Electrodynamic theory of gain amplification for plasmonic nanoparticles coated with a layer of dye molecules

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Abstract

We here present a unified electrodynamic theory of the plasmonic response of metallic nanoparticles assisted by optical gain media, in the case of a nanoparticle coated with a shell of optically active dipoles (fluorescent molecules or quantum dots). We establish a complete description of the optical response based on Green's functions, which allows us to investigate high molecular coverages of the nanoparticle with either regular or random distribution of dye molecules, taking into account not only the interactions between nanoparticle (treated in a multipolar approach) and dye dipoles, but also between dyes molecules, either directly or via the nanoparticle. Our results show a strong amplification of the plasmonic resonance as well as significant modifications of the resonant lineshapes.

1. Introduction

The high level of losses in metamaterials based on metallic nanostructures at optical frequencies is one of the most crucial issues for practical applications. One solution actively explored in the community is the coupling of externally pumped gain elements in the hope to amplify the desired response. The theoretical effort is still very sparse, in particular in the case of devices based on nanoparticles (e.g., spasers). A simple approach by Lawandy [1] has indeed predicted amplification of localized plasmons for spherical nanoparticles in a gain medium. In this paper, we propose a detailed electromagnetic model predicting the optical response of a plasmonic nanoparticle coated by a monolayer of dipolar emitters (representing dye molecules or quantum dots).

2. Electromagnetic model

We consider an aggregate made of a single metal spherical nanoparticle (NP) with radius R surrounded by a layer of N fluorescent molecules located at positions $\mathbf{r}_j$, with $j = 1, 2, ..N$ (we set origin $\mathbf{r} = \mathbf{0}$ at NP center) [see Fig. 1-(a)]. The aggregate is illuminated by an incident plane wave with field $\mathbf{E}^{inc}$. We assume that the aggregate has spherical symmetry, with a uniform (regular or statistical) distribution of fluorescent molecules around the nanosphere. We want to represent the aggregate in terms of its total equivalent polarizability α^a, which relates the total aggregate dipole $\mathbf{p}^a$ to the incident field $\mathbf{E}^{inc}$ as $\mathbf{p}^a = \alpha^a \mathbf{E}^{inc}(\mathbf{r} = \mathbf{0})$.

The induced dipole of each jth molecule can be found from the closed system

$$\mathbf{p}_j = \alpha_m \mathbf{E}_0(r_j) + \frac{4\pi\omega^2}{c^2}\,\alpha_m \sum_{k=1}^{N} \underline{\mathbf{G}}(\mathbf{r}_j, \mathbf{r}_k)\mathbf{p}_k, \tag{1}$$

where ω is angular frequency, c velocity of light, and $\mathbf{E}_0(\mathbf{r})$ is the field scattered by the nanosphere in absence of the N molecules, produced by the incident field $\mathbf{E}^{inc}$. System (1) accounts for all molecule-

ISBN 978-952-67611-0-7

nanoparticle interactions (multipolar) as well as molecule-molecule interactions, both directly and co-operatively mediated by the nanoparticle (see Ref. [3]), with $\underline{\mathbf{G}}$ the dyadic Green function defined below. It also involves the dye molecular polarizability $\underline{\boldsymbol{\alpha_m}} = \alpha_m \underline{\mathbf{I}}$, which is assumed isotropic and identical for all molecules. The quantity α_m is simply modeled as a Lorentzian spectral line $\alpha_m = R_m^3 \times A/[(\omega_0 - \omega) + i\nu]$, with R_m the radius of dye molecules, ω_0 the median emission frequency, ν the collective damping accounting for multiple molecular transitions. The gain amplification parameter A is the sum of transition dipole moments μ_{i1}: $A = \sum_i \mu_{1i}\mu_{i1}/\hbar$, and is dependent on the intensity of the pumping electric field [2].

Our calculations show that the expression for effective dielectric polarizability of the aggregate can be derived as

$$\alpha^a = \frac{1}{|\mathbf{E}^{inc}(\mathbf{r}=\mathbf{0})|^2} \int_V dr \left[\mathbf{E}^{inc}(\mathbf{r})\right]^* \cdot \mathbf{P}(\mathbf{r}) = \alpha^{NP} + \frac{1}{|\mathbf{E}^{inc}(\mathbf{r}=\mathbf{0})|^2} \sum_{j=1}^{N} \mathbf{E}_0(\mathbf{r}_j)\mathbf{p}_j \tag{2}$$

where $\mathbf{P}(\mathbf{r})$ is the total volumetric polarization of the aggregate of volume V and α^{NP} is the bare nanoparticle polarizability (without dye molecules). Note that the last equality in Eq. (2) is valid only in dipolar approximation. The induced dipoles $\mathbf{p}_j$ are found by solving Eq.(1). The Green function $\underline{\mathbf{G}}$ is taken in the near-field approximation (see Ref.[3]):

$$\underline{\mathbf{G}}(\mathbf{r}_j, \mathbf{r}_k) = \frac{1-\delta_{jk}}{4\pi k^2 r_{jk}^3}\left[\frac{3\mathbf{r}_{jk}\mathbf{r}_{jk}}{r_{jk}^2} - \underline{\mathbf{I}}\right] + \sum_{lm} \frac{\bar{\alpha}_l}{(2l+1)k^2} \boldsymbol{\psi}_{lm}(\mathbf{r}_j)\boldsymbol{\psi}_{lm}^*(\mathbf{r}_k)$$

$$-i\frac{2}{9}\sum_{m=-1}^{1}\Big\{\tilde{\alpha}_1\big[\boldsymbol{\psi}_{1m}(\mathbf{r}_j)\boldsymbol{\chi}_{1m}^*(\mathbf{r}_k) + \boldsymbol{\chi}_{1m}(\mathbf{r}_j)\boldsymbol{\psi}_{1m}^*(\mathbf{r}_k)\big] - |\tilde{\alpha}_1|^2 \boldsymbol{\psi}_{1m}(\mathbf{r}_j)\boldsymbol{\psi}_{1m}^*(\mathbf{r}_k)\Big\}, \tag{3}$$

with δ_{jk} the usual Kronecker symbol, $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$, $r_{jk} = |\mathbf{r}_{jk}|$, $k = \frac{\omega}{c}\sqrt{\epsilon}$, $\boldsymbol{\psi}_{1m}(\mathbf{r}) = \boldsymbol{\nabla}[r^{-l-1}Y_{lm}(\hat{\mathbf{r}})]$, $\boldsymbol{\chi}_{1m}(\mathbf{r}) = \boldsymbol{\nabla}[r^l Y_{lm}(\hat{\mathbf{r}})]$, and $\hat{\mathbf{r}} = \mathbf{r}/r$. Y_{lm} denote scalar spherical harmonics, while $\bar{\alpha}_l$ and $\tilde{\alpha}_1$ are quantities directly related to multipolar polarizabilities of the nanoparticle.

3. Numerical results

We consider a gold spherical particle ($R = 10\,\text{nm}$), surrounded by molecular dyes ($R_m = 0.5\,\text{nm}$) all located at the same distance of 1 nm from the particle's surface. The ensemble is embedded in a medium with relative dielectric constant $\epsilon = 1.44$. In our simulations, we take $N = 200$ dye molecules distributed uniformly (randomly) around the nanosphere, assuming that molecular dipoles have random orientations. The gold dielectric function is modified with additional damping introduced into the Drude part due to the nanoparticle small size: $\gamma_{sp} = V_f/R$, where V_f is the Fermi velocity. We take $l = 10$ multipoles into account in our calculations [Eq. 3].

In Fig. 1 we plot our results, giving the aggregate polarizability α^a as a function of photon energy, when the amount of gain in the system is increased. This gain amount corresponds to the dye amplitude parameter A, which is itself controlled by the intensity of the pump field. The amplification parameter A is steadily increased from Fig. 1-(b) to (d). It can be clearly seen in Fig. 1-(b) that the plasmon resonance is amplified as the gain is increased, and also that the resonant lineshapes are gradually distorted – this is indeed related to Fano-type effects in gain-assisted nanoparticles (as we have shown in another work [4]). For values close to $A = 82.15$ [Fig. 1-(c)], the resonance amplification becomes extremely large; we are indeed approaching the point where a singular behaviour is retrieved for the plasmon [1, 4]. Then, as gain is further increased beyond this singular point, the plasmon gradually loses amplitude, but also reverses sign [Fig. 1-(d)]. The behaviour observed for $A = 82.17$ is particularly appealing: the real curve displays a range where the response is strongly negative associated with weak losses; this could have applications for metamaterials where "negative" properties are sought. Finally, one striking result of the model is that

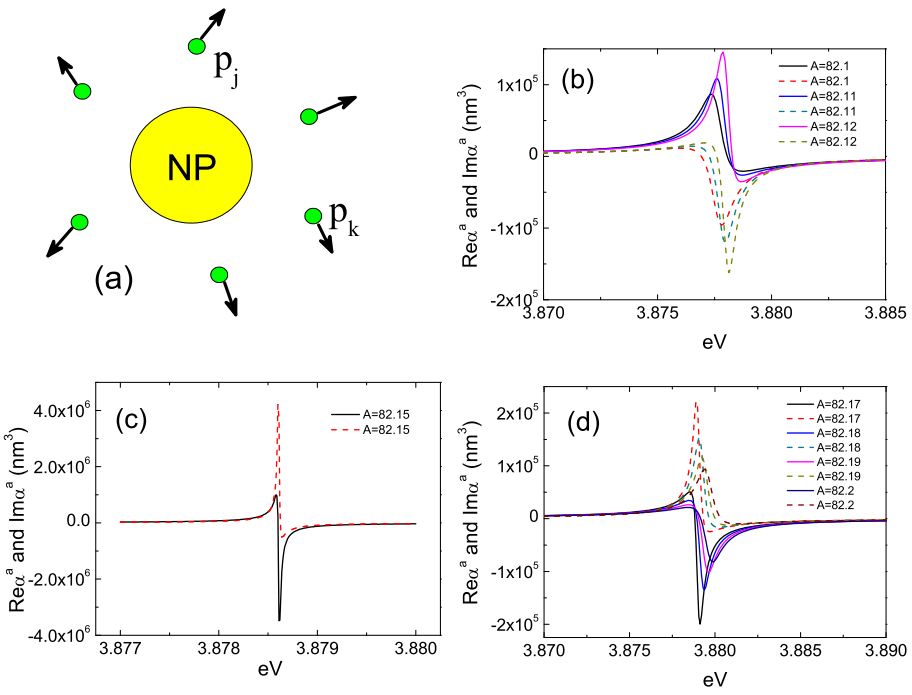

Fig. 1: (a) Gold nanoparticle surrounded with a layer of dye molecules; (b)-(d) Aggregate polarizability (in nm^3) as a function of photon energy (eV) for different values of amplification parameter A (arbitrary units). Real parts: solid lines; Imaginary parts: dashed lines.

the plasmon is strongly blueshifted – this should be ascribed to the strong coupling to optically active elements.

4. Conclusion

We have established a complete electromagnetic model to describe the optical response (total polarizability) of a core-shell aggregate composed of a metallic nanoparticle surrounded by a monolayer corona of externally pumped dye molecules. Our numerical calculations prove that a strong energy transfer occurs and that the presence of the surrounding gain medium leads to quasi-singularity in aggregate response for a well-defined amount, and strongly enhanced plasmons for other values of gain. Some of the observed resonant lineshapes show important distortions compared to usual plasmons (without gain), with interesting features.

Acknowledgments – This work has been funded by the French GIS "Advanced Materials in Aquitaine" under the SAMM project, and by the European FP7-NMP-2008 program under the METACHEM project (grant agreement Nr. 228762).

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