Quantum effects in small plasmonic particles in the UV-VIS range

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The remarkable growth of nanotechnology has been driven by the ability to alter material properties as dimensions are reduced towards 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 towards the low nano-scale domain. Our group has recently examined the plasmonic properties of silver and gold nanospheres and dimers, with radii ranging from 10 to 1nm, extending from the classically described regime to the quantum size regime [2]. As a summary, it can be said that the introduction of quantum mechanically (QM) corrected optical properties becomes in blueshifted [1] and weaker resonances [2]. As a consequence, a dramatic change in the interaction of dimers is observed, especially in the case of gold, where the introduction of QM corrected optical properties quenches the plasmonic resonance and predicts an absence of the expected associated redshift.

In response to an increasing demand to detect and recognize biological toxins [3], to enhance biological imaging and to characterize semiconductor devices at the nanometer scale [4] among other applications, interest in UV plasmonics is rapidly growing. In this work we present what we believe is the first study of quantum effects in small plasmonic particles in the UV-VIS range, comparing UV-candidate materials such as aluminum or gallium with silver and gold. 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, based on fundamental physical phenomena, such as electron transition frequencies ω_{if} and oscillator strengths S_{if}. The overall permittivity expression can then be described as follows [5]

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

where ε_{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 and γ is the scattering frequency, dependent on the nanosphere dimension (particle radius) [1].

As an example, Figure 1 shows a color plot of the QM corrected relative electric permittivity (both real and imaginary parts) as a function of both the incident energy (resonance range) and the particle radius, comparing silver and aluminum. The black dots represent the resonance position (where $\mathrm{Re}\{\varepsilon\} = -2$). The results indicate an increasingly substantial change in the nanoparticle permittivity, with a clear blueshift of the resonance as the radius is reduced below 5 nm.

Figure 2 shows the spectral (as a function of the incident wavelength) extinction efficiency for isolated spherical particles of radius R = 4nm made of silver and aluminum, calculated with both bulk and QM-corrected optical properties. The characteristic blueshift is observed in both cases, whereas the weakening of the resonance is much lower in the case of aluminum, in part due to the larger size parameter compared to that of the silver case.

In summary, in this research we will explore the consequences of introducing QM corrected optical properties when considering very small plasmonic particles in the UV-VIS range, paying special attention to the relative size as compared with the incident wavelength and its effects on their plasmonic properties (blueshifting [1] and weakening [2]).

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Figures

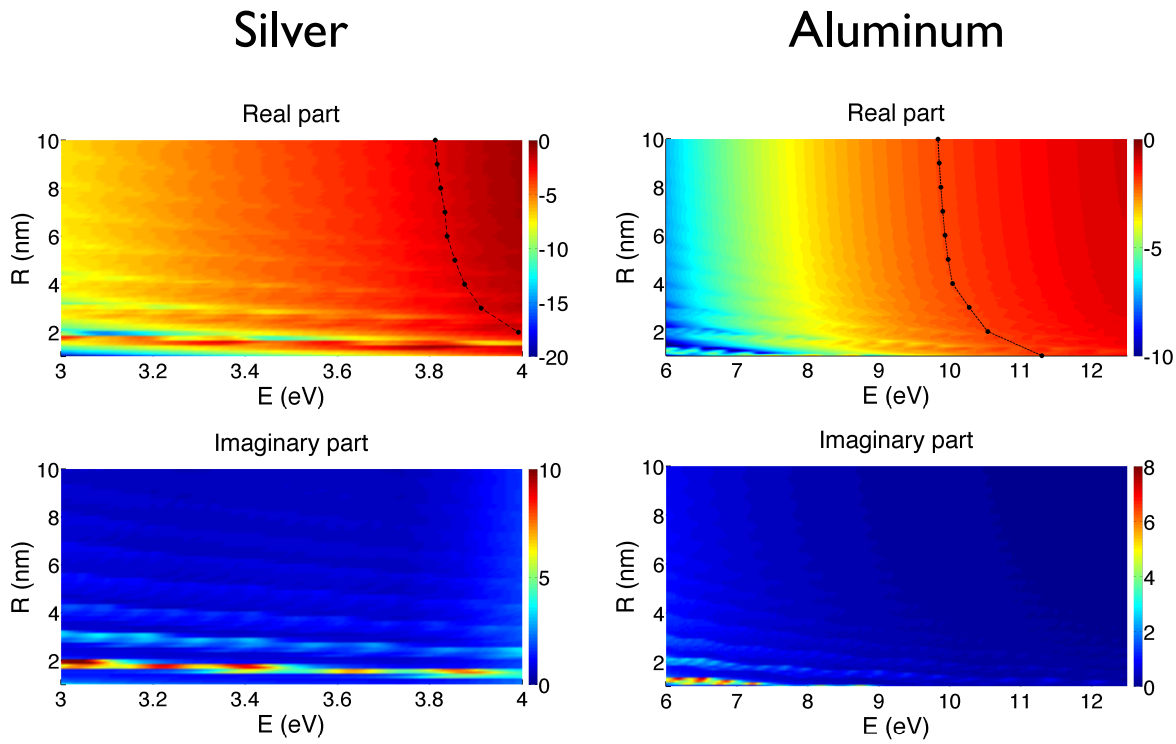

Figure 1: QM corrected relative electric permittivity (both real and imaginary parts) as a function of both the incident energy (resonance range) and the particle radius for silver and aluminum. The black dots represent the resonance position (where Re{ε} = -2)

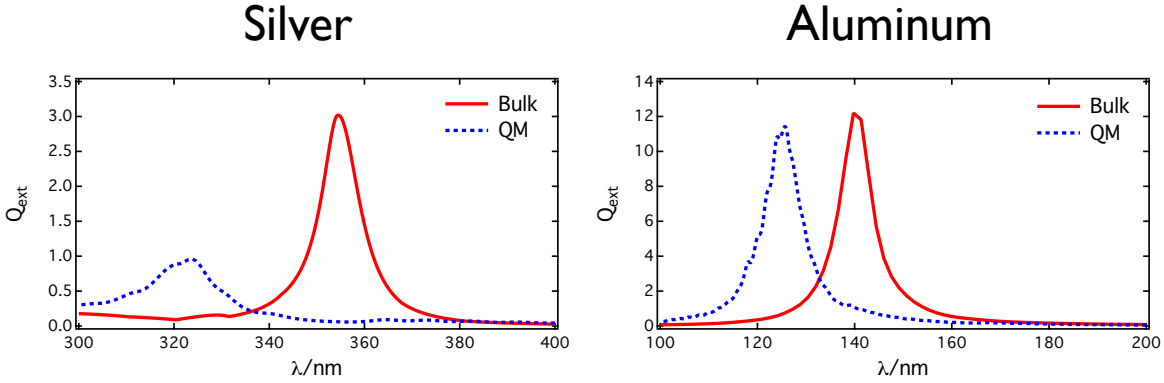

Figure 2: Spectral (as a function of λ) extinction efficiency for isolated spherical particles of radius R = 4nm made of silver and aluminum, calculated with both bulk and QM-corrected optical properties.