

Resonance Fluorescence of a Quantum Dot near a Metallic Nanoparticle: Quantum Interference Effects [†]

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Abstract: In recent years, significant attention has been given to the quantum or nonlinear optical properties of semiconductor quantum dots coupled to plasmonic nanostructures. A phenomenon that has been studied is the modification of the resonance fluorescence spectrum of the quantum dot by the presence of the plasmonic nanostructure. The most common plasmonic nanostructure that has been studied is the metallic (mainly gold or silver) nanosphere and in most studies the quantum dot is modeled as a two-level quantum system. In this work, we model the quantum dot structure with a three-level V-type quantum system, which can naturally arise in quantum dots, and study the resonance fluorescence spectrum near a metallic nanosphere. We show that the present system leads to quantum interference effects due to the presence of the metallic nanoparticle and specifically due to the anisotropic Purcell effect that occurs in the photon emission of the quantum dot near the metallic nanosphere. We then study the resonance fluorescence spectrum, for different distances between the quantum dot and the metallic nanosphere and show that the resonance fluorescence spectrum changes significantly from a single-peak spectrum to a multipeak spectrum. The effects of quantum interference in the resonance fluorescence spectrum are also explored.

Keywords: quantum dot; metallic nanoparticle; resonance fluorescence; quantum interference

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1. Introduction

In recent years, novel optical properties detected in hybrid systems which are composed of quantum emitters, like molecules and quantum dots, and plasmonic (metallic or metal-dielectric) nanostructures have attracted significant attention [1]. The coupling between excitons and surface plasmons can strongly modify a series of optical effects which, until recently, were explored in isolated quantum emitters. Among the various quantum optical effects that have been studied in coupled quantum dot – plasmonic nanostructures of particular interest is the modified incoherent spectrum of fluorescent photons emitted by a quantum dot near a metallic nanostructure and under laser excitation, i.e., the modification of the resonance fluorescence spectrum. This modification mainly occurs due to the alteration of the spontaneous decay rate of the quantum dot near the plasmonic nanostructure and the exciton-plasmon coupling. This effect has been analyzed in quantum dots modeled by a two-level system [1,2], a Λ -type three-level system [3], as well as in more complex energy-level structures, such as the double-V-type [4] and the double- Λ -type four-level systems [5]. In these studies, the quantum dot was assumed to be coupled to either a single metallic nanosphere [1–3] or to more complicated plasmonic structures [4,5]. More specifically, in the double-V-type [4] and the double- Λ -type four-level

systems [5] it was found that the anisotropic Purcell effect is responsible for creating quantum interference effects [6,7] which can also modify the resonance fluorescence spectrum.

In the present work, we model the quantum dot structure with a three-level V-type quantum system and study the resonance fluorescence spectrum near a metallic nanosphere. We show that the current system leads to quantum interference effects due to the presence of the metallic nanoparticle and specifically due to the anisotropic Purcell effect that occurs in the photon emission of the quantum dot near the metallic nanosphere. We then study the resonance fluorescence spectrum, for different distances between the quantum dot and the metallic nanosphere. We demonstrate that the distance separating the quantum dot from the nanosphere determines the number of the peaks observed on the resonance fluorescence spectrum we also investigate the role of quantum interference, which substantially alters the spectral profile, especially for small values of the interparticle distance.

2. Methods

The hybrid structure that is examined in the present study is composed of a gold nanosphere of radius R and a quantum dot described as a V-type three-level scheme (Figure 1), which has been placed at a distance d from the surface of the nanosphere. In order to model the dielectric function of the nanosphere experimental results are used.

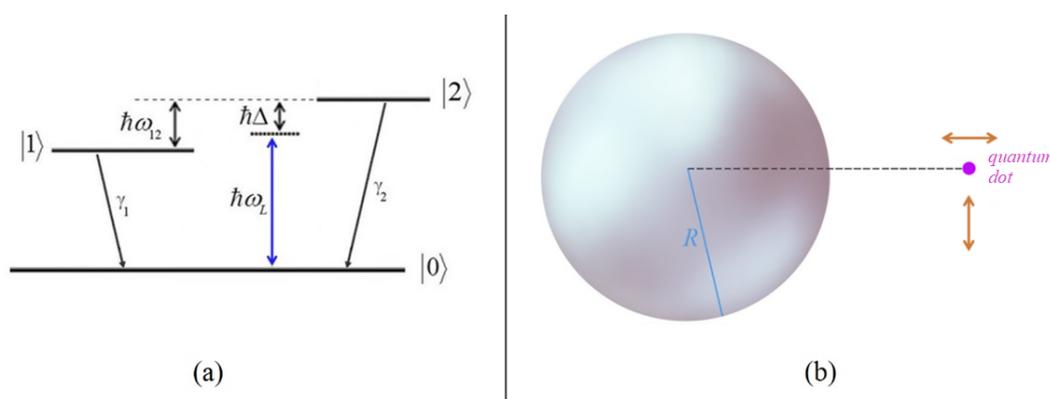


Figure 1. (a) V-type energy-level diagram of a quantum dot interacting with an external field of angular frequency ω_L . We denote the detuning of the field from the $|0\rangle \rightarrow |2\rangle$ resonance by Δ , while the frequency mismatch between the excited levels is ω_{21} and the decay rates corresponding to the $|1\rangle, |2\rangle \rightarrow |0\rangle$ decay pathways are respectively represented by γ_1 and γ_2 , respectively. The $|2\rangle \rightarrow |1\rangle$ transition is dipole-forbidden. (b) the hybrid structure composed of two coupled components: a gold nanosphere and a quantum dot, where the dipole moment oscillates in two alternative orientations, in parallel with, or either, normal to the surface of the nanosphere.

The Hamiltonian that governs the dynamics of the quantum dot, under the assumption that the hybrid structure interacts with a single electromagnetic field of amplitude E_L and angular frequency ω_L , in the dipole approximation, is given by the following expression:

$$H = \sum_{n=1,2} E_n |n\rangle \langle n| + \left[\left(\frac{\hbar \Omega_n}{\hbar} |n\rangle \langle 0| \right) e^{-i\omega_L t} + H.c. \right] \tag{1}$$

with E_n representing the energy of energy level $|n\rangle$ (here we take the energy of the ground state E_0 equal to zero) and $\Omega_n = -\mu_n E_L / \hbar$ denoting the Rabi frequency associated to the transition from the ground state $|0\rangle$ to the excited state $|n\rangle$ ($n = 1, 2$), where μ_n is the relevant dipole matrix element. In the present study, we consider $\Omega_1 = \Omega_2 = \Omega$. Based on the Hamiltonian of Equation (1), we derive the eliminated set of

the density matrix equations that describe the dynamics of the system, under the rotating wave approximation.

The resonance fluorescence spectrum is the real part of the Fourier transformation of the correlation function $\lim_{t \rightarrow \infty} \langle \mathbf{P}^\dagger(\tau + t) \cdot \mathbf{P}(t) \rangle$:

$$S(\omega) = \text{Re} \left[\int_0^\infty \lim_{t \rightarrow \infty} \langle \mathbf{P}^\dagger(\tau + t) \cdot \mathbf{P}(t) \rangle e^{-i(\omega - \omega_L)\tau} d\tau \right] \quad (2)$$

where $\mathbf{P}^\dagger(t) = \mu \sum_{n=1,2} |n\rangle \langle 0|$ denotes the quantum dot's polarization operator. In the present study, we explore the incoherent resonance fluorescence spectrum, which is associated with the dipole polarization fluctuation and calculated based on the formula

$$\Lambda(\omega) = \text{Re} \left\{ \int_0^\infty \lim_{t \rightarrow \infty} \left[\langle \mathbf{P}^\dagger(\tau + t) - \langle \mathbf{P}^\dagger(\infty) \rangle \right] \cdot \left[\mathbf{P}(t) - \langle \mathbf{P}(\infty) \rangle \right] e^{-i\omega\tau} d\tau \right\} \quad (3)$$

where $\langle \mathbf{P}^\dagger(\infty) \rangle$ denotes the mean value of the quantum dot's polarization operator calculated in the steady state. The quantum regression theorem [8] is applied in order to calculate the average value of the two-time correlation functions appearing in Equations (2) and (3), in combination with the equations of motion for the density matrix elements [3,4,6].

The spontaneous emission rates $\gamma_1 = \gamma_2 = \gamma$, with $\gamma = (\Gamma_\perp + \Gamma_\parallel)/2$, are respectively associated with the deexcitation transitions $|1\rangle, |2\rangle \rightarrow |0\rangle$, as seen in Figure 1a, where μ_0 is the vacuum permeability, and $\Gamma_{dir} = \mu_0 \mu^2 \bar{\omega}^2 \text{Im}[G_{dir}(\vec{r}, \vec{r}; \bar{\omega})] / \hbar$ is the spontaneous emission rate, for different directions of the transition dipole ($dir = \parallel$ or \perp , parallel or perpendicular to the surface of the nanosphere), $G_{dir}(\vec{r}, \vec{r}; \bar{\omega})$ representing a projection of the dyadic electromagnetic Green's tensor $\mathbf{G}(\vec{r}, \vec{r}; \bar{\omega})$, on a specified direction, which is calculated based on a rigorous electromagnetic Green's tensor technique [9] and $\bar{\omega} = \sum_{n=1,2} E_n / 2\hbar$. The upper states $|1\rangle$ and $|2\rangle$ are also coupled together, due to the spontaneous emission process, which is responsible for the quantum interference between the two transition pathways in the quantum dot. The parameter associated to the previously discussed coupling is the κ coefficient, which is equal to $\kappa = (\Gamma_\perp - \Gamma_\parallel)/2$. Finally, the degree of quantum interference is defined as $p = \kappa / \gamma$ [7].

3. Parameters and Results

Here, we explore the profiles associated with the resonance fluorescence spectrum (Figure 2), with respect to the detuning of the emitted photon's electromagnetic frequency from the applied electromagnetic field frequency, in γ_0 units, where γ_0 is the spontaneous decay rate of the quantum dot in free space. The spectra presented in Figure 2 are taken for an exactly resonant applied electromagnetic field ($\Delta = 0$), with Rabi frequency Ω and upper states' frequency mismatch ω_{21} , both set equal to $6\gamma_0$, for various distances between the quantum dot and the surface of the gold nanosphere. The radius of the nanosphere is $R = 80 \text{ nm}$. In Figure 2a–c, we respectively take $d = 10 \text{ nm}$, 27 nm and 50 nm . The turquoise solid curve depicts the resonance fluorescence spectrum, in the presence of the interference effects, while, with the blue dashed curve we display the resonance fluorescence spectrum, considering that the interference effects are absent ($\kappa = 0, p = 0$).

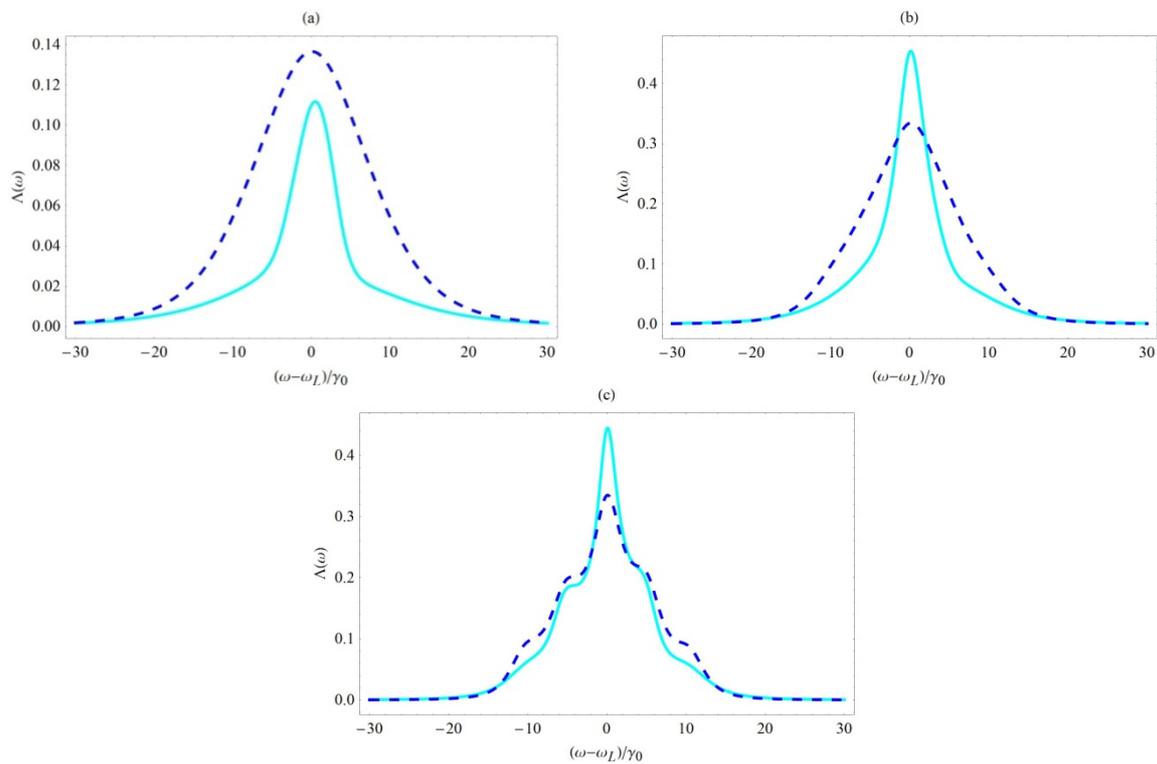


Figure 2. The incoherent resonance fluorescence spectrum, for different distances between the quantum dot and the gold nanosphere (turquoise solid curve: in the presence of interference effects, blue dashed curve: without interference effects – $\kappa = 0$). In (a–c), the distance d between the quantum dot from the surface of the nanosphere is respectively taken equal to 10 nm, 27 nm and 50 nm, while the radius R of the nanosphere is 80 nm, in all cases. Here, we examine the case of exact resonance ($\Delta = 0$), with the Rabi frequency Ω and the frequency mismatch ω_{21} between the two upper states both set equal to $6\gamma_0$.

4. Discussion

In Figure 2a, where the two components of the hybrid system are placed at a short distance from each other ($d = 10$ nm), the value of the decay rate and the coupling coefficient are quite high ($\gamma = 7.87\gamma_0$, $\kappa = 6.96\gamma_0$). Under these circumstances, the profile of the resonance fluorescence spectrum (turquoise solid curve) is single-peaked. More specifically, the resonance is detected for an angular frequency of the emitted fluorescence photons equal to the angular frequency of the applied laser field ($\omega = \omega_L$). If we exclude the influence of the interference effects (by setting $\kappa = 0$), the full-width half maximum as well as the amplitude of the spectral resonance exhibit a substantial increase, as shown with the blue dashed curve. So, the inclusion of interference effects leads to significant narrowing of the lineshape.

In Figure 2b, we take $d = 27$ nm, where the spontaneous emission rate for a transition dipole oriented parallel to the surface of the nanosphere Γ_{\perp} takes its minimum value, there is a transition point, since, by further increasing the center-to-center distance R , the single peaked resonance fluorescence spectrum becomes five-peaked (see Figure 2c). Here, although $\gamma = 3.50\gamma_0$ and $\kappa = 3.10\gamma_0$, the full-width half maximum remains in both cases almost the same to the case with $d = 10$ nm, presented in Figure 2a. Note that the interference factor is practically the same in Figure 2a,b, giving $p \approx 0.88$. However, in this case the amplitude of the spectral resonance is importantly increased. A difference with Figure 2a is that in the absence of the interference effects, the amplitude of

the resonance is found to be considerably lower, as compared to the one with the interference effects accounted for.

Finally, in Figure 2c, where we assume that $d = 50 \text{ nm}$, the value of both the decay rate and the coupling coefficient are importantly decreased ($\gamma = 1.82\gamma_0$, $\kappa = 1.29\gamma_0$), as well as, the interference factor p also decreases, giving $p \approx 0.71$. In this case, we take a five-peaked resonance fluorescence spectrum profile, since two doublets of resonances have arisen at symmetric positions with respect to the central resonance. A dressed-state picture analysis (not shown here), which is valid for high Rabi frequencies, enables us to identify, to a good approximation, the location of the resonances: $\omega - \omega_L = \pm\sqrt{\omega_{21}^2 + 2\Omega^2}$, $\pm\frac{1}{2}\sqrt{\omega_{21}^2 + 2\Omega^2}$. We should also note that the amplitude of the central resonance is the same as the one found in the case of Figure 2b, with $d = 27 \text{ nm}$, under both quantum interference regimes investigated, and the case with the quantum interference leads to a narrower central peak.

5. Conclusions

In summary, in the present study, we explored the incoherent resonance fluorescence spectrum emitted by a quantum dot with a V-type energy-level scheme located in the vicinity of a gold nanosphere. We found that the coupling of the quantum dot to the metallic nanosphere is responsible for the strong modification of the spontaneous decay rates and the quantum interference effects, which occurs due to the anisotropic Purcell effect associated to the photon emission near the metallic nanoparticle. This results to a strong alteration of the resonance fluorescence spectrum profile as the distance between the quantum dot and the metallic nanoparticle changes.

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References

1. Vladimirova, Y.; Zadkov, V. Quantum optics in nanostructures. *Nanomaterials* **2021**, *11*, 1919.
2. Ridolfo, A.; Di Stefano, O.; Fina, N.; Saija, R.; Savasta, S. Quantum plasmonics with quantum dot-metal nanoparticle molecules: Influence of the Fano effect on photon statistics. *Phys. Rev. Lett.* **2010**, *105*, 263601.
3. Carreño, F.; Antón, M.A.; Yannopapas, V.; Paspalakis, E. Resonance fluorescence spectrum of a Λ -type quantum emitter close to a metallic nanoparticle. *Phys. Rev. A* **2016**, *94*, 013834.
4. Carreño, F.; Antón, M.A.; Yannopapas, V.; Paspalakis, E. Control of resonance fluorescence of a four-level quantum emitter near a plasmonic nanostructure. *Phys. Rev. A* **2017**, *95*, 043825.
5. Gu, Y.; Wang, L.; Ren, P.; Zhang, J.; Zhang, T.; Martin, O.J.F.; Gong, Q. Surface-plasmon-induced modification on the spontaneous emission spectrum via subwavelength-confined anisotropic Purcell factor. *Nano Lett.* **2012**, *12*, 2488–2493.
6. Zhou, P.; Swain, S. Ultranarrow spectral lines via quantum interference. *Phys. Rev. Lett.* **1996**, *77*, 3995–3998.
7. Yannopapas, V.; Paspalakis, E.; Vitanov, N.V. Plasmon-induced enhancement of quantum interference near metallic nanostructures. *Phys. Rev. Lett.* **2009**, *103*, 063602.
8. Lax, M. Quantum noise. XI. Multitime correspondence between quantum and classical stochastic processes. *Phys. Rev.* **1968**, *172*, 350–361.
9. Yannopapas, V.; Vitanov, N.V. Electromagnetic Green's tensor and local density of states calculations for collections of spherical scatterers. *Phys. Rev. B* **2007**, *75*, 115124.