Quantum optical response of metallic nanoparticles and dimers

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The optical properties of metallic nanoparticles (NPs) can be described with analytical models based on fundamental quantum mechanical principles, of which the Drude model constitutes the classical limit. Here, we examine the plasmonic properties of silver and gold nanospheres and dimers, with radii ranging from 10 to 1 nm, extending from the classically described regime to the quantum size regime. We have studied the spectral extinction cross section by using the T-matrix method. The results indicate an increasingly substantial change in NP permittivity as the radius is reduced below 5 nm, showing a clear blueshift and weakening of the plasmon resonances for both silver and gold. As a consequence, we observe a dramatic change in the interaction of dimers, especially in the case of gold, where the introduction of quantum mechanically corrected optical properties quenches the plasmonic resonance and predicts an absence of the expected associated redshift.

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The remarkable growth of nanotechnology has been driven by the ability to alter material properties as dimensions are reduced toward the atomic scale. Nanomaterials exhibit physical and chemical properties very different from those of their bulk counterparts, often resulting from enhanced surface interactions or quantum confinement. Therefore, the plasmonic properties of particles in the quantum size regime (radii below 10 nm) have recently received a renewed attention [1], fueled by the race of technologies toward the low nanoscale domain. For instance, it has been shown that cancer treatments based on delivering drugs using nanoparticles (NPs) with radii below 10 nm showed better antitumor efficiency than those using larger particles [2].

Concerning the interaction between metallic NPs, it has also attracted a good deal of interest for the past 10 years. The physics of this interaction is rich and opens nice perspectives for applications, such as single molecule detection [3,4], solar cells [5], or high harmonic generation [6]. Although the plasmon hybridization model [7] is an elegant physical picture of this interaction, in order to properly calculate the optical response of a dimer, numerical simulations are still needed.

In this Letter, we examine the plasmonic properties of both individual nanospheres and dimers made of silver and gold, with radii ranging from 10 to 1 nm, extending from the classically described regime to the quantum size regime. For all dimer cases, the minimum gap considered has been $l_{\mathrm{gap}} = 1$ nm. Very recently, Esteban *et al.* [8] and Savage *et al.* [9] have successfully described the coupling across subnanometer gaps with a quantum-corrected model that includes electron tunneling and tunneling resistivity at the gap. According to Fig. 2 from [8], the electron tunneling transmission vanishes when the gap is larger than ≈8 Å. Then, from 1 nm on, quantum corrections are required due to the size of the particles only. We have studied the spectral extinction cross section by using the T-matrix method [10,11], one of the most powerful and widely used tools for accurately computing light scattering by nonspherical particles, both single and aggregated, based on directly solving Maxwell's equations.

To model the optical properties of quantum-sized plasmonic particles, a revised expression for the permittivity is required. In our analysis, the standard Drude model is recast with Lorentzian terms that are defined quantum mechanically (QM), based on fundamental physical phenomena, such as electron transition frequencies ω_{if} and oscillator strengths S_{if}, treating the relevant conduction electrons as a free electron gas constrained by infinite potential barriers at the physical edges of the particle [12]. Classically, Lorentzian terms can be added to the Drude expression to account for the nearly free nature of electrons in the bulk metal. Here, rather than using Lorentzians to fit the bulk data [13,14], we employ them to explain the changing dielectric function as particle diameter decreases to the quantum size regime. The overall permittivity expression can then be described as follows [12]:

$$\varepsilon(\omega) = \varepsilon_{\mathrm{IB}} + \omega_p^2 \sum_i \sum_f \frac{S_{if}}{\omega_{if}^2 - \omega^2 - i\gamma\omega}, \qquad (1)$$

where $\varepsilon_{\mathrm{IB}}$ is a frequency-dependent correction term to account for the contribution of the d-band valence electrons to interband transitions at higher energies, ω_p is the plasma frequency (9.01 eV/$\hbar$ for silver [1] and 9.01 eV/$\hbar$ for gold [15]), and γ is the scattering frequency, dependent on the nanosphere dimension (particle radius) and the empirical constant γ_{bulk} (0.016 eV/$\hbar$ for silver [1] and 0.07 eV/$\hbar$ for gold [15]).

Figure 1 shows the real and imaginary parts of the relative electric permittivity of silver as we increase the particle radius, for three different energies of the incident radiation. The values of the electric permittivity have been calculated following Eq. (1). A clear convergence to the bulk values (Johnson and Christy [16] and Palik [17]) is observed. The inset of Fig. 1 clearly shows how at $R = 10$ nm the QM-corrected results already converge to bulk results, except for the remain of a small bump belonging to the series of period ≈2 nm.

We now focus on single particles as well as dimers of radius $R = 4$ nm, made of silver and gold. The dimers are

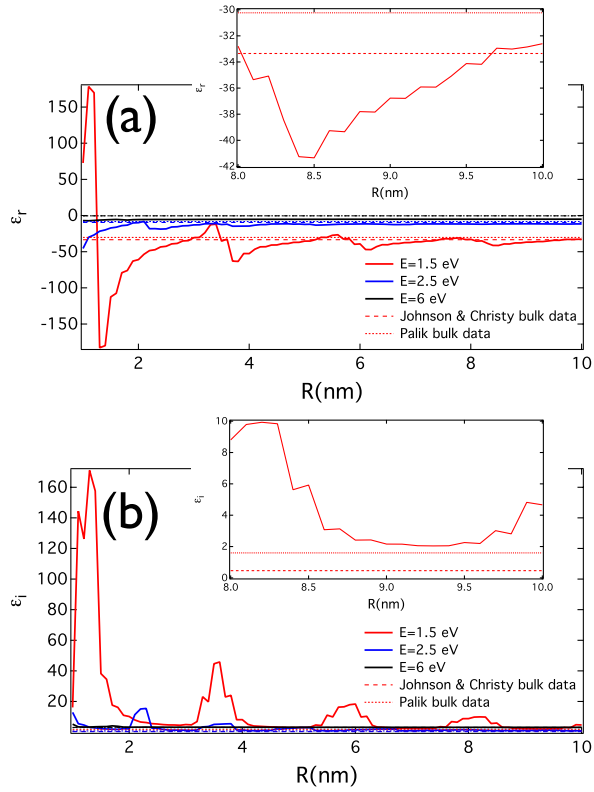

Fig. 1. (Color online) (a) Real and (b) imaginary parts of the relative electric permittivity of silver as a function of the particle radius for three different energies. Bulk values taken from Johnson and Christy [16] as well as Palik [17] are also shown. The insets show zoomed areas between $R = 8$ nm and $R = 10$ nm.

aligned with the incident electric field in all cases. Figure 2 shows the spectral extinction efficiency (cross section normalized by the total geometric section) for these systems, calculated with both bulk and QM-corrected optical properties. The most remarkable feature of the spectral dependence of Q_{ext} shown in Fig. 2 is the fact that, when including QM corrections, resonances shift to smaller wavelengths (blueshift [1]) and also become weaker (lower peaks). The redshift and the peak increment of the dimer resonance with respect to the isolated particle persist in the QM results.

In Fig. 3 we have plotted the spectral relative electric permittivity ($\varepsilon = \varepsilon_r + i\varepsilon_i$) corresponding to the case of a particle with radius $R = 4$ nm, for both silver and gold. As can be seen, in the case of silver, Fig. 3(a), the QM-corrected real part of ε intercepts $\varepsilon_r = -2$ at smaller wavelengths than the bulk results, thus producing a blueshift of the resonant condition. In the case of gold, Fig. 3(b), the QM-corrected ε does not even intercept $\varepsilon_r = -2$, thus we do not see any resonance peak in Fig. 2(b).

On the other hand, the QM-corrected imaginary part of ε is greater than the bulk one for all wavelengths, for both silver and gold. For sufficiently small x, the extinction efficiency equals the absorption, as the scattering may be considered zero [18]:

$$Q_{\text{ext}} \equiv Q_{\text{abs}} = 4x\Im\left\{\frac{\varepsilon - 1}{\varepsilon + 2}\right\}, \tag{2}$$

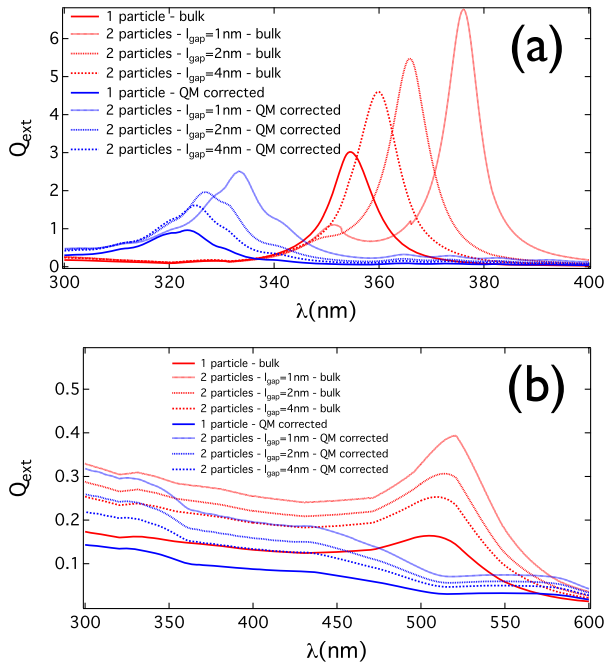

Fig. 2. (Color online) Spectral extinction efficiency for both single particles and dimers of radius $R = 4$ nm made of (a) silver and (b) gold, calculated with both bulk and QM-corrected optical properties.

where $x = 2\pi R/\lambda$ is the size parameter, $\Im$ denotes the imaginary part, and $\varepsilon = \varepsilon_r + i\varepsilon_i$ is the relative electric permittivity. In the resonance condition ($\varepsilon_r = -2$), expression (2) becomes

$$Q_{\text{ext}} \equiv Q_{\text{abs}} = \frac{12x}{\varepsilon_i}. \tag{3}$$

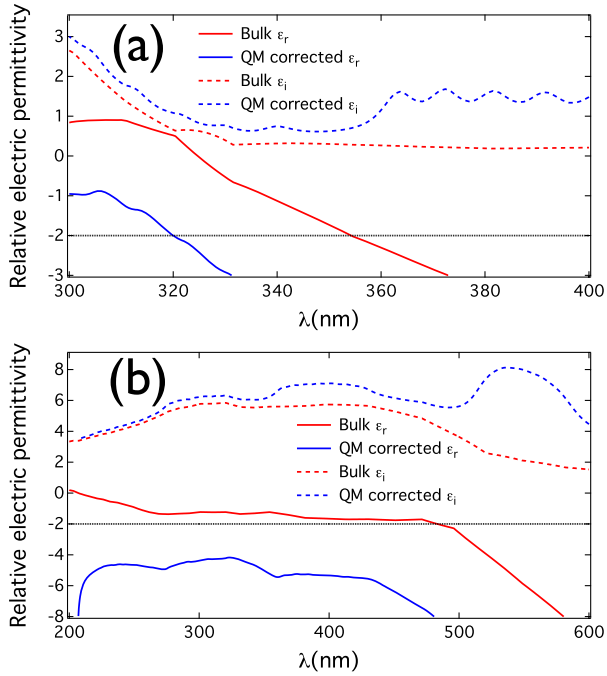

Fig. 3. (Color online) Spectral real and imaginary parts of the relative electric permittivity for the case $R = 4$ nm. Both bulk and QM-corrected values are shown. (a) Silver and (b) gold.

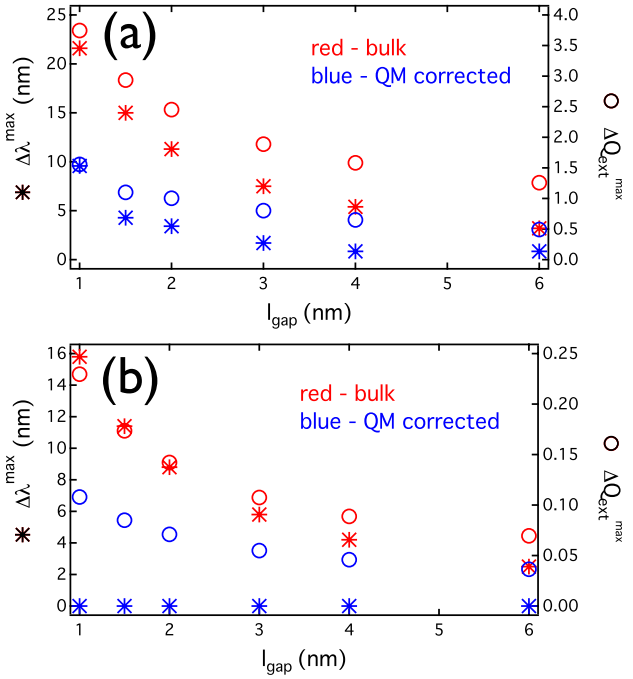

Fig. 4. (Color online) Spectral shift (left axis, "*" symbol) and peak increment (right axis, "o" symbol) of the spectral extinction resonance shown in Fig. 2 as a function of the dimer gap l_{gap}, $\Delta\lambda^{max}$, and ΔQ_{ext}^{max} represent the difference with respect to the isolated particle case. (a) Silver and (b) gold.

According to Eq. (3), the greater the imaginary part, the lower the extinction. This has been reported in the literature as *anomalous absorption* [19], and accounts for the reduction of the peaks. As a result, it is reasonable to think that two particles close to each other with quantum-corrected optical properties will interact less, so that the associated redshifts and peak increments with respect to the isolated case will be smaller, as shown in Fig. 4. Once again, the case of gold [Fig. 4(b)] is especially notorious, since the QM correction quenches the plasmonic resonance and no redshift is observed.

As a summary, the introduction of QM-corrected optical properties becomes in blueshifted [1] and weaker resonances, as shown in Fig. 2. The shifting arises as a consequence of the interception of the real part of the relative electric permittivity with $\varepsilon_r = -2$ (see Fig. 3). On the other hand, the weakening of the resonances is due to the greater imaginary part of the relative electric permittivity when considering quantum corrections (see Fig. 3). According to Eq. (3), the greater the imaginary part, the lower the extinction. The case of silver allows us to test our calculations, while the case of gold shows how important these quantum considerations may be when treating very small particles close to resonance. As a direct consequence, two particles close to each other with quantum-corrected optical properties interact less, therefore producing smaller shifts and lower peak increments in the far-field cross sections, as corroborated by Fig. 4.

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