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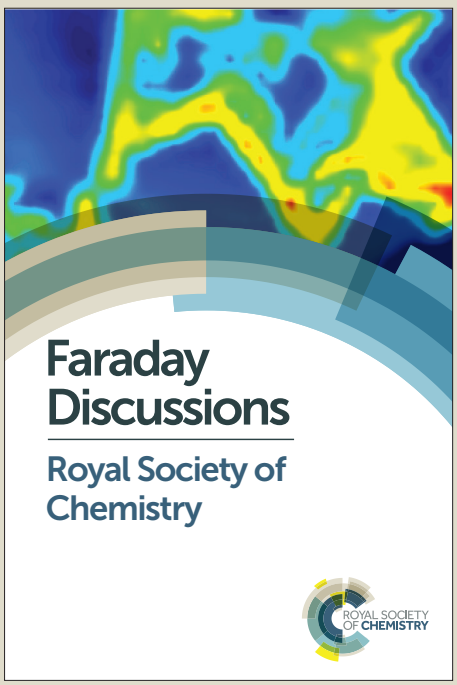

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Relaxation dynamics of a quantum emitter resonantly coupled to a coherent state of localized surface plasmon

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We investigate relaxation dynamics of a quantum dipole emitter (QDE), e.g., a molecule or quantum dot, located near a metal nanoparticle (MNP) exhibiting a dipolar localized surface plasmon (LSP) resonance at the frequency of the QDE radiative transition. A generic three-level QDE, which is pumped with an external laser pulse and brought thereby into an optically active excited state, is considered to be weakly coupled to the resonant LSP described by a coherent state. It is shown that, under the condition of the QDE-MNP characteristic relaxation time being much shorter than that of the QDE in free space but much longer than the LSP lifetime, the QDE relaxation dynamics can be described analytically and features, in general, non-exponential decay with complicated transient behaviour. The main physical consequence of this relaxation process is that the emission, being largely determined by the MNP, comes out with a substantial delay. It is also shown that energy dissipation in the QDE-MNP system is relatively weak with the probability of the photon emission being ~0.75, a number which, rather surprisingly, does not explicitly depend on the metal absorption characteristics. A large number of QDE-MNP system parameters in our analytical description opens new possibilities for controlling quantum emitter dynamics.

Introduction

Interaction of quantum dipole emitters (QDEs), such as molecules or quantum dots, with 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] Coupling of electromagnetic fields in dielectrics and free electron oscillations in metals, which results in surface plasmon excitations, enables localization of light in subwavelength-sized volumes and, in general, command over light-matter interactions at the nanoscale. One of the very fundamental effects occurring as a result of these interactions is the modification of QDE relaxation dynamics due to the presence of metal nanostructures, e.g. MNPs, strongly perturbing local electromagnetic fields. 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 the QDE-MNP interaction can enter the regime of strong coupling, where excitation energy is

coherently transferred between the QDE and MNP in the form of Rabi oscillations.[1,10]

The strong coupling between a QDE and a resonator is a key element of the quantum-optics toolbox. In the absence of energy dissipation, two identical oscillators are strongly coupled even for small coupling constants. In practice, their coupling should be sufficiently strong so that the energy level splitting becomes larger than the width of oscillator resonances or, alternatively, that the period of Rabi oscillations becomes smaller than the oscillator lifetimes. The QDE-MNP system is characterized by an enormous mismatch in the lifetimes of its components due to inevitable light absorption in metals, with the LSP lifetime being of the order of a few femtoseconds in visible.[11] It is clear that, for the strong QDE-MNP coupling regime to be realized, the normal mode splitting should be very large in order to exceed the LSP linewidth or, alternatively, for the Rabi frequency to exceed the LSP damping rate. Considering this requirement from the viewpoint of the QDE decay rate enhanced near a resonant MNP,[3,4,7-10] the MNP-enhanced QDE decay rate should be increased by *many orders of magnitude*, reaching the LSP damping rate.[11] The situation changes when considering the interaction of an ensemble of QDEs with plasmonic resonators due to the square-root scaling of the coupling constant with respect to the QDE concentration.[12] Several successful demonstrations of the strong-coupling regime in various resonant plasmonic configurations interacting with QDE ensembles have been reported during the last 10 years,[1] including recent real-time observations of ultrafast Rabi oscillations between J-aggregate excitons and surface plasmon polaritons supported by a periodic metal nanostructure.[13] However, for the QDE-MNP system, the strong-coupling regime requires very large QDE dipole moments (>>1 a.u.) and very small (<<10 nm) QDE-MNP separations,[10] and is yet to be experimentally realized.

Numerous investigations considering modification of spontaneous emission in various QDE-MNP configurations were focused on the effect of dramatic enhancements of the QDE (radiative and nonradiative) decay rates in the vicinity of the MNP,[3,4,7-9,14,15] *always* implicitly assuming that the relaxation dynamics is purely exponential as obtained in the Weisskopf-Wigner treatment of an individual two-level atom.[16] At the same time, the occurrence of transient effects at early times was noted in the 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 behaviour.[10] Here, we argue that, given an extremely large difference between the relaxation times of the excited QDE and the LSP mode of the MNP, the experimentally accessible 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, occurs via *coherent* interaction between an optically active excited QDE state and a coherent state of the resonant LSP. Recently, we considered a similar system of a generic three-level QDE located near an MNP exhibiting a dipolar resonance (that coincides with the frequency of the QE radiative transition) using a quasi-classical description, in which the QDE was represented by the coherent superposition of the excited and ground states obeying the time-dependent Schrödinger equation (for a two-level system), while the LSP field was considered to be induced in the MNP by the classical electromagnetic field created by the oscillating QDE dipole.[17] For this configuration under pulsed excitation, we have found an *intermediate* regime of relaxation (which we associated with the *self-stimulated* QDE transition[17]) that

occurs in a coherent fashion (like in the strong-coupling regime) with a substantial delay of the emission followed by exponential relaxation dynamics akin to that of modified spontaneous emission in the weak-coupling regime.[3,4,7-9,14-16]

In this work, we develop further our treatment by elaborating the description of the LSP field and introducing the density-matrix formalism for essentially the same configuration as was treated previously.[17] The considered MNP-QDE configuration exhibits the following three main features:

1. Resonant excitation of the LSP is realized as a result of free electron oscillations in the MNP that, for nm-size MNPs, can be regarded as classical current oscillations, since a large number of free electrons (~100 nm^{-3}) is involved and their energy spectrum can be considered continuous. This classical oscillating current is then represented by a quantum *coherent* state[18] of the LSP. Note that the coherent LSP state is fundamentally different from (often considered) LSP states with a definite number of quantized plasmons.[1]
2. The LSP decay rate is larger than the QDE spontaneous emission (decay) rate by five orders of magnitude. Therefore, even for relatively strong QDE-MNP interactions, the relaxation of the QDE-MNP system is much slower than the LSP decay, a feature that allows one to disregard the LSP dynamics and consider the MNP response as being *instantaneous*.
3. The magnitude of a dipole moment associated with the radiative QDE transition is one order of magnitude smaller than that of an LSP dipole moment induced by the QDE, a feature that allows one to consider the MNP acting as an *antenna* of the QDE-MNP system.

In our opinion, these distinct features of the considered MNP-QDE configuration open the possibility for realization of a *unique* (coherent) relaxation dynamics that exhibit characteristic signatures of both weak and strong coupling regimes.

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. Considering the resonant QDE–MNP coupling to be strong enough for significantly decreasing the excited QDE lifetime but weak enough so that the emission rate is still far to smaller than the LSP dissipation rate, we find that the QDE-MNP emission comes with a delay producing a single emission pulse with characteristics that can be controlled by adjusting the system parameters, such as the QDE-MNP separation and MNP dimensions. We further consider energy dissipation in the QDE-MNP system due to the light absorption by the MNP and obtain a *general* result showing that the probability of the photon emission by the system is ~0.75, a number which, rather surprisingly, does *not* explicitly depend on the system parameters, including the metal absorption. We also discuss several publications, whose theoretical and experimental results might have already (albeit indirectly) supported our findings.

Theoretical Framework

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 g into the state s, where it decays nonradiatively into the optically active excited state e, and that the spherical

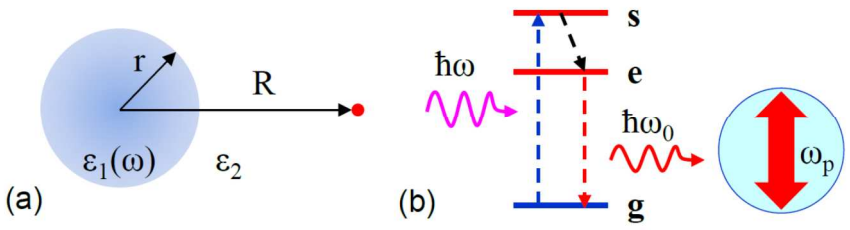

Fig. 1 Schematic of a system with a QDE placed near an MNP, indicating (a) system parameters and (b) QDE energetic levels along with an oscillating current associated with the LSP excitation.

MNP exhibits a dipolar LSP resonance at the frequency ω_0 of the radiative (dipole-allowed) transition $e \rightarrow g$ [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 e, whose modification due to the QDE–MNP coupling is the main subject of this work. 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,[10,19] for instance, to coincide with the QDE radiative transition frequency.

The Hamiltonian of the system can be represented as:

$$\hat{H} = \hat{H}_0 + \hat{H}_1 \ , \tag{1}$$

$$\hat{H}_0 = \frac{1}{2}\hbar\omega_0\left(b_e^+ b_e - b_g^+ b_g\right) + \hbar\omega_p a^+ a \ , \tag{2}$$

$$\hat{H}_1 = q^*\left(b_e^+ b_g + b_g^+ b_e\right)a + q\left(b_e^+ b_g + b_g^+ b_e\right)a^+ \ . \tag{3}$$

Here, ω_0 is the frequency of the radiative QDE transition, $\hbar$ is the reduced Planck constant, b_e^+ and b_e are the creation and annihilation operators of the excited QDE state e, b_g^+ and b_g are the creation and annihilation operators of the ground QDE state g, ω_p is the frequency of the resonant LSP excitation, a^+ and a are the creation and annihilation operators of the LSP, q is the coupling constant characterizing the interaction between the QDE and LSP. By using the unitary transformation: $U_0 = \exp(-iH_0 t/\hbar)$, we transform the system Hamiltonian into one that, within the rotating wave approximation and under the condition of strict resonance ($\omega_0 = \omega_p$), has the following form:

$$\hat{H}' = q^* b_e^+ b_g a + q b_g^+ b_e a^+ \ . \tag{4}$$

The first two of the QDE-MNP system features described in the previous section allow one to significantly simplify the solution procedure. Considering free electron oscillations in the resonantly excited MNP as classical current oscillations (due to a very large number of electrons involved and the continuity of their energy spectrum), we further make use of the concept of coherent states in quantum optics[18] for the description of this classical current. We also assume that, due to an extremely large difference in the decay rates of an LSP and isolated QDE, it is possible and, indeed, highly probable that the relaxation of the QDE-MNP system is much slower than that of the LSP, but much faster than that of the isolated QDE. In such a situation, one can neglect the QDE relaxation due to its spontaneous emission and disregard the LSP dynamics, considering the MNP response as instantaneous. Under these conditions, the wave function of the full QDE-MNP system can be represented

as follows:

$$|\psi>=\left\{\beta_e(t)\left|e>+\beta_g(t)\right|g>\right\}e^{-\frac{1}{2}|\alpha(t)|^2}\sum_{n=0}^{\infty}\frac{\alpha^n(t)}{\sqrt{n!}}|n> \quad . \tag{5}$$

Here, $\beta_e(t)$ and $|e>$ are the probability amplitude and the wave function of the excited QDE state, $\beta_g(t)$ and $|g>$ are the probability amplitude and the wave function of the ground QDE state, $\alpha(t)$ is the eigenvalue of the operator a, $|n>$ is the LSP wave function corresponding to the energy eigenvalue $n\hbar\omega_p$. Eqs. (4) and (5) represent the starting point of our theoretical framework, allowing us to finally obtain relations for the probability density matrix elements of the QDE transitions and for the eigenvalue $\alpha(t)$ of the LSP operators:

$$\frac{\partial<b_e^+b_e>}{\partial t}=\frac{\partial\rho_{ee}}{\partial t}=\frac{i}{\hbar}\{q\alpha^*\rho_{ge}-q^*\alpha\rho_{eg}\} \quad \text{with} \quad \rho_{gg}=1-\rho_{ee} \ , \tag{6}$$

$$\frac{\partial<b_e^+b_g>}{\partial t}=\frac{\partial\rho_{eg}}{\partial t}=-\frac{i}{\hbar}q\alpha^*\{\rho_{ee}-\rho_{gg}\} \quad \text{with} \quad \rho_{ge}=\rho_{eg}^* \ , \tag{7}$$

$$\frac{\partial<a>}{\partial t}=\frac{\partial\alpha}{\partial t}=-\frac{i}{\hbar}q\rho_{ge}-\Gamma\alpha \ , \tag{8}$$

where the LSP relaxation rate Γ is introduced. Here, we operate under the assumption of instantaneous MNP response: $\partial\alpha/\partial t \ll \Gamma\alpha$, hence

$$\alpha\approx-\frac{i}{\hbar\Gamma}q\rho_{ge} \quad . \tag{9}$$

Finally, one can work out the following solution of the system of equations (6-9):

$$\rho_{ee}(t)=\frac{1}{1+e^{2\{\mu(t-\tau)-\varphi\}}} \ , \tag{10}$$

$$\rho_{eg}(t)=\rho_{ge}(t)=\frac{1}{2\cosh\{\mu(t-\tau)-\varphi\}} \ , \tag{11}$$

where

$$\mu=\frac{|q|^2}{\hbar^2\Gamma} \quad \text{and} \quad \varphi=\ln\left[\frac{\rho_{ee}^{(\tau)}}{\rho_{gg}^{(\tau)}}\right] \ , \tag{12}$$

$\rho_{ee}^{(\tau)}$ and $\rho_{gg}^{(\tau)}$ are the probability density matrix elements at the initial moment $t=\tau$.

It is seen that the relaxation dynamics of the QDE-MNP configuration is characterized by the parameter μ that influences both the time delay in reaching the maximum QDE transition rate [Eq. (11)] and the relaxation rate at later moments of time [Eq. (10)]. This important system characteristic is related to the basic parameters of the considered configuration. 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, i.e., that $\lambda \gg R \gg r$. Then, by making use of the electrostatic approximation we obtain for the coupling constant q, which represents the energy of the QDE-MNP (dipole-dipole) interaction, the following expression:

$$q=\frac{1}{4\pi\varepsilon_0\varepsilon_d}\frac{2\boldsymbol{d}_{eg}\cdot\boldsymbol{d}_p}{R^3} \ , \tag{13}$$

where ε_0 is the vacuum permittivity, ε_d is the relative permittivity of the dielectric

environment, $\boldsymbol{d}_{eg}$ is the dipole moment of QDE radiative transition, and $\boldsymbol{d}_p$ is the dipole moment associated with the LSP transition. In the vicinity of the LSP resonance, the polarizability δ of the MNP can be expressed as follows:[20]

$$\delta = \frac{1}{\hbar}\frac{|\boldsymbol{d}_p|^2}{\omega-\omega_p-i\Gamma} = 4\pi\varepsilon_0\varepsilon_d r^3\frac{\varepsilon_m-\varepsilon_d}{\varepsilon_m+2\varepsilon_d} \quad , \tag{14}$$

where $\varepsilon_m = \varepsilon_m^{'} + i\varepsilon_m^{''}$ is the metal permittivity. Using the condition of strict resonance $\omega_0 = \omega_p$ and, alternatively, $\left|\varepsilon_m^{'} + 2\varepsilon_d\right| \ll \varepsilon_m^{''}$ one obtains:[21]

$$\left|\boldsymbol{d}_p\right|^2 = \frac{12\pi\hbar\varepsilon_0\varepsilon_d^2 r^3}{\frac{\partial\varepsilon_m^{'}(\omega_p)}{\partial\omega_p}} \quad \text{and} \quad \Gamma = \frac{\varepsilon_m^{''}(\omega_p)}{\frac{\partial\varepsilon_m^{'}(\omega_p)}{\partial\omega_p}} \quad . \tag{15}$$

Finally, the characteristic relaxation rate μ of the QDE-MNP system can be expressed via the system parameters by substituting Eqs. (13) and (15) into Eq. (12):

$$\mu = \frac{3|\boldsymbol{d}_{eg}|^2 r^3}{\pi\hbar\varepsilon_0\varepsilon_m^{''}R^6} \quad . \tag{16}$$

The QDE relaxation dynamics is strongly influenced by the excitation of the LSP mode that opens a very efficient relaxation channel. The QDE-induced dipole moment of the MNP, which plays a role of an antenna in the QDE-MNP system, can be represented in the following form:

$$\boldsymbol{p} = \frac{3i\varepsilon_d r^3}{\varepsilon_m^{''}R^3}\frac{\boldsymbol{d}_{eg}e^{-i\omega_0 t}}{cosh\{\mu(t-\tau)-\varphi\}} \quad . \tag{17}$$

The above expressions [Eqs. (10), (11), (16) and (17)] constitute the main theoretical outcome 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. Note that these expressions are also consistent with those obtained previously by us using the quasi-classical approach, in which the QDE was represented by the coherent superposition of the excited and ground states obeying the time-dependent Schrödinger equation (for a two-level system), while the LSP field was considered to be induced in the MNP by the classical electromagnetic field created by the oscillating QDE dipole.[17] In this respect, the above derivation can be considered as the justification of the previously used approach.

Results and Discussion

One of the most important assumptions made in our theoretical framework described in the previous section 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. (16) and the Weisskopf-Wigner result[16] as follows:

$$\beta = \frac{\mu}{\gamma_0} = \frac{9}{\varepsilon_m^{''}\sqrt{\varepsilon_d}}\left(\frac{\lambda_0}{2\pi R}\right)^3\left(\frac{r}{R}\right)^3 \quad , \tag{18}$$

with λ_0 being the vacuum wavelength corresponding to the QDE transition frequency ω_0. For a typical dielectric environment with $\varepsilon_d = 2.25$ (e.g., glass or polymer), the resonance condition (i.e., $\varepsilon_m' = -4.5$) is met, for gold, at the wavelength of ~530 nm with $\varepsilon_{m(g)}'' = 2.35$ and, for silver, at ~400 nm with $\varepsilon_{m(s)}'' = 0.22$.[22]

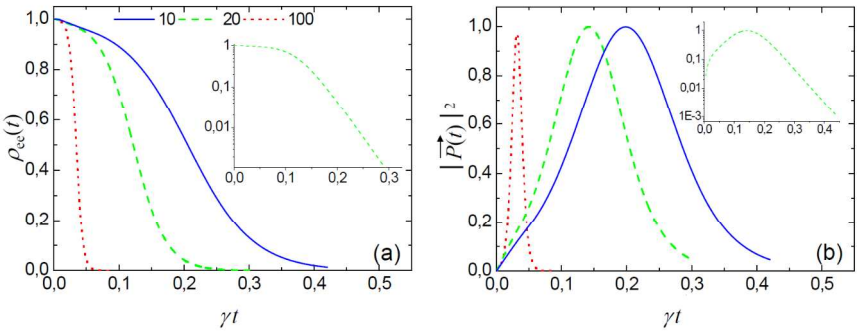

Fig. 2 Relaxation dynamics of the QDE-MNP configuration for different ratios of the established and initial relaxation rates μ/γ, showing (a) population decay of the excited state e [Eq. (10)] and (b) the squared magnitude of the MNP dipole moment [Eq. (17)] normalized to its maximum value. Insets display the same dependencies in the logarithmic scale for the case of $\mu/\gamma = 20$.

Considering an MNP with the 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 $\beta \approx 77$ 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[10,19] and red-shifting the MNP resonance towards smaller metal absorption.[22]

The QDE relaxation described by Eqs. (10) and (11) begins at some moment of time when the QDE optically active state e, which is created by nonradiative decay of the excited state s, is partially relaxed into the ground state g, so that $\rho_{gg}^{(\tau)} > 0$. This starting process can occur due to other inducements always found in an open system, for example, due to the free-space spontaneous emission, i.e., without the influence of the QDE-MNP interaction, because the MNP dipole moment [Eq. (17)] is still negligibly small. Let us now assume that the QDE relaxation at *initial* moments of time can be described via an exponential decay, so that $\rho_{ee}^{r} = exp(-\gamma t)$. It is reasonable to expect that this initial QDE relaxation is very similar to that of the free-space spontaneous emission, i.e., that $\gamma \sim \gamma_0$. Applying the continuity condition at the transition between these two processes to both functions, $\rho_{ee}^{r}(t)$ and $\rho_{ee}(t)$, and their derivatives, one can determine the characteristic time $\tau = 1/2\mu$ and $\rho_{ee}^{(\tau)}/\rho_{gg}^{(\tau)} = \sqrt{2\mu/\gamma} \gg 1$. Note that the time τ does not depend on the initial QDE relaxation rate γ, after which starts the investigated process. Therefore, the present consideration allows one to analyze the whole relaxation process. The QDE relaxation dynamics depends strongly on the efficiency of the QDE-MNP interaction, which is characterized by the relaxation rate ratio μ/γ. Sharp step-like behavior, which is observed for very large ratios μ/γ, changes to more gradual population decay for smaller ratios μ/γ [Fig. 2(a)]. Emission of radiation from the QDE-MNP system is determined primarily by the square magnitude of the (induced) MNP dipole moment [Eq. (17)], whose maximum is attained after a certain delay time $t_d = [1 + ln(2\,\mu/\gamma)](2\mu)^{-1}$. For strong QDE-MNP interactions (very large μ/γ), the emission peak is narrow and occurs close to the initial moment of time [Fig. 2(b)]. Note that, in practice, $\mu/\gamma \sim \beta$ [Eq. (18)] that can attain rather large values in realistic conditions as discussed above. It should also be noted that the

delay time t_d is of the same order of magnitude as the width (at half maximum) of the emission peak. This interesting feature might be found useful when conducting and analyzing the corresponding experiments.

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, which is in turn excited in the MNP by the QDE dipole moment. It can be shown that this field represents in fact a π pulse, which ensures the QDE transition into 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 Ref. 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.[23] 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 Ref. 8).

As already mentioned the MNP serves as a radiative antenna in the QDE-MNP configuration. The energy dissipation in this configuration (that causes photon loss) occurs due to inevitable ohmic losses in the MNP. Then the probability of non-radiative decay of the system can be determined by relating the energy dissipated in the system[24] to the photon energy:

$$P = \frac{\frac{1}{2}\int_0^\infty Re[\boldsymbol{p}\cdot\dot{\boldsymbol{E}}^*]dt}{\hbar\omega_0} \quad , \tag{19}$$

where $\boldsymbol{E}$ is the electric field induced at the MNP, which is characterized by the dipole moment $\boldsymbol{p}$ [Eq.(17)], by the QDE dipole moment $\boldsymbol{d}_{eg}$:

$$\dot{\boldsymbol{E}}^* = \frac{i\omega_0}{4\pi\varepsilon_0\varepsilon_d R^3}\frac{\boldsymbol{d}_{eg}^* e^{i\omega t}}{cosh\{\mu(t-\tau)-\varphi\}} \quad . \tag{20}$$

In the discussed case, when $\rho_{ee}^{(\tau)} \gg \rho_{gg}^{(\tau)}$, one obtains after performing integration in Eq. (19) a very simple formula for the loss probability: $P \cong 0.25[1-(3\gamma/8\mu)] \approx 0.25$. Under the condition of the resonant QDE-MNP coupling, the transition from the QDE optically active state e to the ground state g occurs during the time interval of $\sim 2t_d$ (Fig. 2), implying the transition rate of $\sim 0.5/t_d$. Assuming that the excitation of the upper state s by the pump [Fig. 1(b)] together with the subsequent relaxation to the QDE optically active state e takes considerably less time (also that the pump rate is smaller than any of the system relaxation rates), we can evaluate the fluorescence enhancement due to the QDE-MNP resonant coupling:

$$\eta = (1-P)\frac{1/2t_d}{\gamma_0} \cong \frac{3}{4}\frac{\mu}{\gamma_0[1+ln(2\mu/\gamma)]} \approx \frac{3}{4}\frac{\beta}{1+ln(2\beta)} \quad , \tag{21}$$

which is substantial [Eq. (18)] and can easily reach several orders of magnitude.

The most interesting physical finding of our work, viz., the spontaneous 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 justifies the derivation of Eq. (4) and ensures the $\pi/2$ phase delay in the QDE-MNP system (electromagnetic) feedback, while the latter is needed to realize the desirable weak-coupling regime. The appropriate interaction can be realized at practically any wavelength with non-spherical MNPs[19] 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.[25] Another possibility would be to place a QDE near a metal surface, a configuration that is resonant if $\varepsilon'_m(\omega_0) \approx -\varepsilon_d$, with the strong-coupling regime requiring sub-nanometer QDE-surface distances.[26] Our approach can also be applied in this case, provided that $|\varepsilon'_m + \varepsilon_d| \ll \varepsilon''_m$ and $2\varepsilon_d \gg \varepsilon''_m$, resulting in similar emission dynamics with the relaxation parameter μ given by

$$\mu_1 = \frac{|\boldsymbol{d}_{eg}|^2}{8\pi\hbar\varepsilon_0\varepsilon''_m R^3} \quad , \tag{22}$$

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 R^{-6} scaling in Eq. (16) is transformed, for this configuration, into the R^{-3} scaling [Eq. (22)], which is also expected to be the case for small QE-MNP separations with the dipolar MNP response to the homogeneous field becoming strongly multipolar and approaching that of a flat metal surface.[27] The condition $\varepsilon'_m(\omega_0) \approx -\varepsilon_d$ defines the physical situation, where the predicted relaxation dynamics can be observed. In the visible region of the spectrum, where the magnitude of the real part of the dielectric constant of metals, such as gold and silver, is large enough, semiconductor substrates can be used. In this case, excitons, which are typically localized in the vicinity of the interface, can be playing the role of individual QDEs. Indeed, very recent time-resolved spontaneous emission measurements in the configuration, consisting of a semiconductor (CdS) nanocrystal separated from a metal (silver) surface by a 8-nm-thin dielectric (MgF_2) layer, revealed that the spontaneous emission reaches its maximum with a significant delay in time.[28] This delay (a few hundred ps) is significantly larger than the characteristic time of reaching the equilibrium state (a few ps), with the overall time dependence being quite similar to our results (cf. Fig. 2 here and Fig. 3 in Ref. 28).

Conclusions

Summarizing, we have considered the relaxation dynamics of a generic QDE excited with short pump pulses and located near a MNP that exhibits a dipolar LSP resonance at the frequency of the QDE radiative transition. It has been shown that, under the condition of the QDE-MNP characteristic relaxation time being much shorter than that of the QDE in free space but much longer than the LSP lifetime, the QDE relaxation dynamics can be described analytically and features, in general, non-exponential decay with complicated transient behaviour. Our theoretical analysis resulted in the following main conclusions: (*i*) the relaxation dynamics in the resonantly coupled QDE-MNP system exhibits step-like behaviour 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*) energy dissipation in the QDE-MNP system is relatively weak with the probability of the photon emission being ~0.75, a number which, rather surprisingly, does not explicitly depend on the metal absorption characteristics. 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[19] and semiconductor[25] nanoparticles, the experimental observation of the predicted effect seems feasible,[28] while the possibility of tuning the delay time by changing the QDE-MNP separation can be exploited in many applications, e.g., for practical implementation of a nanoscopic ruler,[29] or optimization of scanning single QDE fluorescence lifetime imaging,[30] as well as in fundamental studies within quantum plasmonics.[1]

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