properties of the electron gas then enter through the density–density susceptibility $\chi_s(\mathbf{r}, \mathbf{r}', \omega)$ and the exchange-correlation potential $\partial V_{\text{xc}}/\partial\rho$. The result we thus obtain is fairly general.

Appendix

The self-consistent problem and the boundary conditions being linear, the octupolar part of $\delta\rho^{(3)}$ may be treated independently. Since now the relevant functions are of the form

$$g_3(\mathbf{r}) = g_3(r)Y_3^0(\theta, \varphi) \tag{A1}$$

they can be expanded, when $r < a$, as

$$g_3(\mathbf{r}) = \sum_h C_h j_3(hr)Y_3^0(\theta, \varphi)g_3(h) \tag{A2}$$

where j_3 is the spherical Bessel function of third order and the h are chosen so that

$$\left[\frac{dj_3(x)}{dx} \right]_{x=ha} = 0. \tag{A3}$$

The constant C_h is

$$C_h = \{2a^{-3}[j_3^2(ha) - j_2(ha)j_4(ha)]^{-1}\}^{1/2} \tag{A4}$$

and the inverse transform is

$$g_3(h) = C_h \int_V d\mathbf{r} j_3(hr)Y_3^0(\theta, \varphi)g_3(\mathbf{r}). \tag{A5}$$

The susceptibility $\chi'_s(h, h', \omega)$ is defined similarly to $\chi_s(k, k', \omega)$:

$$\chi'_s(h, h', \omega) = C_h C_{h'} \int \int d\mathbf{r} d\mathbf{r}' j_3(hr) j_3(h'r') Y_3^0(\theta, \varphi) Y_3^0(\theta', \varphi') \chi_s(\mathbf{r}, \mathbf{r}', \omega) \quad (\text{A6})$$

and the quantities equivalent to $\bar{\mathcal{F}}$ and $\bar{\mathcal{F}}^*$ are denoted $\bar{\mathcal{G}}$ and $\bar{\mathcal{G}}^*$. The octupolar moment is obtained from the potential outside the sphere which is of the form

$$\delta\phi_2 = \frac{1}{\varepsilon_2(\omega)} \frac{o^{\text{NLS}}}{r^4} \sqrt{\frac{4\pi}{7}} Y_3^0(\theta, \varphi). \quad (\text{A7})$$

The octupolar density $O_{\text{NLS}}^{(3)}(\omega) = No^{\text{NLS}}$ is then obtained as

$$\begin{aligned} O_{\text{NLS}}^{(3)}(\omega) = & -Na^2 \frac{7a\varepsilon_2(\omega)}{a + 4\varepsilon_2(\omega)\bar{\mathcal{G}}(a, \omega)} \frac{3a\varepsilon_2(\omega)}{a + 2\varepsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)} \left| \frac{3a\varepsilon_2(\omega)}{a + 2\varepsilon_2(\omega)\bar{\mathcal{F}}(a, \omega)} \right|^2 \\ & \times \int \int \int \int d\mathbf{r} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \chi^{\rho+\rho+\rho}(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \omega, -\omega, \omega) \\ & \times \bar{\mathcal{G}}(\mathbf{r}, \omega) \bar{\mathcal{F}}(\mathbf{r}_1, \omega) \bar{\mathcal{F}}^*(\mathbf{r}_2, \omega) \bar{\mathcal{F}}(\mathbf{r}_3, \omega) P_3(\cos \theta) \\ & \times \cos \theta_1 \cos \theta_2 \cos \theta_3 |E_0(\omega)|^2 E_0(\omega). \end{aligned} \quad (\text{A8})$$

The octupolar contribution to the radiated wave is much weaker than the dipolar one first because of a factor $\kappa^2 a^2$ where $\kappa = 2\pi/\lambda$ in the equivalent source term and secondly because the fourth factor which appears in (A8) is not resonant at the same frequency as the other three. In the local approximation, $\bar{\mathcal{G}}(\mathbf{r}, \omega)$ and $\bar{\mathcal{G}}^*(\mathbf{r}, \omega)$ reduce to $r^3/3\varepsilon_1(\omega)a^2$.

References

- [1] Perenboom J A A J, Wyder P and Meier F 1981 *Phys. Rep.* **78** 173
- [2] Mie G 1908 *Ann. Phys., Lpz* **25** 377
- [3] Maxwell-Garnett J C 1904 *Phil. Trans. R. Soc. London* **203** 385; 1906 **205** 237
- [4] Kreibig U and Zacharias P 1970 *Z. Phys.* **231** 128
- [5] Doyle W J 1958 *Phys. Rev.* **111** 1067
- [6] Doremus R H 1964 *J. Chem. Phys.* **40** 2389; 1965 **42** 414
- [7] Kreibig U and Fragstein C V 1969 *Z. Phys.* **224** 307
Kreibig U 1970 *Z. Phys.* **234** 307; 1974 *J. Phys. F: Met. Phys.* **4** 999; 1977 *J. Physique* **38** C2-97
- [8] Kawabata A and Kubo R 1966 *J. Phys. Soc. Japan* **21** 1765
- [9] Ruppin R and Yatom H 1976 *Phys. Status Solidi b* **74** 647
- [10] Genzel L, Martin T P and Kreibig U 1975 *Z. Phys.* **B 21** 339
- [11] Dasgupta B B and Fuchs R 1981 *Phys. Rev. B* **24** 554
- [12] Wood D M and Ashcroft N W 1982 *Phys. Rev. B* **25** 6255
- [13] Zaremba E and Persson B N J 1987 *Phys. Rev. B* **35** 596
- [14] Ekardt W 1984 *Phys. Rev. Lett.* **52** 1925
- [15] Ricard D, Roussignol P and Flytzanis C 1986 *Opt. Lett.* **10** 511
- [16] Hache F, Ricard D and Flytzanis C 1986 *J. Opt. Soc. Am.* **B 3** 1647
- [17] Hache F, Ricard D, Flytzanis C and Kreibig U 1988 *Appl. Phys. A* **47** 347
- [18] Hache F, Ricard D and Girard C 1988 *Phys. Rev. B* **38** 7990
- [19] News D M 1970 *Phys. Rev. B* **1** 3304
- [20] Zangwill A and Soven P 1980 *Phys. Rev. A* **21** 1561
- [21] Girard C and Hache F 1987 *Chem. Phys.* **118** 249
- [22] Senatore G and Subbaswamy K R 1987 *Phys. Rev. A* **35** 2440
- [23] Lindhard J 1954 *K. Dan. Vidensk. Selsk. Mat-Fys Medd* **28** no 8