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Spectral shift between the near-field and far-field optoplasmonic response in gold nanospheres, nanoshells, homo- and hetero-dimers

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ABSTRACT

We investigate the shift between near- and far-field spectral properties in a set of different gold nanostructures using the multipole expansion of the electromagnetic fields. The optical behavior of isolated spheres, gold-silica nanoshells, homo- and hetero-di7mers is studied computationally as a function of the particle size. We show that in isolated nanospheres, both homogeneous and shell-like, the red-shift between near- and far-field peak intensities increases with nanoparticle dimension and has a universal character that can be attributed to the different spectral behavior of the radial component of the enhanced field, dominating in the near-field, with respect to its transverse part, which determines the far-field properties. Calculations on dimers of closely separated nanospheres, instead, highlight that the spectral shift between the maximum field intensity, calculated at the dimer nanocavity center, and the maximum extinction or scattering, computed in the far-field, strongly depends on both the radius of the monomers and the gap distance. The shift can turn from positive (i.e. red-shift) to negative (i.e.blue-shift) depending on the values of the nanostructure parameters. Our results call into question the universality of the energy red-shift, with relevant implications for the optimization of the efficiency in surface enhanced spectroscopies.

1. Introduction

Metal nanoparticles (MNPs) feature unique optical properties, that stem from their capability to support localized surface plasmons (LSPs), i.e. collective oscillations of the free conduction electrons driven by light, spatially confined at the MNP surface [1–3]. When resonantly excited, MNPs act as antennas for light [4], strongly amplifying and confining the light field at nanometric scale [5–8]. Varying size, shape, and materials, nanoantennas can be made resonant from the near-ultraviolet to the mid-infrared [9–12], making nanoantennas an ideal platform for enhanced spectroscopies [13–18], nanoscale imaging [19,20], light harvesting [21], and molecular sensing [22,23].

The relevant progress in the use of spectroscopic techniques sensitive to the electromagnetic fields at or near the particle surfaces, such as Surface-Enhanced Raman Spectroscopy (SERS) [24,25] or Surface Enhanced Infrared Absorption/Scattering (SEIRA/SEIRS) [26] motivated a keen interest in optimizing the optical interaction of MNPs with light at the nanoscale [3,27]. This involves engineering of the LSP resonances [9–12,28], optimization of the enhancement factor [29–32], exploitation of higher LSP resonance orders [33], polarization control of the near-field coupling [34–37].

Intense research has been carried out towards this goal in the last decades assuming that the LSP resonance energies, determined by the peak positions in extinction and scattering spectra, can be readily used to choose the excitation energy that maximizes the field enhancement. This is not true, in principle. Extinction and scattering measurements are, in fact, carried out with sources and detectors positioned at distances much larger than the wavelength, providing information on the capability of a particle to absorb and scatter light in the far field. In plasmon-enhanced spectroscopies, conversely, the signal amplification is governed by the ability of the nanoparticles to convert freely propagating light into local fields, the near-fields, confined close to the nanoparticle surface, that do not propagate into the far-field. Measuring the near-field properties, however, is by far less practical and requires more sophisticated scattering-type near-field optical microscopy techniques [38]. Only recently Alonso et al. [39] have succeeded to experimentally prove that in the mid-IR the excitation energy at which the maximum near-field enhancement occurs in linear nanoantennas is red-shifted with respect to the peak absorption observed in the far-field IR spectra. Red-shift arguments, however, have been used for a long time to justify

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discrepancies concerning the spectral dependence of the SERS enhancement factor. In SERS both the laser and the Stokes photon wavelengths must be resonant with the nanoantenna in order to benefit of the $|E|^4$ plasmonic enhancement [29,40]. Maximum SERS amplification is therefore expected when the excitation wavelength (λ_L) is slightly blue-shifted with respect to the nanoantenna resonance (λ_{LSP}) so that also the Stokes field wavelength (λ_R, red-shifted with respect to the laser) falls within the LSP resonance half-width, and thus the condition $\lambda_{LSP} \approx (\lambda_L + \lambda_R)/2$ is verified [29,30]. Differences between the extinction peak and the maximum SERS excitation wavelength have been observed on gold and aluminum nanoparticle arrays [41], on silver islands [42] and, more recently, in nanotriangles [43], near-field coupled gold nanorods [44] and nanospheres [45]. In the latter cases SERS is found maximum by exciting in the NIR (785 nm) although the MNPs resonate in the visible (550–650 nm), with vanishingly small extinction in the NIR. Guillot et al. [46] observed a more intriguing effect: while Wokaun's condition holds in the visible range (633 nm), in the NIR (785 nm excitation) maximum enhancement is obtained when $\lambda_L > \lambda_{LSP}$, i.e. when the excitation is red-shifted with the LSP peak [47,48].

These observations have triggered a theoretical interest to get more physical insight on the phenomenon. From Mie theory it is known that a red-shift has to be expected between the far-field extinction/scattering and the near-field scattering (defined as the integral of the scattered field intensity on the nanoparticle surface) on individual nanospheres of gold, silver and copper [49]. The shift is negligible for small nanoparticles (radius of few tens of nm) but increases with the particle dimensions up to about 200 nm for gold nanospheres of 100 nm radius. This red-shift can be interpreted in consideration of the different spectral behavior of the radial component of the near-field, that does not propagate in the far-field. Similar red-shifts between the near-field at the edges (calculated at 1 nm from the surface) and the far-field scattering are also predicted for single gold linear nanoantennas [28]. The red-shift is found to change along the surface, diminishing as the evaluation point is moved from the edge to the center of the antenna arm [50]. Red shifts are also predicted numerically on gold individual nanocylinders and ellipsoids [51], and on silver nanosphere dimers [52]. The physical reason of this phenomenon is currently under debate. It has been attributed to retardation effects [28] and radiation damping phenomena [53–55]. Zuloaga and Nordlander [54] used a mechanical analogy with a harmonic oscillator to show that the spectral red-shift between the plasmon-induced near-field (proportional to the oscillation amplitude) and the extinction cross-section (correlated to the kinetic energy) is a universal consequence of the presence of damping [56]. Moreno et al. [57] showed that the shift in dipolar nanoparticles arises naturally because of the different spectral responses of the evanescent (near-field) and propagating (far-field) wave components of the scattered field, and confirmed the universality of this phenomenon when the dipolar contribution is dominant.

Some important questions, however, are still open: (i) whether the red-shift depends on the distance from the nanoparticle surface, (ii) how the shift compares among homogeneous, silica core-shell and homo- /hetero-dimers of nanospheres with similar dimensions; and finally, (iii) whether the universality of the red-shift, demonstrated when the dipolar contribution is predominant and intrinsically associated to the presence of some damping, can be extended to systems in which the multipolar orders are not negligible. Such issues are of particular interest in plasmon enhanced spectroscopies. For example, the presence of multipolar orders [33] is crucial in SERS with nanoshells, dimers and aggregates that are among the most efficient SERS substrates [58,59]. Moreover, in SERS nanosensors the target molecules are absorbed on the overall surface of the particles or, in presence of functionalization layers, at some controlled distance from it. Thus, it is extremely important to correctly model the multipolar response of the plasmonic system in the near-field.

In this paper we address such problems by comparing the spectral dependence of the near-field electromagnetic intensity (calculated along the polarization direction) with the far-field scattering and extinction cross sections on homogenous spheres, nano-shell particles and nanosphere dimers. This is done through an analytical and computational approach based on the multipole expansion of the electromagnetic fields, whose convergence can be carefully tested throughout the computation [60,61]. This approach is not subject to any restriction on the choice of the nanosphere size and refractive index and gives a complete and accurate description, up to all the required multipole orders, of the interaction of the electromagnetic radiation with homogeneous and nano-shell particles at the nanoscale. Finally, we extend the study to gold homo- and hetero- dimers by applying the transition matrix (T-matrix) formalism [61,62], which offers unique advantages in the study of the light scattering of spherical particle aggregates [61,63,64], to perform angular orientation averages on randomly distributed particles [61,65,66], and to simulate the optical response of plasmonic nanoparticles [67,68].

Our computational results confirm the universality of the energy red-shift between near-field and far-field measurements for homogeneous and nano-shell MNPs. The red-shift in nano-shell particles is found to be remarkably smaller than on homogeneous spheres of equal dimensions. Finally, for metal dimers we show that, for some particular choices of the radii of the coupled particles, we get the occurrence of an energy blue-shift between near-field and far-field quantities, and specifically between the near-field energy density peaks and the far-field peaks in the scattering cross section. The blue-shift is not observed if calculations are performed in the dipolar approximation, highlighting the important role of the multipoles on such coupled systems.

2. Background theory

We start our investigation modeling an isolated gold sphere with radius r_0. Let us define a laboratory reference frame coinciding with the center of the sphere (see Fig. 1a) and assume that the incident field is a plane wave

$$\boldsymbol{E}_{\rm inc} = E_0\, \hat{\boldsymbol{e}}_{\rm inc} \exp[{\rm i}\boldsymbol{k}_{\rm inc}\cdot\boldsymbol{r}] \tag{1}$$

with amplitude E_0, polarized along the $\hat{\boldsymbol{e}}_{\rm I} \equiv \hat{x}$ direction, propagating along the direction $\hat{\boldsymbol{k}}_{\rm inc} \equiv \hat{z}$, with wavevector $\boldsymbol{k}_{\rm inc} = k\hat{\boldsymbol{k}}_{\rm inc}$, where $k = n\omega/c$, ω is the light frequency, c the speed of light in vacuum and n the refractive index of the surrounding medium, that we assume to be non-magnetic, isotropic, and homogeneous. An exact solution to the scattering problem can be found expanding both the incident, the scattered, and the internal (within the particle) field in a series of vector multipole fields. For the incident plane wave we have [61]

$$\boldsymbol{E}_{\rm inc} = E_0 \sum_{plm} \boldsymbol{J}_{lm}^{(p)}(\boldsymbol{r}, k) W_{lm}^{(p)}\left(\hat{\boldsymbol{e}}_{\rm inc}, \hat{\boldsymbol{k}}_{\rm inc}\right) \tag{2}$$

where $\boldsymbol{J}_{lm}^{(p)}$ denotes vector multipole fields which are defined by

$$\boldsymbol{J}_{lm}^{(1)} = j_l(kr)\boldsymbol{X}_{lm}, \quad \boldsymbol{J}_{lm}^{(2)} = \frac{1}{k}\nabla\times\boldsymbol{J}_{lm}^{(1)},$$

where the superscripts 1 and 2 are the values of a parity index p that distinguishes the magnetic multipoles ($p=1$) from the electric ones ($p=2$), j_l are spherical Bessel functions, and $\boldsymbol{X}_{lm}$ are vector spherical harmonics [69]. The amplitudes $W_{lm}^{(p)}$ for a plane wave are known [61]. For homogeneous spherical scatterers with refractive