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Radiative coupling of high-order plasmonic modes with far-field

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Abstract

In the last few years, hybrid systems consisting of punctual sources and metallic nanostructures have been assembled and studied. Furthermore, the radiative coupling between the two counterparts has become a crucial aspect to be explored in nanophotonics and plasmonics. In this paper a numerical framework based on the Discrete Dipole Approximation is presented as a simple computational scheme to analyze the decay dynamics of an emitter when it is located in the near proximities of metallic nanoparticles. This approach allows to go beyond the analytically solved cases and to predict the optical response of more complex shaped nanoparticles. Here the excitation of dipole and higher-order modes is studied as a function of the applied radiation with a particular attention paid to the changes induced in the response by approaching the source to the metal. Numerical results, obtained for Ag spheroids and conically shaped nanoparticles, are explained by analyzing the charge density induced on the surface of the nanoparticles, this allowing to distinguish dark from radiative modes in a straightforward way.

Keywords: Plasmonics; Nanoantennas; Dipole decay rates

1. Introduction

Over the last years the development of nano-optic techniques has affirmed the importance of exploiting plasmonic nanoantennas, like metallic nanoparticles or nanotips, to strongly enhance the absorption and the emission of radiation by a punctual receiver or emitter [1–7]. As is well known, thanks to the excitation of collective oscillations of the free electrons plasma (named localized surface plasmon resonances) [2], metallic nanostructures are able to enhance in a significant way the photonic density of states in their surroundings and in this way to strongly perturb the perturb the excitation and decay dynamics of proximate emitters, i.e. fluorophores or QDs [8]. Similar to radiowave and microwave antennas, their purpose is to convert the energy of free propagating radiation to localized energy, and vice versa. Several experimental works have demonstrated that the internal dynamics of any source of radiation can be tuned if the photonic environment is resonant with its radiative transitions [1,9–11]. Anyway, despite these evidences, the problem of mutual interaction between an emitter and a plasmonic antenna still presents lacking points and a lot of questions in molecular plasmonics results open, especially for what concerns complex-shaped nanoparticles that cannot be solved analytically.

For what concerns theory, the study of electrodynamic coupling between molecules and plasmonic antennas can be treated in different ways, according to

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the approximation adopted to describe the counterparts. Even if several options can be identified in literature, usually the molecule is described as a classical oscillating dipole, and the metal nanoparticle as a macroscopic entity characterized by its own frequency-dependent dielectric function [3].

In the work here presented, the description of the metal–emitter system and of the perturbations induced by metal on the decay dynamics of the emitter is performed in the framework of classical electrodynamics, well useful for weak-coupling regimes of interaction [12]. A numerical framework based on the Discrete Dipole Approximation (DDA) is applied: it turns out to be a simple and useful scheme to investigate coupling problems involving geometries which do not lend themselves to an analytical treatment. The idea underlying the analysis consists in accurately describing the nanoparticle shape through DDA to get a faithful description of the optical response of the metallic component to the emitter location, like recently done in literature with similar approaches [13–23]. The reliability of such numerical approach, as well as its generality in calculating the total and nonradiative decay rates has been recently demonstrated [24–26]. Here we are interested in the radiative behavior of the antenna. The radiative power of a polarizable system can be derived by starting from the flux of the Poynting vector through a surface enclosing it. Thus, being the scattered electric field in the far-field (radiation) zone due to the several multipoles in which the bound charge can be expanded (electric dipole, magnetic dipole, electric quadrupole and so on), it will contain contributions from modes of several order [27]. For metal nanoparticles whose dimensions are small if compared to the applied radiation wavelength, the major contribution to re-radiation can be ascribed to the dipole mode. The excited system assumes a fluctuating electric dipole moment and this causes electromagnetic radiation to be produced. Dipole radiation is thus considered the most important channel for radiative decay. Here we will show the potentialities and the criticalities of this approximation. Higher-order modes are not always dark modes and can produce a significant contribution in the electromagnetic coupling of plasmons with far field radiation. The analysis here reported aims at shedding light on the physical nature of the resonances appearing in the nanoparticles spectra and on the contributions that higher-order modes with respect to the dipolar one, can assume in large or elongated nanoparticles for which retardation effects can be significant and a net dipole moment different from zero can appear. In particular, a radiative contribution from the quadrupole mode is recognized for large silver prolate spheroids. This possibility for high-order modes to behave like bright modes is then confirmed by presenting the optical response of conically shaped nanoparticles to a plane wave excitation.

Numerical results, obtained for the different analyzed scatterers, assess that the decay rates of a dipole can be significantly tailored by tuning either the size or the shape of a nanoparticle and this could result of interest for measures of time-resolved fluorescence spectroscopy [28,29] and scanning near-optical microscopy [30,31].

2. Methods

The analysis here presented has been done in the framework of the Discrete Dipole Approximation [32] which is an useful method to numerically solve Maxwell equations for particles or arbitrary shapes and compositions. Also named *Coupled Dipole Approximation*, such numerical method is based on the discretization of the target into an array of N polarizable dipolar elements organized on a cubic lattice. The polarization of each element is the result of the interaction with the local electromagnetic field produced by all other elements plus the external field. The used implementation is ADDA [33,34] which allows to perform parallel simulations by partitioning the target into slices along one direction and thus to strongly reduce the run time. For what concerns the prescription for the polarizability, LDR (lattice dispersion relation) being this good enough to obtain a satisfactory level of accuracy ($<10\%$) for high discretization levels [35]. Here, like in other recent works [24–26], the ADDA code has been modified in order to consider dipolar fields as incident radiation. This should resemble the well known situation in molecular plasmonics, in which a metallic structure is irradiated by a point-like source like a chromophore or a small fluorophore. If we assume a point-like dipole $\tilde{\mathbf{p}}_0$ located at $\mathbf{r}_0$ and oscillating with frequency ω emitting electromagnetic radiation near a metallic nanoparticle, this nanoparticle will reflect and/or scatter back the radiation by generating an electric field $\tilde{\mathbf{E}}_{\mathrm{scat}}$ due to the polarization of the N internal dipoles. The idea underlying the present analysis is thus to numerically describe this key quantity. By solving in a self-consistent way a system of $3N$ coupled complex equations, DDA allows to calculated the N polarizabilities $\tilde{\mathbf{p}}_i$ describing the polarization response of the target to a particular excitation, so that the surface charge density as well as scattered field experienced by the dipole [36] can be easily calculated.