Near field enhancement due to the optical response of small nanoparticles

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In this work, we propose to describe the behavior of the optical response of small metal nanoparticles (particles below 10 nm of radius) as a function of size. We use classical models as well as quantum approaches to study the nanoparticles dielectric function in the whole range of nanometers using two infinite confinements, cubic and spherical, which are simple enough to obtain information of the quantum size effects on the optical response, measured on the enhancement field factor and absorption spectra, to find the limit of pure classical models at the nano-scale finding out enhancement factors of the order of $10^3$ for small silver nanoparticles. We confirm the plasmon resonance frequency through the absorption spectra, besides that, we have studied the role played by Localized Surface Plasmon Resonance (LSPR) in small metal nanoparticles as a function of the particle size and the environment, which are in good agreement with reported experiments and have found a limit of the classical behavior of small nanoparticles.
I. INTRODUCTION

Nano-Plasmonics studies the optical properties of nanostructured materials based on the study of the interaction of an external electric field or electron charged beams with an interface dielectric-metal. The response of the conduction electrons of a nano-material is a collective resonant motion, called Localized Surface Plasmon Resonance (LSPR) which depends both on geometrical and compositional factors as the size, composition, shape, number of nanoparticles and the dielectric environment [1–4] as well as the nature of the incident light, e.g. polarization, intensity and wavelength. Although for nanoparticles of tens of nanometers in size, this behavior is well understood, for particle sizes smaller than 10 nm, there is controversy about the origin of reported LSPR blueshifts as the particle size decreases below 10 nm. Due to the length scale of nanometers, this is an interesting open problem that is worth to be carefully examined. One possible explanation is quantum size effect, which takes into account the discretization of energy levels [5–7] and therefore improve the actual description of the optical response of small nanoparticles, making classical theories insufficient for explaining several phenomena that appear due to the nature of nanoscopic systems. The main interest in understanding the plasmonic resonances of small nanoparticles lies in the physics of the limit between classical and quantum descriptions and therefore in its applications in biology, catalysis and quantum optics.

The plasmonic effect on isolated nanoparticles under the influence of a longitudinal polarized electromagnetic wave, produces a strong electric near field enhancement, which can be related to the incident electric field, known as the enhancement field effect [8], and gives information about the LSPR. Recently, EELS experiments [5] on single metal nanoparticles, corroborate the blueshifts of the LSPR as the particle size decreases.

In this work, we propose to improve the description of the optical response of the small nanoparticles, which determines the values of the optical constants to be used in the solution of the Maxwell equations to obtain the near field enhancement and the optical absorption. In particular, particle sizes smaller than 10 nm are of special interest due to their natural quantum features that make them an important subject to understand the limit of pure classical phenomena, where it is found that the ratio surface-volume plays a crucial role.
II. CLASSICAL DIELECTRIC OPTICAL RESPONSE

The classical dielectric function of a metal, can be described by a simplified model where the conduction electrons are considered like a free electron gas with a number $n$ of charges per volume unit moving on a background of positive ion cores. Based on a classical motion equation for an electron in a plasma, under the influence of an external electric field and assuming a harmonic response, the dielectric function as a function of the oscillation frequency of the external field for a free electron gas is given by

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega}, \quad (1)$$

where $\omega_p$ represents the bulk plasma frequency defined by $\omega_p^2 = ne^2/\epsilon_0 m$. The term $\gamma = 1/\tau$ corresponds to a damping collision frequency in terms of the relaxation time of the free electron gas $\tau$. By means of the dielectric function defined in (1), one can obtain the refractive index $\eta$ (related with the polarization), and the extinction coefficient $\kappa$ of a system (related with the optical absorption) through the equations

$$\eta^2 = \frac{\epsilon_1}{2} + \frac{1}{2} \sqrt{\epsilon_1^2 + \epsilon_2^2} \quad (2)$$

and

$$\kappa = \frac{\epsilon_2}{2n}, \quad (3)$$

These last two quantities are of great importance, due that these have all the optical information we can include as input parameters in the subsequent simulations.

III. QUANTUM APPROACHES

A. Free electron gas in a cubic infinite box

When the size of a particle becomes smaller, the continuous electronic band of a nanoparticle should break up into observable discrete states. Such effects have been observed in experiments with thin films and metallic nano-particles [5–7], showing a notably difference between the results obtained for light-mater interaction in the quasi-static regime (particles until 10-100 nm of radius) and the quantum regime (particles below 10nm of radius). As a first approximation, to describe the optical response of a valence electron gas in a metal nanoparticle, Genzel and Martin [6] showed a
simplified quantum model where the free (valence) electron gas is confined in a cubic potential well with infinite sides, where the dielectric function of a single metal nanoparticle is given by

$$\epsilon(\omega) = \epsilon_\infty + \frac{\omega_p^2}{N} \sum_{i,f} \frac{s_{if}(F_i - F_f)}{\omega^2_{if} - \omega^2 - i\omega \gamma_{if}},$$  \hspace{1cm} (4)$$

where the terms $s_{if}$, $\omega_{if}$ and $\gamma_{if}$ are respectively, the oscillator strenght, the eigen-frequency and the damping for the dipole transition from an initial state $i$ to another, final state $f$ and $F_i$ and $F_f$ are the values of the Fermi-Dirac distribution function for the initial and final states. The oscillator strenght $s_{if}$ corresponds to the dipolar form in the $z$-direction in terms of the initial $|i\rangle$ and final $|f\rangle$ states

$$s_{if} = \frac{2m\omega_{if}}{\hbar} |\langle f|z|i\rangle|^2.$$  \hspace{1cm} (5)$$

with the parameter $m = M/N$ in terms of the mass of electron $M$ and the atom valence number $N$. Using the orthogonallity of eigen-functions, the term $\omega_{if}$, can be written by

$$\omega_{if} = \Delta l(2l + \Delta l) \frac{E_0}{\hbar}.$$  \hspace{1cm} (6)$$

If only transitions in the $z$ direction is considered, $s_{if}$ takes the form

$$s_{if}^2 = \frac{64}{\pi^2} \frac{l^2(l + \Delta l)^2}{\Delta l^3(l + \Delta l)^3} \delta(h_i, h_f) \delta(k_i, k_f),$$  \hspace{1cm} (7)$$

where $\{h, k, l\}$ are the set of quantum numbers associated to each direction $\{x, y, z\}$ in the momenta space. Due to the form of the eigen-functions in this type of confinement potential, the number of dipole transitions in the sum of the dielectric function depends only on the initial and final values of the quantum number $l$ corresponding solely to initial states within the Fermi surface through final states just outside the Fermi surface, $l_F$.

The final expression for the dielectric function obtained in [6] (in which only transitions with $\Delta l = 1$ are considered) reads

$$\epsilon(\omega) = \epsilon_\infty + \omega_p^2 \sum_{\Delta l} \frac{1}{\sum_l} \frac{S_{l,\Delta l}}{\omega_{l,\Delta l}^2 - \omega^2 - i\omega \gamma_{l,\Delta l}},$$  \hspace{1cm} (8)$$

where

$$S_{l,\Delta l} = \frac{32}{\pi l_F} \frac{l^2(l + \Delta l)^2}{\Delta l^2(l + \Delta l)^2}.$$  \hspace{1cm} (9)$$

Using eq.(8), we plot the real and imaginary parts of the dielectric function vs. the incident photon energy for nanoparticles with $L = 1.6, 3.6, 4.8, 6.4, 8$ and $16 \text{ nm}$ (we can relate the lenght of the cube $L$ with the radius of a nanosphere by the expresion $L = (\frac{4\pi}{3})^{1/3}R$), comparing with the classic
Drude approach given by eq. (1) in the case of \( L = 16 \text{nm} \) (see Fig.1). We observe that the dielectric functions predicted by the quantum model disagree notably with the classical results in the range studied. The main difference is that both \( \Re[\epsilon] \) and \( \Im[\epsilon] \) exhibit a nonmonotonic behavior according to the quantum model, versus the monotonic response using classical Drude theory. However, as the length reaches the limit of 16 nm, the agreement with the classical description is good.

### B. Free electron gas in a spherical infinite well

Considering the derivation made for Scholl et al., where the conduction electrons are considered as a free electron gas constrained by an infinite spherical potential well, the corresponding transition frequencies \( \omega_{if} \) of conduction electrons from occupied states \( i \) to unoccupied states \( f \) immediately outside of it from eq.(5) are defined by \( \omega_{if} = \frac{E_f - E_i}{\hbar} \), where \( E_i \) and \( E_f \) are the initial and final energies, respectively, with associated initial \( |i\rangle \) and final \( |f\rangle \) states.

Solving the corresponding Schrödinger equation, for an electron constrained to a spherical potential, with the appropriate boundary conditions we obtain a set of wavefunctions of the form

\[
\psi(r, \theta, \phi) = \frac{1}{|j_{l+1}(\alpha_{nl})|} \sqrt{\frac{2}{R^3}} j_l \left( \frac{\alpha_{nl} R}{R} \right) Y^m_l(\theta, \phi),
\]

where, \( j_l \) represents the spherical Bessel functions, \( Y^m_l \) the standard spherical harmonics, and \( \alpha \) is a zero of \( j_l \). The energy eigen-values \( E \) for this problem results in a quantized form associated to the \( l \)th spherical Bessel function by the expression

\[
E = \frac{\hbar^2 \alpha^2_{nl}}{2MR^2},
\]

where \( \alpha_{ln} \) is the \( n \)th zero of \( j_l \), i.e. \( j_l(\alpha_{ln}) = 0 \) for \( n = 0, 1, 2, \ldots \). The oscillator strenght of eq.(5) can be calculated, taking \( z = r \cos \theta \) in the expression

\[
|\langle f|z|i\rangle| = \int_0^{2\pi} \int_0^\pi \int_0^R r^2 \sin \theta dr d\theta d\phi \Psi^*_n f_{l_f m_f}(r, \theta, \phi) r \cos \theta \Psi_{n_i l_i m_i}(r, \theta, \phi),
\]

where the angular integral has the form

\[
I_{ang} = \sqrt{\frac{(l_i + m_i + 1)(l_i - m_i + 1)}{(2l_i + 1)(2l_i + 3)}} \delta_{l+1,l} + \sqrt{\frac{(l_i + m_i)(l_i - m_i)}{(2l_i + 1)(2l_i - 1)}} \delta_{l-1,l}
\]

and, the radial term,

\[
I_{rad} = \frac{1}{|j_{l+1}(\alpha_{nl})|} \frac{1}{|j_{l+1}(\alpha_{nl})|} \left( \frac{2}{R^3} \right) \int_0^R dr j_{l_f} \left( \frac{\alpha_{nl} R}{R} \right) r^3 j_l \left( \frac{\alpha_{nl} R}{R} \right).
\]
Then, the integral to calculate is simply

\[ |\langle f|z|i\rangle| = \frac{I_{\text{ang}}}{|j_{l_f+1}(\alpha_{n_f i_f})||j_{l_i+1}(\alpha_{n_i i_i})|} \left( \frac{2}{R^3} \right) \int_0^R dr j_{l_f}(\frac{\alpha_{n_f i_f}}{R} r) r^3 j_{l_i}(\frac{\alpha_{n_i i_i}}{R} r), \tag{15} \]

which is different to zero only for values between \( \Delta l = l_f - l_i = \pm 1 \).

One simple form to calculate the allowed energies in this problem \[5\] is to take the approximate solution for the Bessel zeros \( \alpha \)

\[ E = \frac{\hbar^2 \pi^2}{8MR^2} (2n + l + 2)^2, \]
\[ = \frac{\hbar^2}{2MR^2} \left[ \pi \left( n + \frac{l}{2} + 1 \right) \right]^2, \tag{16} \]

and for the wavefunctions, to employ the asymptotic approximation \[9\]

\[ j_l(x) \approx \frac{1}{x} \cos \left[ x - \frac{\pi}{2}(l + 1) \right], \tag{17} \]
valid only for \( x \gg l^2/2 + l \).

|   | \( n = 0 \) | \( n = 1 \) | \( n = 2 \) | \( n = 3 \) | \( n = 4 \) |
|---|-----|-----|-----|-----|-----|
| \( l = 0 \) | 376.03 | 1504.11 | 3384.25 | 6016.45 | 9400.71 |
| \( l = 1 \) | 769.26 | 2273.77 | 4530.04 | 7538.31 | 1129.86 |
| \( l = 2 \) | 1265.57 | 3151.57 | 5785.61 | 9170.69 | 13307.4 |
| \( l = 3 \) | 1860.45 | 4134.43 | 7148.86 | 10912.1 | 15426.0 |
| \( l = 4 \) | 2550.93 | 5219.83 | 8617.81 | 12760.9 | 17653.2 |

**TABLE I.** Comparison between energies given by eq.(11) upper and by eq.(16) lower in units of meV when \( R = 1 \) nm for various values of \( l \) and \( n \).

In order to compare the exact expression with the approximation given in reference \[5\], we compare the energies given by eq. \( (11) \) and eq.(16) for \( R = 1 \)nm in Table. \[1\] where we observe a good
agreement only for \( l = 0 \), and a significant overestimation for \( l > 0 \). Besides this, in Figure 2 we show \( j_l(kr) = j_l(\alpha_n r/R) \) and its asymptotic approximation given by eq. (17) versus \( r/R \) and \( n = 1 \). As we can see, the asymptotic approximation and the Bessel functions are identical for \( l = 0 \), but the approximation deviates remarkably from the actual function when \( l = 1, 2, \) and \( 3 \). Recall that this deviation occurs for \( r/R < 1 \), i.e. inside the nanosphere. Therefore, we conclude that the asymptotic approximation in eq. (17) is not acceptable to describe the wavefunction of a free electron inside metallic nanospheres.

Using a similar treatment as in the infinite cubic confinement potential, we calculate the real and imaginary parts of the dielectric function vs. the incident light energy for a nanosphere varying its radius from 1 to 10 nm (see Fig 3) where the dielectric functions predicted by the quantum model disagree notably with the classical results in the radius range studied (given by eq.(1)). The main difference is that both \( \Re[\epsilon] \) and \( \Im[\epsilon] \) exhibit a nonmonotic behavior according to the quantum model, as well as in the cubic case, due mainly to the natural chosen confinement potential and the number of states involved adequately.

IV. ENHANCEMENT FIELD FACTOR AND ABSORPTION SPECTRA FOR SMALL NANOPARTICLES

The interaction of metallic nanoparticles with an electromagnetic wave, produces an enormous near field, which can be calculated solving the Maxwell equations in matter. Generally in literature it is usually incorrect to use the bulk optical constants to define the nature of matter, at least for particles below 10 nm of radius, when the quantum nature is evident. Accordingly, to solve the problem of light-nanoparticle interaction, we use the analytical expressions of \( \eta \) and \( \kappa \) previously calculated for each particle size and confinement potential to solve the vector Maxwell equations numerically, by means of a standard finite elements method (FEM). We define the enhancement field factor (EFF) as the norm of the ratio between the scatter electric near field just in the north pole of the spherical nanoparticle \( \vec{E}_{out} \) and an incident \( z \)-polarized electric field \( \vec{E}_{inc} \) (see sketch in Figure 4).

\[
EFF = \frac{|\vec{E}_{out}|^2}{|\vec{E}_{inc}|^2}
\]  

(18)

For an isolated silver particle with different sizes \( (R = 1, 2, 3, 4, 5 \) and 10 nm), we compare the solu-
tions for three different sets of optical constants, which are taken as input parameters. Firstly, we use bulk optical constants taken from experiments of Johnson and Christie [10], where we observe the EFF increase with the nanoparticle size, due to the higher charge concentration, as usually in a classic framework without any resonance energy shift (Figure 5.a). Secondly, we show the EFF for a single silver nano-particle using the infinite cubic confinement potential (Figure 5b), and finally (Figure 5c) the infinite spherical confinement potential. For the last two cases, we observe a fine structure in the plasmonic resonance when the particle size decreases and the resonance shows a blue shift around of $1 - 1.5 \text{eV}$. This fine structure appearance is a consequence of the transitions between discrete electronic states and the blue shift is due to strong near field effect, which increases as the particle decreases. This new feature indicates a more energetic plasmon for smaller particles, as seen in Figure 5b. We also show the comparison of EFF for a single particle $R = 10 \text{ nm}$ using Drude parameters and quantum parameters. The last one shows a slightly blue shift and EFF twice greater than in the former. However, for smaller particles, the EFF decreases and blue-shifts remarkably for the cubic confinement.

The nanoparticle of $R = 2 \text{ nm}$ under the quantum confinement potential, does not show a definite maximum, as expected, instead of it, appear many little transitions in the range from 3.5 to 5 eV. The 1 nm particle has again a higher peak to 4 eV but still has a minor peaks at 6 and 7 eV, corresponding to electronic transitions. The region between $R = 3$ and 2 nm is a frontier where the surface reaches the main importance and the optical response is dominated by the electronic transitions at the Fermi level, while for smaller particles the strong confinement makes again the core electrons to respond to the external perturbation, although in a weaker way due to the small number of charges present. For $R = 2 \text{ nm}$ the competition between surface and volume is clear. Recently R. C. Monreal et. al. [11] discuss the influence of quantum size effect in small Ag nanoparticles as a competition to the spill out that can move the surface plasma energy toward the red or the blue. In our work we suppose infinite potential and therefore neglect the spill out effect, however we find the competition between surface and volume processes at very small nanoparticles. These spectra are in good agreement with the results found in reference [5], although clearly we see that the use of an infinite spherical potential gives us a richer structure in both EFF and absorption spectra (see Figure 6), besides showing the blue shifts as a function of nanoparticle size. The use of a cubic potential confinement allows to know the experimental blue shift in the plasmon resonance, but does not have the same rich structure than the spherical. This can be interpreted as a consequence
of the high degenerance in the cubic case.

Figure 6 also shows the resonance value from each absorption spectra for both confinement potential (cubic and spherical), dependent on the surrounding environment: air, with refractive index \( n = 1.0 \) and SiO (glass) with \( n = 1.5 \), in which we observe that the LSPR in both spectra change significantly with this parameter, showing that in the glass case, the plasmon resonance values are more defined and follow a well marked tendency relative to real experiments (see [5] and [11]).

We conclude that independent from the confinement used to obtain the values of the dielectric function the size effect is important for plasmon formation in small nanoparticles making clear a frontier between \( R \sim 3, 4 \) nm. Another considerations related with the ratio Surface/Volume (S/V) should bring understanding of the origin of the plasmon formation. The S/V ratio increases from 6\% (\( R = 10 \)nm) to 60\% (\( R = 1 \) nm). Between \( R = 2 \) nm and \( R = 1 \) nm this ratio doubles. In following table we see the relationship between R and the ratio S/V. The collective plasmonic behavior is seen for S/V less than 15\%. This ratio maintains under 50\% for \( R < 4 \) nm up to \( R = 2 \)nm. In this range there is a competition between surface and volume effects, but for \( R = 1 \) nm the percentage of surface electrons is 60\% and definitely the surface effects dominate.

| \( R \) (nm) | 1 nm | 2 nm | 3 nm | 4 nm | 5 nm | 10 nm |
|-------------|------|------|------|------|------|-------|
| S/V         | 60   | 30   | 20   | 15   | 12.5 | 6     |

TABLE II. Percentage surface-volume ratio Vs. nanoparticle (sphere) radius.

For \( R = 1 \) nm, where 60\% of the atoms are at the surface, the response comes mainly from the surface, while for \( R = 2 \)nm at the surface are only 30\% and the electronic transitions are strong enough to absorb the energy of the field.

V. CONCLUSIONS

We present a mathematically more detailed quantum description of the dielectric response for small metal nanoparticles (less than 10 nm) using two different confinement potentials. We study the optical response of isolated nanoparticles as a function of particle size, by obtaining the enhance-
ment near field factor and absorption spectra. For small particles, we can see a richer spectrum in the optical response, that can be described as a consequence of the evident quantum nature at the nanoscale.

We also present the localized surface plasmon resonance in small nanoparticles as a function of size, carrying out a finite elements method to solve the complete vector Maxwell equations. We can conclude that the use of a cubic potential confinement, allows to explain the experimental blue shift in its plasmon resonance. Because we study spherical nanoparticles is physically meaningful the use of spherical confinement, so we found in this case a better description of the electronic transitions in addition to the blueshift. However, the spherical confinement should be more precise physically and therefore the appearance of electronic transitions become clear.

We obtain plasmon resonance energy as function of diameter of nanoparticles in good agreement with up to now reported experiments. Therefore our calculation shows that the simple models that take into account confinement explain satisfactorily the optical behavior of small nanoparticles, and allow us to fix a limit for diameters between 2 and 4 nm as the frontier between classical and quantum behavior. Effects such as spill out recently reported are important and we are now working on it.

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FIG. 1. a) Real and b) imaginary parts of the dielectric function for a silver nanoparticle of length \( L = 1.6, 3.6, 4.8, 6.4, 8 \) and 16 nm. using an infinite cubic confinement potential.

FIG. 2. Comparison between \( j_l \) and its asymptotic approximation \([17]\) versus \( r/R \) for different \( l \)'s and \( n = 1 \).
FIG. 3. a) Real and b) imaginary parts of the dielectric function for a silver nanoparticle of radius $R = 1, 2, 3, 4, 5,$ and 10 nm using an infinite spherical confinement potential.

FIG. 4. Sketch of the calculation of the enhancement field factor.

FIG. 5. Enhancement field factor (EFF) for a single metallic nanosphere using the bulk optical constants in a), infinite cubic potential in b) and infinite spherical potential in c). We compare in a) and b) with the classical result (Drude). Inset in b): Quantum results for $R = 1, 2$ and 5 nm. In all cases, we have a refraction index of the surrounding medium $n_m = 1$. 
FIG. 6. Absorption spectra for a silver nanoparticle using the optical constants from the quantum model: Infinite cubic potential (a and b) and infinite spherical potential (c and d) for different particle sizes (L=1.6, 3.2, 4.8, 6.4, 8 and 16 nm and R=1, 2, 3, 4, 5 nm and 10 nm). The graphs a) and c) correspond to a refractive index of surrounding medium $n = 1.0$ and the graphs b) and d) to $n = 1.5$. 