

# Theoretical study of nonlocal effects in the optical response of metallic nanoshells

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## ABSTRACT

The optical response of metallic nanoshell which includes coated dielectric particles is investigated in the long-wavelength limit in which the nonlocal response of the metal is taken into account. Using our recent formalism which calculates the nonlocal multipole polarizability of such a shell, we have studied how these nanoshells interact with both the far field and near field of a light source. For the far field case, both absorption and scattering cross sections for an incident plane wave are calculated in the dipole approximation. For the near field case, we study how the fluorescence properties of an emitting molecule in the vicinity of a nanoshell are affected, by including all higher multipolar response of the shell. It is found that the nonlocal effects are most prominent for higher order multipoles, and hence for the description of molecules in close proximity interacting with the nanoshell.

**Keywords:** nanoshell, nonlocal effects, near field

## 1. INTRODUCTION

Of the many exciting recent developments in the study of plasmonics from metallic nanostructures [1], the metallic nanoshell stands out as a unique system and has been very actively studied in the past decade [2-12]. This is due both to the capability of these shells in enhancing various optical processes, as well as the high tunability in their plasmon resonance frequencies via the control of the shell thickness relative to the size of the core. Experimentally, both dielectric [2-4] and hollow [5,6] cores can be fabricated using methods of colloidal chemistry. Furthermore, by varying the metal shell thickness towards the thin shell limit (in the order of a few nm), the plasmon frequency can be adjusted across the whole visible spectrum --- from near UV to near IR [3].

Theoretically, most of the previous investigations on the optical property of this system have applied classical electrodynamics in the form of the Mie scattering theory [3,4,10-12], although in a few cases microscopic theory such as the time-dependent density functional theory (TDDFT) has also been formulated [7,8]. While the Mie approach is

limited to the bulk dielectric response of the nanoshell, the previous application of TDDFT is mostly limited to dipolar response of the system, as in the study of the photoabsorption by these shells [7,8]. It will be therefore of interest if one can investigate the optical response of these nanoshells to all order of multipoles, accounting for the microscopic quantum mechanical nature of the metallic electrons in these systems. Among the various microscopic effects, we shall here emphasize the nonlocal response effects which become prominent when the surface-to-volume ratio of the system increases as the size of the system shrinks. Another surface effect which has been found significant in these systems is the interface scattering between the metallic electrons and the shell boundaries. This can lead to a damping rate in the dielectric function much greater than the one for bulk metals in case of good conductors (e.g. Ag) and thin shells of nanometer thickness, and can often be accounted for in a semi-empirical way in the process of fitting experimental data [4,12], although microscopic theories also exist in the literature which predict significant effects due to the dielectric properties of the environment in which the nanoshell is situated [13]. Since our interest here is mainly in exploring the significance of the nonlocal effects *relative* to the local dielectric response theory, we shall simply follow the semi-empirical approach by re-parametrizing the damping constant ( $\Gamma$ ) in the local (Drude) model by using  $\Gamma = \Gamma_{\text{BULK}} + Av_F/d$ , where the second term accounts for the interface scattering rate with  $v_F$  the Fermi velocity,  $d$  the shell thickness, and  $A$  an adjustable geometric factor. Note that this phenomenological surface-scattering term will be included *both* in the local and nonlocal models in our following study.

We have recently formulated a nonlocal theory for the multipole polarizability of a metallic nanoshell [14], in an approach parallel to the previous theory of Fuchs and Claro (FC) for a spherical particle [15]. In the following, we shall first give a brief summary of our results obtained in Ref. [14], and then apply them to study the fluorescence characteristics of an emitting molecular dipole in the vicinity of such a nanoshell. As we shall see, in the description of the molecule-nanoshell interaction, the near field plays a significant role and all the multipolar response of the nanoshell must be accounted for. It turns out that it is in the higher multipolar interaction that the nonlocal effects will become most prominent, as will be illustrated by our following numerical examples.

## 2. BRIEF SUMMARY OF PREVIOUS RESULTS

Consider a spherical shell of inner radius  $a$  and outer radius  $b$ , respectively, as shown in Fig. 1. We assume the region outside the shell ( $b < r$ ) is vacuum and the inner core ( $r < a$ ) is filled with a dielectric of dielectric constant  $\epsilon'$ , while the shell region ( $a < r < b$ ) is filled with metal described by a nonlocal dielectric function  $\epsilon(\vec{k}, \omega)$  which is both temporal and spatial dispersive. In a recent work, we have applied the so-called semi-classical infinite barrier (SCIB) model [15], and obtained the following results for the nonlocal  $\ell^{\text{th}}$  multipole polarizability of a nanoshell [14]:

$$\alpha_\ell = - \left( \frac{l\beta + b\gamma}{(l+1)\beta - b\gamma} \right) b^{2l+1} \equiv \Delta_\ell b^{2l+1}, \quad (1)$$

where the quantities  $\beta$  and  $\gamma$  are defined as follows:

$$\beta = l \frac{a^{l+1}}{b^{l-1}} F(a,b) + (l+1)b^2 F(b,b) + \frac{2}{\pi} \epsilon' ab^2 l(2l+1) [F(a,a)F(b,b) - F(a,b)F(b,a)],$$

(2)

$$\gamma = \frac{\pi l(l+1)}{2} \frac{1}{2l+1} \left[ \left( \frac{a}{b} \right)^{2l+1} - 1 \right] - \varepsilon' a l^2 F(a, a) - \varepsilon' l(l+1) \frac{a^{l+1}}{b^l} F(b, a), \quad (3)$$

and the function  $F(x, y)$  is defined as in Ref.15 in the form of an integral:

$$F(x, y) = \int \frac{j_l(kx) j_l(ky)}{\varepsilon(k, \omega)} dk, \quad (4)$$

with  $j_l$  being the spherical Bessel function. Note that by setting the inner radius  $a = 0$  in the above results, one obtains back the results for a solid nanosphere which were first derived in the previous work by Fuchs and Claro [15]. On the other hand, in the local limit, we have:

$$F(x, y) \rightarrow \frac{1}{\varepsilon} \int j_l(kx) j_l(ky) dk = \frac{\pi}{2\varepsilon(2l+1)} \frac{x^l}{y^{l+1}}, \quad (5)$$

and one can show that the result in Eq. (1) indeed reduces back to the one from a local response theory with the factor  $\Delta_l^L$  given by:

$$\Delta_l^L = \frac{(\varepsilon - \varepsilon')l[l + \varepsilon(l+1)]a^{2l+1} + l(1 - \varepsilon)[\varepsilon' l + \varepsilon(l+1)]b^{2l+1}}{(\varepsilon - \varepsilon')(\varepsilon - 1)l(l+1)a^{2l+1} - (\varepsilon' l + \varepsilon(l+1))b^{2l+1}}. \quad (6)$$

Note that by using the undamped Drude model for  $\varepsilon$ , the poles of Eq.(6) yield the following quadratic equation for the plasmon resonance frequencies of the nanoshell:

$$\left[ 2l^2(\varepsilon' + 1) + l(\varepsilon' + 3) + 1 \right] y^3 - \left[ (\varepsilon' - 1)l(l+1)X^{2l+1} + l^2(\varepsilon' + 3) + 4l + 1 \right] y - l(l+1)(X^{2l+1} - 1) = 0 \quad (7)$$

where  $\sqrt{y} = \left( \frac{\omega_l}{\omega_p} \right)$  is the  $l^{\text{th}}$ -multipole resonance frequency normalized to the bulk plasmon frequency of the metal,

and  $X \equiv a/b$  is the ratio of the two radii. In the limit for a hollow metallic nanoshell,  $\varepsilon' = 1$  and the solution to (7) leads back to the well-known results for the plasmon frequencies in the local theory as follows [7]:

$$\omega_{l\pm}^2 = \frac{\omega_p^2}{2} \left[ 1 \pm \frac{1}{2l+1} \sqrt{1 + 4l(l+1) \left( \frac{a}{b} \right)^{2l+1}} \right]. \quad (8)$$

The two modes  $\omega_{l\pm}$  corresponds to the antisymmetric (+) and symmetric (-) coupling between the sphere and cavity modes, respectively, and can be accounted for by a plasmon hybridization model [16]. Eq. (8) shows clearly the tunability of the resonance frequency in terms of the geometrical parameters. Furthermore, by filling the inside with a dielectric, this tunability can be made even more versatile to cover a broader range of frequencies.

We have studied numerically the above nonlocal (NL) optical effects as implied by Eqs. (1) – (4) by calculating the photoabsorption, scattering, and extinction cross sections of a Ag nanoshell of a few diameters in sizes [14] and have come to the following conclusions: (1) these NL effects are significant for shells of size as small as 3nm and/or shell thickness  $\sim 1$ nm; (2) these effects are observable even in the presence of large scattering effects between the metallic

electrons and the shell interfaces; and (3) these effects are especially prominent when higher multipolar interactions are involved between the light source and the nanoshell. In Fig. 2 we show separately the absorption and scattering efficiency for a Ag-glass nanoshell with  $a = 2.5\text{nm}$  and  $b = 3.0\text{nm}$ . Note that extinction is dominated by absorption for a shell of such a small dimension. In addition, we have also studied the NL effects on the plasmon resonant frequencies as predicted by Eq. (7) for this nanoshell. The results are reproduced in Fig. 3, where we have computed the results using both the hydrodynamic and Lindhard-Mermin dielectric functions [see, e.g., Ref. 15] in Eq. (4) above, and compared the results with those obtained from the Drude model in the local description of the metal of the nanoshell. The significance of our conclusion in (3) above is evident from these results.

### 3. MOLECULAR FLUORESCENCE IN THE PROXIMITY OF A NANOSHELL

Previously, we have limited ourselves to the study of how optical far-fields interact with the nanoshell in which the various cross-sections were calculated in the long-wavelength approximation. Because of this approximation, mainly the dipolar response of the nanoshells has been included in our previous study of the NL effects [14]. However, as discussed above, the NL effects are most significant in the higher multipolar responses of the shell, we shall here extend our study to the near-field interaction between the light source and the shell. To this end, we have here studied the modifications of various fluorescence properties of an emitting molecular dipole in the vicinity of such a nanoshell. The corresponding problem with a metallic nanosphere replacing the shell has been studied previously by both the TDDFT [17] and SCIB [18] approaches, significant deviations were found compared to those results obtained from a classical Drude description of the metallic response.

According to a well-known phenomenological model [18], for an emitting molecular dipole interacting with a substrate structure, the decay and modified emission frequency of the molecule can be expressed by the following equations, with the results normalized to the natural decay rate of the system:

$$\Gamma/\Gamma_0 = 1 + \frac{3q}{2k^3} \text{Im}(G), \quad (9)$$

$$\Delta\omega/\Gamma_0 = -\frac{3q}{4k^3} \text{Re}(G), \quad (10)$$

where  $q$ ,  $\Gamma_0$  and  $k$  are respectively the quantum yield, natural decay rate and the natural emission wave number of the molecule. In Eqs. (9) and (10), the  $G$  factor is defined as

$$G = \sum_l \Delta_l \frac{f_l b^{2l+1}}{r^{2l+4}}, \quad (11)$$

with  $f_l = (l+1)^2$  [ $f_l = l(l+1)/2$ ] for tangential [radial] dipole and  $r$  being the radial coordinate of the molecule. It should be noted that in the  $G$  factor, the polarizabilities of multipoles for all orders are taken into account, and numerically we have to sum over sufficient number of terms to reach to a converged value. In Fig. 4, we present the calculated modified decay rate and emission frequency-shift as functions of the natural frequency of the molecule with  $r = 4.0\text{nm}$ ,  $a = 2.5\text{nm}$  and  $b = 3.0\text{nm}$ . Although the results of the two nonlocal theories including the hydrodynamic and Lindhard-Mermin models are very close, one can observe their distinct feature compared to Drude model. The shallow dip at  $\omega = 0.6\omega_p$  ( $\omega = 0.75\omega_p$ ) for local (nonlocal) cases in Fig. 4a corresponds to the gap between symmetric and antisymmetric modes illustrated in Fig. 3. Since the calculation here involves the overall contributions from all higher order multipoles, the "peaks" in the spectrum are not as distinct as those in the simple

dipole spectrum for the absorption/extinction coefficients. Rather, they will depend on the relative contribution of each of the multipole terms." In Fig 4b a corresponding behavior of variation can be seen as well. One should note that the detailed information of each multipole is not manifested due to the large damping constant because we choose  $A = 1.0$ . In addition the frequency-shift in the local case (Fig. 4b) turns positive when the natural frequency is higher than all the plasmon modes. In the nonlocal case, however, the antisymmetric modes have resonance frequency too high to allow such change to occur in the range of frequency we consider. In Fig. 5, the decay rate and frequency-shift are shown as functions of the position of the molecule, for radial dipoles and natural frequency  $\omega = 0.7\omega_p$ . One can easily observe the extremely sensitive change of the results with position as well as large deviation between local and nonlocal results.

#### 4. SUMMARY

In this paper, we have investigated the far field as well as near field response of a metallic nanohell. We found that the nonlocal effects manifested not only in the extinction coefficient of the nanoshell, but also more significantly in the radiation properties of a molecule in the vicinity of the nanoshell.

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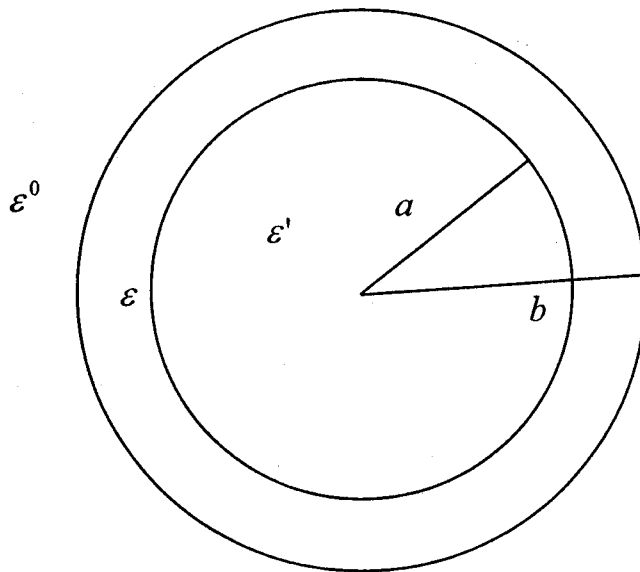


Fig. 1 The geometry of a nanoshell with inner radius  $a$  and outer radius  $b$ . Note that we have considered a vacuum environment ( $\epsilon^0 = 1$ ) in all our calculations.

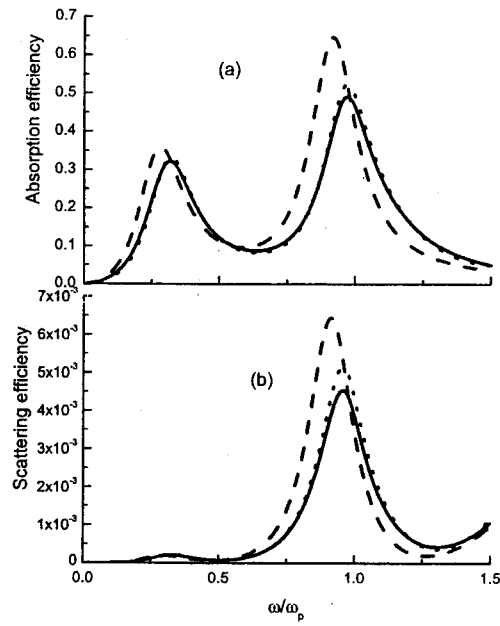


Fig. 2 (a) Absorption efficiency and (b) scattering coefficient for a nanoshell with  $a = 2.5nm$  and  $b = 3.0nm$  evaluated by Drude model (dashed line), hydrodynamic model (dotted lines), and Lindhard-Mermin model (solid lines).

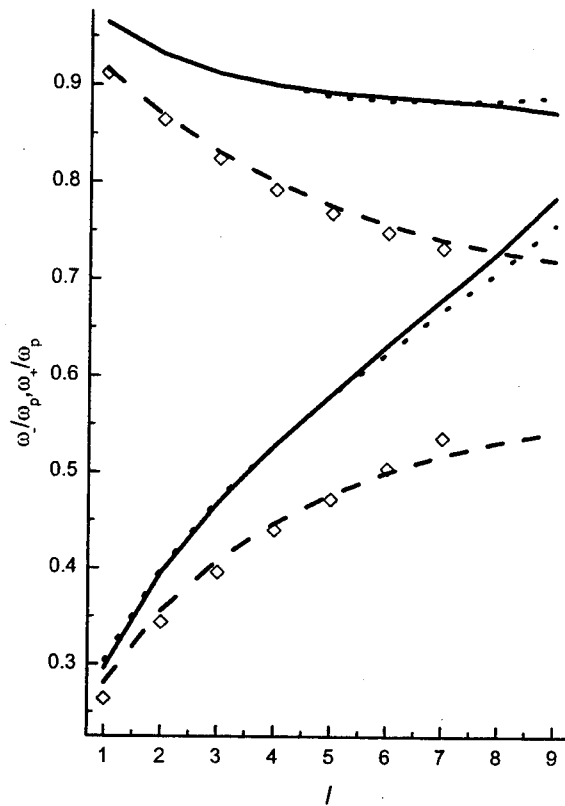


Fig. 3 The two surface plasmon mode frequencies for a Ag-glass nanoshell with outer radius  $b = 3.0$  nm and inner radius  $a = 2.5$  nm evaluated by Drude model (hollow diamond), hydrodynamic model (dotted lines), and Lindhard-Mermin model (solid lines) as functions of the multipolar order  $l$ . Also shown (dashed lines) are the results for the ideal Drude case (without damping) as obtained from Eq. (7).



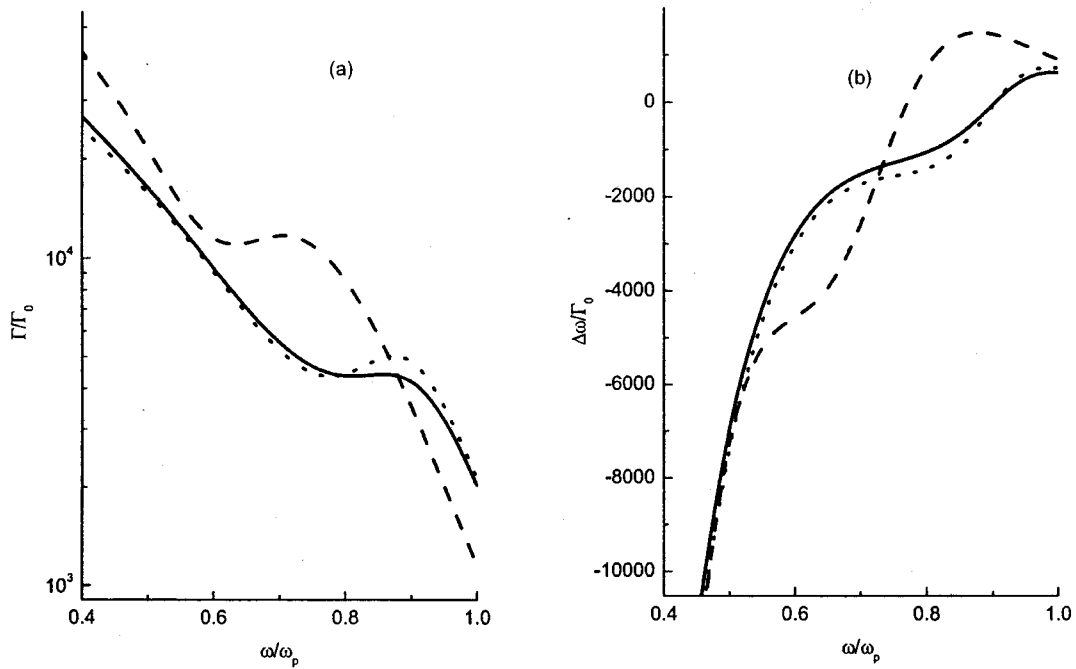


Fig. 4 Calculated (a) decay rate (b) frequency-shift as functions of natural frequency of a molecule with radial coordinate  $r = 4.0nm$ . The shell has  $a = 2.5nm$  and  $b = 3.0nm$ . Results from different models are labeled in the same way as in Fig. 2

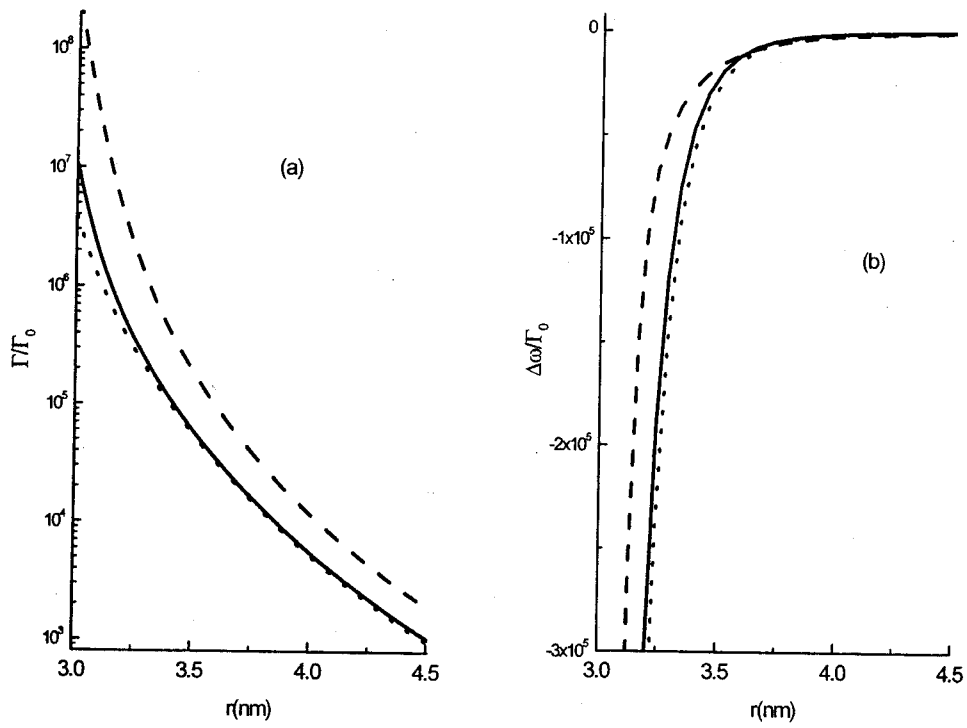


Fig. 5 Calculated (a) decay rate (b) frequency shift as functions of the position of a molecule with natural frequency  $\omega = 0.7\omega_p$ . The shell has  $a = 2.5nm$  and  $b = 3.0nm$  .. Results from different models are labeled in the same way as in Fig. 2