Decay Rates near layers of Au Nanospheres

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Abstract

The decay rate of quantum emitters near a layer of Au nanospheres is studied in the framework of a Green's tensor formalism. The localized surface plasmons that can be excited on the gold spheres provide a strong avenue for transporting the energy from the donors to the acceptors. The effect of the layer when compared to a single sphere depends on the concentration and distance in a non-trivial way, having a maximum at a finite distance.

1 Introduction

Since Purcell's work on this topic [1], it has been known that the electromagnetic properties of quantum emitters (fluorescent molecules, quantum dots) can be modified by placing them in suitable surroundings. The decay rate of a quantum emitter [2–9] has been investigated in a host of geometrical arrangements of their surroundings.

In this contribution we consider the decay rates of quantum emitters near a layer of Au nanospheres and investigate the effect of the spheres on these rates. Section 2 sets up the theoretical framework used in this investigation, namely that of the Green's tensor. Section 3 presents the results of numerical simulations performed within the Green's tensor formalism, as well as a discussion of these results. Finally, Section 4 is reserved for conclusions and outlook.

2 Theoretical Framework

We now consider the theoretical framework used to model the decay and energy transfer rates in the presence of the layer of Au nanospheres. For this we use a Green's tensor technique, widely employed for this type of investigations and readily amenable to numerical work.

2.1 Decay rates and the Green's tensor

The decay rate of an emitter placed in the proximity of a sphere can be calculated with the aid of the Green's tensor of the sphere, as [6]

$$\gamma(\mathbf{r},\omega) = \frac{2\mu^2\omega^2}{\hbar c^2 \varepsilon_0} \mathrm{Im}[\hat{\mu}_i \mathscr{G}_{ij}(\mathbf{r},\mathbf{r},\omega)\hat{\mu}_j], \tag{1}$$

where μ is the transition dipole moment of the emitter between its excited and ground states, $\mathscr{G}(\mathbf{r},\mathbf{r},\omega)$ is the Green's tensor of the electromagnetic field at the position $\mathbf{r}$ of the emitter.

Wishing to keep the discussion of the results as broad as possible, we forgo calculating the absolute decay rates and focus on their normalized values, i.e. the ratio of these rates near the layer of Au nanospheres and in free-space. The normalized rate is given as:

$$\tilde{\gamma}(\mathbf{r},\omega) = \frac{6\pi c}{\omega} \mathrm{Im}\hat{\mu}_i \mathscr{G}_{ij}(\mathbf{r},\mathbf{r},\omega)\hat{\mu}_j. \tag{2}$$

If, in the above expressions, $\mathscr{G}_{ij}(\mathbf{r},\mathbf{r},\omega)$ is the Green's tensor of a single sphere, these formula gives the decay rate in the presence of a single sphere.

Considering now a number N of Au nanospheres distributed over a planar surface, we calculate the decay rate by summing over the contributions from each Au nanosphere. While this is strictly not correct, it is a good approximation if the nanosphere concentration over the surface is small enough that multiple scattering events are very unlikely. We are currently working on developing the full formalism for an arbitrary distribution of spheres with arbitrary concentration.

From Eq. (2) it is clear that, in order to calculate the relative decay rate, a knowledge of the Green's tensor for the single sphere is required.

2.2 The Green's tensor for a single homogeneous sphere

The Green's tensor for a single homogeneous sphere of radius a and dielectric permittivity $\varepsilon(\omega)$ can be expanded in spherical harmonic, leading to, for example, the radial-radial component being given by [10]

$$\mathscr{G}_{rr}(\mathbf{r}_A,\mathbf{r}_B,\omega) = ik\sum_{n,m} a_n n(n+1)\frac{\zeta(\rho_A)\zeta(\rho_B)}{\rho_A^2\rho_B^2} P_n^m(\cos\theta_A)P_n^m(\cos\theta_B)\,\mathrm{e}^{im(\phi_A-\phi_B)}, \tag{3}$$

where $\zeta(\rho) = \rho\, h^{(1)}(\rho) = kr h^{(1)}(kr)$ is a Riccati-Bessel function, $k=\omega/c$ is the wavenumber, $\mathbf{r}_{A(B)} = (\rho_{A(B)}, \theta_{A(B)}, \phi_{A(B)})$ is the position vector of the donor(acceptor) in spherical coordinates, $P_n^m(\cos\theta)$ is the associated Legendre polynomial of degree m and order n and, finally, a_n represent the Mie scattering coefficients of the sphere.

3 Results and Discussion

In calculating the decay and energy transfer rates near a layer of Au nanospheres, the material properties of the particles play a crucial role. We have modeled the dielectric permittivity of the Au nanospheres through the following expression

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_D^2}{\omega^2 + i\gamma_D\omega + i\gamma_D^a\omega} + \frac{\Delta_\varepsilon\omega_L^2}{\omega_L^2 - \omega^2 - i\gamma_L\omega} \tag{4}$$

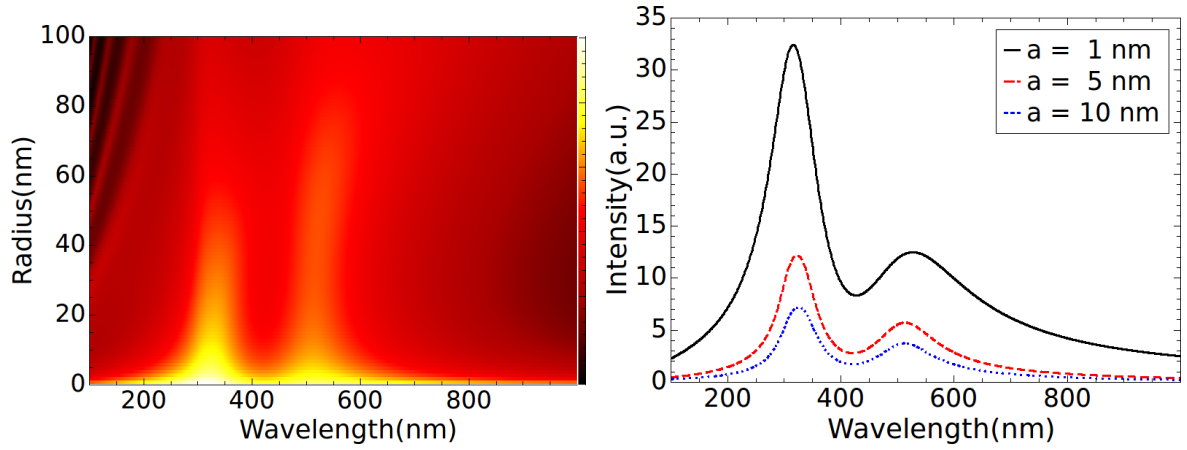
where $\varepsilon_\infty = 6.889$ is the static permittivity, $\omega_D = 8.96\,\mathrm{eV}$ is the plasma frequency for a Drude model for Au, $\gamma_D = 0.07\,\mathrm{eV}$ is the collision frequency of the Drude model, $\Delta_\varepsilon = 1.78$ is an oscillator strength for a single-resonance Drude-Lorentz model, $\omega_L =$ eV is the resonance frequency of the Drude-Lorentz model and $\gamma_L = 0.95\,\mathrm{eV}$ is the collision frequency of this model. A further correction $\gamma_D = A\frac{v_F}{2a}$ is introduced to account for surface scattering contribution to the dielectric permittivity, which for nanospheres smaller than approximately 50 nm cannot be neglected for Au. In this correction, $v_F \approx 1.4\,\mathrm{nm/fs}$ is the Fermi velocity of bulk Au, a is the radius of the Au sphere and A is a dimensionless parameter with values between 0.25 and 1.

3.1 Plasmonic resonances in Au nanospheres

Considering that we are investigating metallic (Au) nanospheres, their surface plasmon polariton (SPP) resonances will play a crucial role in the calculations that follow. Fig. 1 shows the SPP resonances for a Au sphere for $n=1$ and as a function of wavelength and radius. There are two resonances visible in this figure, one in the near-UV and one in the visible, around 500 nm. This second peak is the one we are interested in and we observe it slightly red-shifts as the radius of the Au nanosphere is increased. This red-shift is due to the surface scattering correction introduced in the dielectric permittivity of the Au nanosphere

3.2 The decay rate of an emitter

We now consider a quantum emitter located at a distance d above a layer of Au nanospheres of radius a. The geometrical arrangement is presented in Fig. 2, where the quantum emitter is depicted as a point electric dipole. We now consider the decay rate of this emitter as a function of the distance d to the layer of Au nanospheres, for several concentrations of spheres in the layer. For the radius of the spheres we take a value $a = 2.75\,\mathrm{nm}$, i.e. the



(a) (b)

Figure 1: Plasmon resonances of a Au nanosphere.

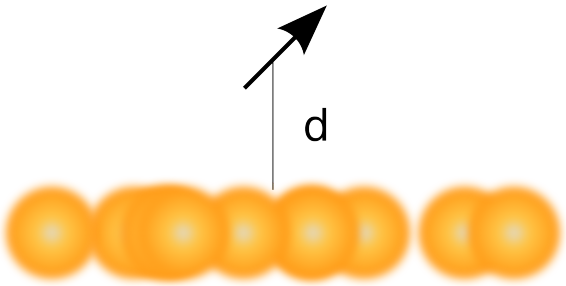


Figure 2: Geometrical arrangement

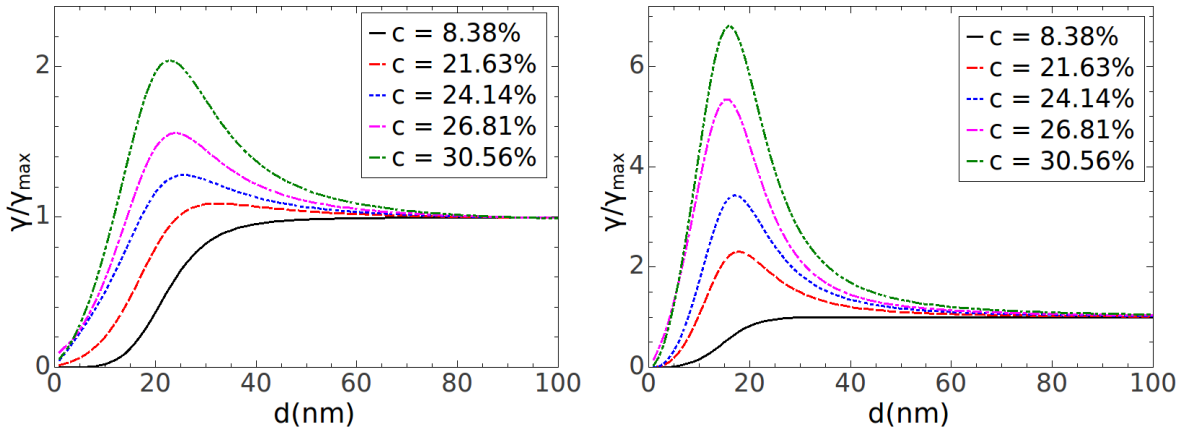
spheres have a diameter of $2a = 5.5\,\text{nm}$. For this dimension, the scattering component of the extinction by the sphere is negligible when compared to the absorption component, so that the decay process of the quantum emitter will be dominated by absorption in the Au spheres.

The calculation procedure used is as follows: for a given concentration c of Au nanospheres, given as a fractional filling in what follows, the spheres are randomly distributed over a square of side $L = 200\,a$ and area $L^2 = (2a)^2 \times 10^4$, containing a maximum of 10^4 spheres arranged in a square lattice. Given that the spheres are randomly distributed, a large number of realizations (> 1000) is averaged over in order to smooth out any statistical fluctuations.

Fig. 3 presents the decay rate of an emitter above thi[illegible]er of Au nanospheres as a function of the distance d to the layer. This decay rate is normalized to the maximal decay rate γ_{max} defined as the decay rate of the same emitter located at a distance d from the surface of a single sphere of radius a. With this definition γ_{max} is the maximum possible contribution from a single Au nanosphere.

As Fig. 3 shows, for concentrations up to $c \approx 10\%$, the presence of a layer of Au nanospheres does not have an appreciable effect on the decay rate of the emitter. This can be inferred from the fact that the normalized decay rate $\gamma/\gamma_{\text{max}}$ does not exceed 1. The fact that it seems to approach 0 at small distances d is a consequence of the fact that, at these small distances, the decay rate is very sensitive to fluctuations in d and, therefore, any such fluctuation will a value much smaller than γ_{max}.

As the concentration of Au nanospheres is increased, one can see from Fig. 3 that the normalized decay rate of the donor above the layer is actually [illegible]imal for a finite distance d to the layer. The reason for this is, again, the competition between the additional contributions from multiple spheres (which become more significant as the concentration is increased) and the maximal decay rate γ_{max}; this competition leads to an optimum distance where the contribution from the layer of spheres is maximal when compared to γ_{max}. The distance d_{max} of the peak in



(a) Perpendicular dipole moment

(b) Parallel dipole moment

Figure 3: Decay rate above a layer of Au nanospheres; the dipole moment is (a) perpendicular and (b) parallel to the plane of the spheres, for different concentrations. The emission wavelength is $\lambda \approx 540\,\text{nm}$, close to the SPP resonance.

Fig. 3 is, as one would expect, concentration dependent, its value decreasing with increasing concentration. As we mentioned before, it is not correct to use this model of independent Au spheres as the concentration is increased much further, since multiple scattering events must then be taken into account, especially for spheres comparable to the wavelength of light.

4 Summary, Conclusions and Outlook

In this contribution we have investigated the decay rate of a quantum emitter above a layer of Au nanospheres. We have calculated the decay rate close to the SPP resonance of a single sphere and for several orientations of the dipole moment of the emitter and concentrations of the Au nanospheres. Comparing the decay rate a distance d above the layer of Au nanospheres to the decay rate at the same distance from a single sphere, we have found that for low concentrations and at large distances d, the layer contribution reduces to that of a single sphere. As the distance d is decreased, and still at low concentrations, the decay rate is more sensitive to the random distribution of Au spheres and the normalized decay rate $\gamma/\gamma_{\text{max}}$ drops off abruptly.

As the concentration of Au spheres is gradually increased, the normalized decay rate $\gamma/\gamma_{\text{max}}$ reaches a maximum at a finite d. At these concentrations the contribution from multiple spheres becomes comparable to the main contribution for a single sphere. The value d_{max} where this maximum occurs depends on concentration.

The model used in this contribution considers the Au spheres as independent. We are currently extending this model to take into account multiple scattering from an arbitrary distribution of Au spheres and will investigate the decay rates, as well as the energy transfer rates between quantum dots near layers of Au nanospheres.

Acknowledgments

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