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Influence of the confinement potential on the size-dependent optical response of metallic nanometric particles

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ABSTRACT

In this paper, different confinement potential approaches are considered in the simulation of size effects on the optical response of silver spheres with radii at the few nanometer scale. By numerically obtaining dielectric functions from different sets of eigenenergies and eigenstates, we simulate the absorption spectrum and the field enhancement factor for nanoparticles of various sizes, within a quantum framework for both infinite and finite potentials. The simulations show significant dependence on the sphere radius of the dipolar surface plasmon resonance, as a direct consequence of energy discretization associated to the strong confinement experienced by conduction electrons in small nanospheres. Considerable reliance of the calculated optical features on the chosen wave functions and transition energies is evidenced, so that discrepancies in the plasmon resonance frequencies obtained with the three studied models reach up to above 30%. Our results are in agreement with reported measurements and shade light on the puzzling shift of the plasmon resonance in metallic nanospheres.

1. Introduction

In the last decade, metallic nanoparticles have drawn attention because of their boundary-located excitations originated from conduction electrons, so-called Localized Surface Plasmon Resonances (LSPRs) [1–4]. Those LSPRs are widely understood in terms of collective oscillations of the conduction electron gas, and their frequencies typically lie in the terahertz range [5–7].

Considerable experimental and theoretical efforts in this energy range have been made to fully understand the physics underlying the optical response of those structures since applications encompass diverse fields such as cancer therapy [8], nanophotonic devices [9–11], biosensing [12], and catalysis [13,14], among others [15–17].

Nowadays, light absorption and scattering are well-known to depend on the material, size and shape of the nanoparticles, because of the increment of the surface to volume ratio [18–21]. However, experimental difficulties in classifying and isolating such small structures on the one hand, and the computationally demanding atomistic calculations in this regime where the number of atoms is at the order of 10^2–10^3, on the other hand, make the characterization of that dependence a challenging problem.

Regarding the size dependence of the LSPRs in metallic nanospheres, Scholl et al. reported few years ago a strongly fluctuating behavior in the 1–5 nm radius range, as observed by using Electron Energy-Loss Spectroscopy (EELS) [22]. That unexpected result was later challenged by H. Haberland [23], and Kisma et al. [24], by basically arguing that the asymptotic regime (where quantum confinement effects start being negligible) is valid for diameters as low as 2 nm or less.

In this work, we perform a computationally inexpensive method to study the optical response of silver nanoparticles in this controversial size range, articulating classical electrodynamics (pertinent because of the very high number of photons involved in the related experimental set-ups), with a quantum treatment of the conduction electrons.

We calculate dielectric functions under three different approaches for the confining potential representing the nanospheres. Significant quantitative differences among the optical responses obtained from those approaches are observed, although the results from all three models are found qualitatively consistent with the available experimental measurements.

The paper is structured as follows: In the first part, the theoretical framework underlying the calculations is provided. In the second part, we present the numerical simulation results and a discussion. Concluding remarks are drawn at the last part.

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2. Theoretical framework

We carry out the simulations in two fundamental stages: first, we obtain the dielectric function for each of the confinement models, and then we calculate two physical observables (absorption cross section and field enhancement), associated to each of those potentials.

2.1. Dielectric function

When a charge carrier is trapped in a region of size at the order of the corresponding de Broglie's wavelength (nanometric scales for conventional materials), values of energy allowed for that particle are discrete and spectral continuity cannot be considered anymore [25,26]. This is the case for conduction electrons in metallic nanospheres. That makes any classical model used in describing the electron gas response to exciting radiation, to fail at some point under reduction of the metal size. However, what that limit is, persists as a matter of debate [22,24].

Experimentally, contrastive behaviors between the 10–100 nm and the 1–10 nm regimes have been reported [22,27,28]. However, independent computational studies in that later regime are scarce because it is simultaneously too big for atomistic calculations [24], and too small for a continuous classical modeling [29].

Free electron approaches as the Drude and the hydrodynamical models, which considers the valence electrons as classical particles, are the most widely used to obtain the dielectric function of metal nanoparticles [30–35]. However, a quantum model seems more appropriate for studying electrons in nanometric structures [29,36].

In this study, we use a dielectric function first introduced by Cini and Ascarelli [37], that considers the charge carriers as quantum particles subject to spatial trapping. Accordingly, the dielectric function of a single metallic nanoparticle under the influence of an electromagnetic wave with frequency ω is given by

$$\epsilon(\omega) = \epsilon_\infty + \frac{\omega_p^2}{N} \sum_{i,f} \frac{s_{if}(F_i - F_f)}{\omega_{if}^2 - \omega^2 - i\omega\gamma_{if}}, \tag{1}$$

where ϵ_∞ is the interband contribution of core electrons, $\omega_p = \left(\frac{4\pi ne^2}{m*}\right)^{(1/2)}$ is the bulk plasmon frequency, N is the total number of conduction electrons (in silver, the same as the number of atoms in the nanoparticle), and ω_{if} and γ_{if} are respectively, the frequency and damping for a transition from an initial state i to a final state f. Temperature dependence is included through F_i and F_f which are the Fermi–Dirac distribution values for the initial and final states [27]. The oscillator strength for the transition between states $|i\rangle$ and $|f\rangle$ is defined as

$$s_{if} = \frac{2m_0\omega_{if}}{\hbar} |\langle f|z|i\rangle|^2, \tag{2}$$

where $|\langle f|z|i\rangle|$ is the corresponding transition dipole moment, under z-linearly polarized incident light [38].

Fig. 1(a) presents a schematic diagram of the excitation process and the corresponding stimulated transitions between single particle populated and unoccupied discrete energy states. This model neglects the correlation effects, which in the considered size regime are expected to exist but not to dominate. Hence, the Schrödinger equation for the electron conducting gas is solved in the non-interacting approach, i.e. in the one electron picture.

Since the eigenenergies and eigenstates of the electron are required for the calculation of the dielectric function, its particular features are expected to depend significantly on the potential used to model the carrier confinement. Then, details of the different cases studied in these calculations are presented in the next subsection.

2.2. Spherical confinement

Atomistic calculations in small silver clusters show that their shapes are well described as icosahedra or decahedra [39]. However as the particle size increases, their geometries exhibit more facets, ultimately resembling spheres [40]. According to Figure 3 in Ref. [22], for a radius larger than 1 nm, the spherical approximation fits well the nanoparticle shape.

In this work, the dielectric functions for the various studied sizes are obtained within three different approaches for the spherical confining potential, namely: (A) infinite confinement with asymptotic eigenenergies and wave functions, (B) infinite confinement with exact eigenenergies and wave functions, and (C) finite confinement with numerical eigenenergies. The first two models share the infiniteness of the potential barrier modeling the particle boundary, while the last two share the accuracy in the energy values.

2.2.1. Infinite confinement

The hard-wall spherical well is one of the few potentials with an exact known solution. Hence, given the shape of the nanostructures under study, plus the assumption of an absolutely impenetrable barrier, the wave functions and allowed energies of a conduction electron of effective mass m^* confined in a particle of radius R, are, respectively,

$$\psi_{n,l,m}(r,\theta,\phi) = \frac{1}{|j_{l+1}(\alpha_{nl})|}\sqrt{\frac{2}{R^3}} j_l\left(\frac{\alpha_{nl}}{R}r\right) Y_l^m(\theta,\phi) \tag{3}$$

and

$$E_{n,l} = \frac{\hbar^2\alpha_{ln}^2}{2m^*R^2}, \tag{4}$$

where j_l represents the lth spherical Bessel functions, Y_l^m the standard spherical harmonics, and α_{nl} the nth zero of j_l [41].

Thus, the eigenenergies and eigenfunctions of each electron in the non-interacting conduction gas are in principle fully determined, so that the necessary oscillator strengths and transition energies for the dielectric function can be obtained. However, because there is not a recurrent relation between zeros of spherical Bessel function with different l, the calculation results at last in a numerical problem.

As proposed in Ref. [22], the asymptotic approximation that provides wave functions and energies in a compact form, can be used to simplify the calculations. Within such an approximation [42], the spherical Bessel functions appearing in Eq. (3) and the eigenenergies in Eq. (4) are correspondingly reduced to

$$j_l(x) \approx \frac{1}{x}\cos\left[x - \frac{\pi}{2}(l+1)\right] \tag{5}$$

and

$$E_{n,l} = \frac{\hbar^2}{2m^*R^2}\left[\pi\left(n + \frac{l}{2} + 1\right)\right]^2. \tag{6}$$

Using the approximation given by Eqs. (5) and (6), straightforward calculation of the dielectric function can be carried out at a minimum computational cost. Nevertheless, a price is paid in accuracy because these expressions are only suitable for small l and $x \gg l^2/2 + l$ [41] [model (A)], as can be seen in Table 1, where we present a comparison between energies given by Eq. (4) with the corresponding ones from Eq. (6) for a nanoparticle of radius $R = 1$ nm. Complete agreement is observed for $l = 0$, whereas a noticeable overestimation by the approximation becomes significant as l increases.

Fig. 1(b) shows $j_l(\alpha_{ln}r/R)$ and its asymptotic approximation [Eq. (5) into Eq. (3)], as functions of the normalized radius for different values of l ($n = 1$). It is worth to note that for $l = 0$ both

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