

Relaxation dynamics of a quantum emitter resonantly coupled to a metal nanoparticle

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The presence of a metal nanoparticle (MNP) near a quantum dipole emitter, when a localized surface plasmon mode is excited via the resonant coupling with an excited quantum dipole, dramatically changes the relaxation dynamics: an exponential decay changes to step-like behavior. The main physical consequence of this relaxation process is that the emission, being largely determined by the MNP, comes out with a substantial delay. A large number of system parameters in our analytical description opens new possibilities for controlling quantum emitter dynamics. © 2014 Optical Society of America

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Controlled modification of spontaneous emission is one of the central issues of quantum electrodynamics. Coupling between quantum dipole emitters (QDEs), such as molecules or quantum dots, and metal nanoparticles (MNPs) at optical frequencies allows control over the flow of electromagnetic energy and lies at the core of an explosively growing field of quantum plasmonics [1]. Recent advances in nano-optics, especially experiments with single molecules interacting with well-defined metal nanostructures [2–4], often referred to as nanoantennas, serve as a strong impetus for further developments in this direction [5,6]. The most often discussed effect of QDE–MNP interaction is concerned with the modification (enhancement or quenching) of fluorescence yield determined by the balance between radiative and nonradiative decay rates, both enhanced near MNPs [3,4,7–9]. It is also expected that the QDE–MNP interaction can even enter the regime of strong coupling, where excitation energy is coherently transferred between QDE and MNP in the form of Rabi oscillations [10].

Modification of spontaneous emission in various QDE–MNP configurations has been considered from different perspectives [3,4,7–9] but *always* assuming that the relaxation dynamics is *purely exponential* as obtained in the Weisskopf–Wigner treatment of an individual two-level atom [11]. In this Letter, we investigate the conditions ensuring that, under *pulsed* excitation of the *resonantly* coupled QDE–MNP system, the relaxation dynamics changes drastically: it is no longer described by an exponential decay but exhibits step-like behavior. One should note here that the most important feature of any QDE–MNP system is an extremely large difference between the relaxation times of the excited QDE and localized surface plasmon (LSP) mode of the MNP. It is clear then that the strong QDE–MNP coupling is extremely difficult to realize, since it would imply achieving the Rabi frequency that exceeds the LSP damping rate [10]. At the same time, the regime of *weak* coupling, in which the QDE–MNP relaxation time is much shorter than that of the QDE in free space but much longer than the LSP lifetime, is relatively easy to realize using reasonably large QDE–MNP distances [10]. Under these conditions and in the absence of the external illumination,

it becomes crucial to properly take into account self-action of the excited QDE, in which its dipole field generates an LSP mode that acts back on the QDE, thus providing a feedback in the QDE–MNP system. It turns out that in the case of weak and resonant QDE–MNP coupling, namely when the frequency of LSP resonance *coincides* with the frequency of the QDE radiative transition, the relaxation dynamics of *coherent* QDE excitation can be described *analytically* and features, in general, a step-like decay in time, deviating thereby *significantly* from the widely adopted exponential behavior [3,4,7–9]. It is further demonstrated that radiation emission, which is produced primarily by the MNP, comes out with a considerable time delay, opening thereby new possibilities for controlling the QDE–MNP emission process. We discuss also other possible realizations of the considered configuration.

The QDE–MNP system under consideration is schematically presented in Fig. 1 and consists of a generic three-level QDE [9,10] and a spherical MNP. It is assumed that an external pump laser brings the QDE from the ground state 0 into the excited state 2, where it decays nonradiatively into the optically active state 1, and that the spherical MNP exhibits a dipolar LSP resonance at the frequency ω_{10} of the radiative (dipole-allowed) transition $1 \rightarrow 0$ [Fig. 1(b)]. This allows us to separate the excitation dynamics, which is not influenced by the presence of the MNP, from the relaxation dynamics of the state 1, whose modification due to the QDE–MNP coupling is the main subject of this work. Physically, a very similar situation can be realized with a two-level QDE

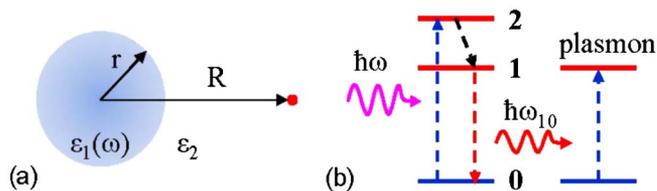


Fig. 1. Schematic of a system with a QDE placed near an MNP, indicating (a) system parameters and (b) QDE energetic levels along with the localized (dipolar) surface plasmon resonance of the MNP.

under one- or two-photon (pulsed) excitation. Note that the shape of an MNP is not important in this context and can be chosen specifically in order to produce a dipolar resonance at a given frequency [10,12], for instance, to coincide with the QDE radiative transition frequency.

We start our consideration when the QDE state can be described by a *coherent superposition* of the optically active state 1 and ground state 0, with the LSP *not* being excited. This can be achieved, for example, by using a weak laser pulse at the frequency ω_{10} sent on the three-level QDE that is brought into the optically active state 1 as described above. The two-level QDE can be brought directly into the superposition state by a strong laser pulse at the frequency ω_{10} with the characteristics being close to that of a π -pulse, that is, a pulse needed to ensure one Rabi flopping. All these laser pulses are assumed to be very short, lasting on the time scale that is commensurable with typical LSP lifetimes (which are several orders of magnitude shorter than QDE relaxation times). We further assume that the (weak) QDE–MNP coupling is sufficiently strong so that the QDE relaxation is determined by this coupling and not by interaction with vacuum fields as in the Weisskopf–Wigner treatment [11]. Similarly, we disregard other possible dissipative and dephasing processes. We anticipate thereby that the relaxation rate in our configuration will be significantly larger than the QDE relaxation rate γ_0 in free space.

The framework determined by the above assumptions allows one to represent the QDE wave function during the transition for the excited coherent superposition state to the ground state in the following form:

$$\Psi(t) = a_1(t)\phi_1 \exp\left(-\frac{i}{\hbar}E_1t\right) + a_0(t)\phi_0 \exp\left(-\frac{i}{\hbar}E_0t\right), \quad (1)$$

where ϕ_1 and ϕ_0 are the wave functions of the QDE states 1 and 0, characterized by the energies E_1 and E_0 , respectively, while $a_1(t)$ and $a_0(t)$ are the corresponding probability amplitudes describing the transition $1 \rightarrow 0$. The QDE dipole moment is thereby given by

$$\vec{D}(t) = a_1 a_0^* \vec{d}_{10} \exp(-i\omega_{10}t) + a_0 a_1^* \vec{d}_{10}^* \exp(i\omega_{10}t), \quad (2)$$

with the asterisk denoting the complex conjugate and $\vec{d}_{10} = \int \phi_1 e \vec{r} \phi_0^* dV$ and $\hbar\omega_{10} = E_1 - E_0$ being the dipole moment and energy of the transition $1 \rightarrow 0$, respectively.

Let us assume that the QDE dipole moment is collinear with the QDE–MNP axis and that the MNP center-to-QDE distance R is considerably larger than the MNP radius r [Fig. 1(a)], with all dimensions being much smaller than the wavelength λ of light, that is, that $\lambda \gg R \gg r$. In this electrostatic approximation, the MNP can be considered as being subjected to the homogenous electric field created by the oscillating QDE dipole. The LSP induced in the MNP by this field creates in its turn the electric field at the QDE site that can be written in the following form:

$$\vec{E}_{\text{sp}} = \frac{a_1 a_0^* \vec{d}_{10}}{\pi \epsilon_0 \epsilon_2} \frac{\epsilon_1 - \epsilon_2}{\epsilon_1 + 2\epsilon_2} \frac{r^3}{R^6} \exp(-i\omega_{10}t) + \text{c.c.}, \quad (3)$$

where c.c. stands for complex conjugate, ϵ_0 is the vacuum permittivity, and $\epsilon_1 = \epsilon_{1r} + \epsilon_{1i}$ and ϵ_2 are the relative permittivities of the MNP and dielectric environment, respectively. In obtaining the above relation, we assumed that temporal variations of $a_1(t)$ and $a_2(t)$ are insignificant during the LSP lifetime, that is, that the QDE–MNP dynamics is very slow in comparison with the LSP damping, an assumption that is consistent with the weak-coupling regime. Note that, if the QDE dipole moment is perpendicular to the QDE–MNP axis, the electric field given by Eq. (3) should be decreased by four times. Using the time-dependent Schrödinger equation for a two-level system in the driving field given by Eq. (3) and carrying out standard manipulations, one obtains the following system of two coupled equations for the probability amplitudes:

$$\frac{da_0}{dt} = \frac{i(\epsilon_1^* - \epsilon_2)|\vec{d}_{10}|^2 r^3}{\pi \hbar \epsilon_0 \epsilon_2 (\epsilon_1^* + 2\epsilon_2) R^6} a_1^* a_1 a_0, \quad (4a)$$

$$\frac{da_1}{dt} = \frac{i(\epsilon_1 - \epsilon_2)|\vec{d}_{10}|^2 r^3}{\pi \hbar \epsilon_0 \epsilon_2 (\epsilon_1 + 2\epsilon_2) R^6} a_0^* a_0 a_1. \quad (4b)$$

The obtained equations can be further simplified and made amenable to analytical treatment by considering the resonance configuration and relatively low LSP damping, that is, with the following conditions being satisfied: $|\epsilon_{1r} + 2\epsilon_2| \ll \epsilon_{1i}$ and $3\epsilon_2 \gg \epsilon_{1i}$. In this case, the coupled equations become reduced to

$$\frac{da_0}{dt} = \mu a_1^* a_1 a_0 \quad \text{and} \quad \frac{da_1}{dt} = -\mu a_0^* a_0 a_1, \quad (5)$$

with

$$\mu = \frac{3|\vec{d}_{10}|^2}{\pi \hbar \epsilon_0 \epsilon_{1i}} \left(\frac{r}{R}\right)^3 \frac{1}{R^3}. \quad (6)$$

Note that Eq. (5) implies that $|a_0|^2 + |a_1|^2 = \text{const}$. Imposing the initial conditions $a_0(\tau) = a_{00}$ and $a_1(\tau) = a_{10} = \sqrt{1 - a_{00}^2}$ allows us to write the solution:

$$a_0(t - \tau) = \frac{a_{00}}{\sqrt{a_{00}^2 + a_{10}^2 \exp[-2\mu(t - \tau)]}}, \quad (7a)$$

$$a_1(t - \tau) = \frac{a_{10}}{\sqrt{a_{10}^2 + a_{00}^2 \exp[2\mu(t - \tau)]}}. \quad (7b)$$

The QDE relaxation dynamics is strongly influenced by the excitation of the LSP mode that opens a very efficient relaxation channel. This channel is primarily nonradiative, but the MNP dipole moment does contribute to the emission process, dominating in fact over the QDE radiation. The total dipole moment of the QDE–MNP system can be represented in the following form:

$$\vec{P} = \left(1 - \frac{6i\varepsilon_2 r^3}{\varepsilon_{1i} R^3}\right) \frac{\vec{d}_{10} \exp(i\omega_{10}t)}{2 \cosh[\mu(t - \tau) - \ln(a_{10}/a_{00})]} + \text{c.c.} \quad (8)$$

The above expressions [Eqs. (6)–(8)] constitute the main theoretical result of our work, providing simple analytical formulas for the QDE–MNP relaxation and emission dynamics and demonstrating that the dynamics is in general quite complicated. The value of parameter μ determines the characteristic relaxation rate of the excited QDE state. Note that the QDE relaxation described by Eq. (7) begins at some time moment τ , when the QDE is in the initial coherent superposition state represented by the initial amplitude conditions, which are determined by the processes used to create such a state as described above. Considering different initial conditions, one notices that, after transient behavior at early times, the QDE relaxation exhibits monoexponential decay with the decay rate given by μ and independent on the initial conditions [Fig. 2(a)]. At the same time, the emission power, which is proportional to the squared magnitude of the total dipole moment [Eq. (8)], can be significantly delayed depending on the QDE initial state [Fig. 2(b)], a somewhat unexpected feature that opens exciting possibilities for controlling the QDE emission dynamics.

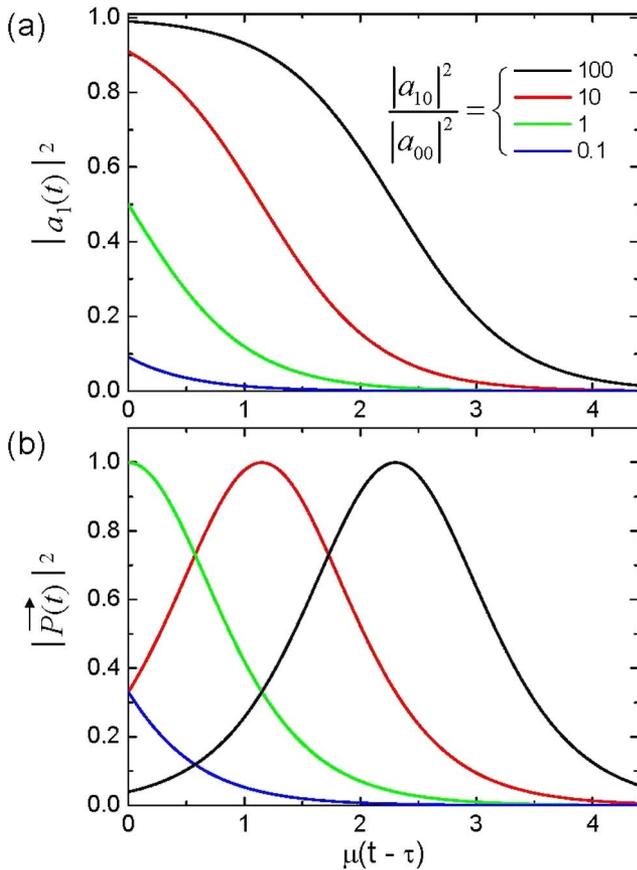


Fig. 2. Relaxation dynamics of the QDE–MNP configuration for different ratios of initial level populations, showing (a) population decay of the excited state 1 [Eqs. (7a)] and (b) the squared magnitude of the total dipole moment [Eq. (8)] normalized to its maximum value.

One of the most important assumptions made is related to the strength of the QDE–MNP coupling, which should ensure considerably larger relaxation rates μ than that for the QDE in free space (γ_0). Their ratio can be evaluated now with the help of Eq. (6) and the Weisskopf–Wigner result [11] as follows:

$$\beta \cong \frac{\mu}{\gamma_0} = \frac{9}{\varepsilon_{1i} \sqrt{\varepsilon_2}} \left(\frac{\lambda_0}{2\pi R}\right)^3 \left(\frac{r}{R}\right)^3, \quad (9)$$

with λ_0 being the vacuum wavelength corresponding to the QDE transition frequency ω_{10} . For a typical dielectric environment with $\varepsilon_2 = 2.25$ (e.g., glass or polymer), the resonance condition (i.e., $\varepsilon_{1r} = -4.5$) is met; for gold, at the wavelength of ~ 530 nm with $\varepsilon_{1i}(g) \cong 2.35$; and for silver, at ~ 400 nm with $\varepsilon_{1i}(s) \cong 0.22$ [13]. Considering an MNP with radius of 5 nm and the QDE distance to the MNP center being 15 nm (in order to be within the electrostatic dipole description), one obtains the ratio $\beta \approx 17$ for gold and ≈ 77 for silver, justifying thereby the above assumption, $\mu \gg \gamma_0$. It is interesting that the effect is already pronounced at relatively large (~ 10 nm) distances between QDEs and the MNP surface, which are in the range of distances explored in the recent experiments with 10-nm-size gold nanoparticles [8]. It is also transparent that even larger ratios can be achieved by exploiting the LSP shape dependence [10,12] and redshifting the MNP resonance toward smaller metal absorption [13].

The described QDE relaxation process can be considered as the *self-stimulated* QDE transition from the excited coherent superposition state into the ground state because it is stimulated not by an external (to QDE) monochromatic light but by the feedback field from the LSP [Eq. (3)], which is in turn excited by the QDE dipole moment [Eq. (2)] generated by the QDE coherent amplitudes [Eq. (7)]. It can be shown by substituting the amplitudes from Eq. (7) into the feedback field given by Eq. (3) that this field represents in fact a π pulse, which ensures the QDE transition to the ground state.

We would like to mention that the occurrence of transient effects at early times was noted in the theoretical consideration of molecular dynamics modified by the presence of an MNP, stressing the following (at later times) exponential decay in the case of weak coupling but without further analysis of transient behavior [10]. Numerical analysis based on the SPP quantum-mechanical description indicated however the occurrence of the emission peak with a certain delay in time in a fashion similar to our results (cf. Fig. 2 here and Fig. 2 in [10]). It is also relevant to mention the reported observation of non-Markovian dynamics of a quantum dot resonantly coupled to a micropillar cavity, resulting in a nonexponential decay in time [14]. Finally, we believe that such a delay could have actually been present (but not elucidated) in the recent experiments with 10-nm-size gold nanoparticles connected by DNA to individual fluorophores (see Fig. 1(d) in [8]).

The most interesting physical finding of our work, namely the radiation emission delay under pulsed excitation, is in fact quite general. Indeed, it is only required that a QDE is placed near a resonator that, at the

frequency of QDE radiative transition, features a well-defined dipolar resonance with the damping rate, which is substantially larger than the QDE relaxation rate in free space. The former ensures the $\pi/2$ phase delay in its electromagnetic feedback, which is essential for arriving at Eq. (5), while the latter is needed to realize the desirable weak-coupling regime. The appropriate interaction can be realized at practically any wavelength with nonspherical MNPs [12] or by using low absorbing dielectric (semiconductor) nanoparticles having large permittivity values and supporting strong Mie resonances that can be chosen propitiously by adjusting the particle shapes and sizes [15]. Another possibility would be to place a QDE near a metal surface, a configuration that is resonant if $\epsilon_{1r}(\omega_{10}) = -\epsilon_2$, with the strong-coupling regime requiring subnanometer QDE–surface distances [16]. Our approach can also be applied in this case, provided that $|\epsilon_{1r} + \epsilon_2| \ll \epsilon_{1i}$ and $2\epsilon_2 \gg \epsilon_{1i}$, resulting in similar emission dynamics with the relaxation parameter given by

$$\mu_1 = \frac{|\vec{d}_{10}|^2}{8\pi\hbar\epsilon_0\epsilon_{1i}R^3}, \quad (10)$$

with R being in this case the QDE–surface distance and considering that the QDE dipole moment is perpendicular to the metal surface. Note that the $1/R^6$ scaling in Eq. (6) is transformed, for this configuration, into the $1/R^3$ scaling [Eq. (10)], which is also expected to be the case for small QDE–MNP separations with the dipolar MNP response to the homogeneous field becoming strongly multipolar and approaching that of a flat metal surface.

In summary, we have considered the relaxation dynamics of a generic QDE excited with short pump pulses and located near an MNP that exhibits a dipolar LSP resonance at the frequency of the QDE radiative transition. Our theoretical analysis resulted in the following conclusions: (i) the relaxation dynamics in the resonantly coupled QDE–MNP system exhibits step-like behavior, deviating thereby significantly from the generally accepted exponential decay [3,4,7–9]; (ii) the QDE–MNP radiation emission reaches its maximum with a significant delay in time; and (iii) a large number of system parameters in our analytical description opens new possibilities for controlling the QDE relaxation and emission dynamics. Given the variety of resonant plasmonic

[12] and semiconductor [15] nanoparticles, the experimental observation of the predicted effect seems feasible, while the possibility of tuning the delay time by changing the QDE–MNP separation can be exploited in many applications, such as for realizing a nanoscopic ruler [17], as well as in fundamental studies within quantum plasmonics [1].

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