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Reversible Population Dynamics at the Nanoscale for a Quantum Emitter Near a WSe_2 Monolayer †

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Abstract: We investigate the spontaneous emission dynamics of a two-level quantum emitter in proximity to an atomically thin tungsten diselenide (WSe_2) layer at various distances of the emitter from the layer and various free-space decay rates of the emitter. Depending on the distance and the decay rate value, our studies cover the range of weak to strong coupling regime of the light-matter interaction between the quantum emitter and the electromagnetic continuum modified by the WSe_2 layer. We find that the decay dynamics is Markovian under weak coupling conditions, and it becomes strongly non-Markovian, characterized by oscillatory population emitter dynamics, on the top of the overall population decay, as well as population trapping in the emitter.

Keywords: quantum emitter; two-dimensional material; transition-metal dichalcogenide; Purcell effect; spontaneous emission; Non-Markovianity measure

1. Introduction

The interaction of quantum emitters (QEs) with photonic antennas created by nanoscale structures may lead to several interesting phenomena with many important potential applications in current and future technology [1]. There are two distinct regimes of light-matter interaction between a QE and its modified photonic environment, the weak coupling (or weak light-matter interaction) regime and the strong coupling (or strong light-matter interaction) regime, where the QE has completely different spontaneous emission (SE) response. In the weak coupling regime, an initially excited QE shows an exponential SE dynamics (Markovian response), but the spontaneous decay rate can be markedly different from free-space vacuum, and can be either enhanced or suppressed due to the Purcell effect [2]. In the strong coupling regime, there is a coherent exchange of energy between the QE and its modified nanophotonic environment, which manifest itself in splitting in the emission or absorption spectrum in the frequency regime (the so-called Rabi splitting) and non-exponential SE dynamics (non-Markovian response) [3]. Several studies have been devoted to the study of reversible, non-Markovian, SE dynamics of a two-level quantum emitter near plasmonic nanostructures [4]. Different nanostructures that have been proposed as photonic structures for creating strong coupling with QEs are made of two-dimensional (2D) materials [5]. The simplest 2D nanostructure is a single layer made by the 2D material, modelled as an infinite sheet.

In this work we investigate the SE dynamics of a QE near a transition-metal dichalcogenide monolayer, in particular, a tungsten diselenide WSe_2 layer. We use electromagnetic calculations for obtaining the Purcell factor and the spectral density, where we describe its optical response by experimental data. We then combine the results of the electromagnetic response with quantum dynamics calculations and study the SE dynamics of the QE for different distances from the WSe_2 layer and different QE free-space decay rates. We show that at short distances strong coupling occurs and the

QE exhibits non-Markovian SE response. The SE dynamics, as studied from the excited state population dynamics, leads to different population time evolution for different distances and free-space decay rates. The phenomena found in the population evolution include Markovian and non-Markovian dynamics with decaying Rabi oscillations, and even population trapping. Besides population evolution, we also discuss the non-Markovian SE dynamics using the non-Markovianity measure defined by Breuer, Laine and Pillo (BLP) [6].

2. Theory

We investigate the SE dynamics of a QE interacting with a single photon near an atomically-thin WSe_2 layer, as shown on the left side in Figure 1. We consider a coordinate system with the xy-plane coinciding with the WSe_2 layer and the Z-axis perpendicular to it; the QE is located in vacuum at $\mathbf{r}_{QE} = (0, 0, D)$ with respect to this coordinate system.

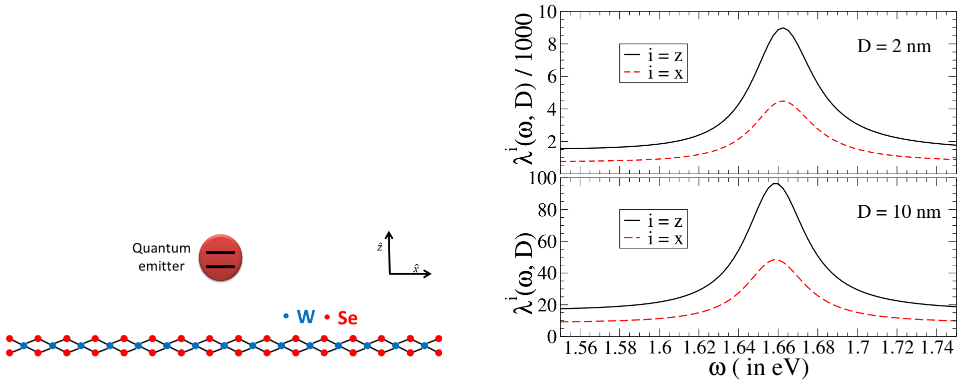

Figure 1. (color online) (**Left**): Schematic representation of a two-level QE in proximity to an atomically-thin layer of WSe_2. (**Right**): Directional Purcell factors of a QE at distance $D = 2$ nm and $D = 10$ nm from an atomically-thin WSe_2 layer along the perpendicular (z) and parallel (x) directions.

We write the total Hamiltonian of the system as [7] (we use $\hbar = 1$ throughout in this work)

$$\begin{aligned} \hat{H} &= \omega_0 |1\rangle\langle 1| + \int d^3\mathbf{r}' \int_0^\infty d\omega \omega \hat{\mathbf{f}}^\dagger(\mathbf{r}', \omega) \cdot \hat{\mathbf{f}}(\mathbf{r}', \omega) + \\ & \int_{-\infty}^{\infty} d\omega \int d^3\mathbf{r}' g(\mathbf{r}', \omega)(|0\rangle\langle 1| + |1\rangle\langle 0|)[\hat{\mathbf{f}}^\dagger(\mathbf{r}', \omega) + \hat{\mathbf{f}}(\mathbf{r}', \omega)] \,. \end{aligned} \tag{1}$$

Here, the first term describes the energy of the QE, the second term describes the electromagnetic field's energy and the last term describes the interaction of the QE with the electromagnetic field. Here, ω_0 is the transition frequency of the QE, $\hat{\mathbf{f}}^\dagger(\mathbf{r}', \omega)$, $\hat{\mathbf{f}}(\mathbf{r}', \omega)$ are the electromagnetic field's creation and annihilation operators, which obey the usual commutation relations [8], and $g(\mathbf{r}', \omega)$ is the coupling coefficient between the QE and the electromagnetic field given by

$$g(\mathbf{r}', \omega) = -i\sqrt{\frac{1}{\pi\epsilon_0} \frac{\omega^2}{c^2}} \sqrt{\epsilon_I(\mathbf{r}', \omega)} \hat{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega) \cdot \boldsymbol{\mu} \,, \tag{2}$$

where $\boldsymbol{\mu}$ denotes the electric dipole moment of the QE and $\hat{\mathbf{G}}(\mathbf{r}, \mathbf{r}', \omega)$ describes the classical electromagnetic Green's tensor. Also, $\epsilon_I(\mathbf{r}, \omega)$ denotes the imaginary part of the dielectric function of the system and c is the speed of light in vacuum.

We now write the general wavefunction of the QE and electromagnetic field as

$$|\psi(t)\rangle = c_1(t)e^{-i\omega_0 t}|1, \{0\}\rangle + \int d^3\mathbf{r}' \int_{-\infty}^{\infty} d\omega c_0(\mathbf{r}', \omega, t)e^{-i\omega t}|0, \{\mathbf{1}_{\mathbf{r}', \omega}\}\rangle \,, \tag{3}$$

and substitute it into the time-dependent Schrödinger equation, using the above Hamiltonian. Here, $|n,a\rangle = |n\rangle \otimes |a\rangle$, where $|1,\{0\}\rangle$ denotes the excited state of the QE $|1\rangle$ and the zero photon electromagnetic field state (vacuum state) $|\{0\}\rangle$, and $|0,\{\mathbf{1}_{\mathbf{r}',\omega}\}\rangle$ denotes the lower state of the QE $|0\rangle$ and the one photon electromagnetic field state $|\{\mathbf{1}_{\mathbf{r}',\omega}\}\rangle$. We then obtain the subsequent integro-differential equation for the excited state's probability amplitude $c_1(t)$,

$$\dot{c}_1(t) = -\int_0^t dt' \int_0^\infty d\omega J(\omega) e^{-i(\omega-\omega_0)(t-t')} c_1(t'), \tag{4}$$

where $J(\omega)$ denotes the spectral density given by

$$J(\omega) = \frac{\Gamma_0(\omega_0)}{2\pi} \lambda^k(\omega, D), \quad k = \perp, \parallel . \tag{5}$$

Also, $\Gamma_0(\omega_0)$ denotes the free-space vacuum decay rate of the QE and $\lambda^i(\omega, D)$, with $k = x, z$, denotes the directional Purcell factor due to the presence of the WSe_2 layer at $\mathbf{r}_{QE} = (0, 0, D)$. The free-space decay rate reads $\Gamma_0(\omega_0) = \frac{\omega_0^3 \mu^2}{3\pi\epsilon_0 c^3}$ [7]. Below, we calculate the excited state probability amplitude dynamics of the QE $c_1(t)$ numerically using the effective mode differential equation methodology [7]. The calculations are performed in the energy range 1.4 eV to 5 eV.

The directional Purcell factor is crucial for quantifying the influence of the photonic environment created by the WSe_2 layer on the QE's SE process, which is defined as:

$$\lambda^i(\omega, \mathbf{r}) = \frac{\Gamma^i(\omega, \mathbf{r})}{\Gamma_0(\omega)} = 1 + \frac{6\pi c}{\omega} \hat{n}_i \cdot \mathrm{Im}\, \hat{\mathbf{G}}(\mathbf{r}, \mathbf{r}, \omega) \cdot \hat{n}_i, \tag{6}$$

where $\Gamma^i(\omega, \mathbf{r})$ is the directional relaxation rate of a QE, placed in vacuum, in proximity to the WSe_2 layer, and $\hat{\mathbf{G}}$ is the induced part of the electromagnetic Green's tensor, due to the layer, calculated at the QE position, which represents the response of the WSe_2 layer under consideration to a point-like dipole excitation [8], and $\hat{n}_i$ $(i = z, x)$ is the unit vector along the direction of the transition dipole moment. The Purcell factors for a QE with z- and x-oriented transition dipole moment located at $z = D = 2$ nm and $z = D = 10$ nm are presented on the right side in Figure 1. More details on the calculation of the Green's tensor and the corresponding Purcell factors are given in refs. [9–11].

3. Results and Discussion

In the left panel in Figure 2 we present the SE dynamics of a QE with z-oriented transition dipole moment and transition frequency $\omega_0 = 1.6625$ eV located at $D = 2$ nm from the WSe_2 layer for various free-space decay widths Γ_0 in the range from 413.57 µeV to 0.83 µeV. As the Γ_0 value increases from 0.83 µeV to 413.57 µeV, the features of the decay dynamics alter gradually from Markovian to strongly non-Markovian with decaying population oscillations of various amplitudes and frequencies depending on the actual value of Γ_0. The dynamics also shows population trapping for the largest Γ_0 value. In the latter case, there are fast oscillations of the excited state population in the initial 20 fs, with a period of about 8.5 fs, which corresponds to energy of 0.486 eV, i.e. about 30% of the transition energy of the QE. This indicates that the (ultra)strong coupling regime of the light-matter interaction between the QE and the WSe_2 layer is attained [12]. Under such coupling conditions, a bound state between the electromagnetic continuum, as modified by the presence of the WSe_2 layer, and the two-level QE is formed [13,14], which results in about 30% of the initial population remaining in the QE at times longer than 60 fs.

In the right panel in Figure 2 we present the SE dynamics of a QE with z-oriented transition dipole moment and transition frequency $\omega_0 = 1.6585$ eV, located at $D = 10$ nm from the monolayer, for various free-space decay widths Γ_0 in the range from 413.57 µeV to 82.71 µeV. Again we observe that as the Γ_0 value increases the features of the decay dynamics alter gradually from Markovian to non-Markovian with decaying population oscillations of various amplitudes and frequencies depending on the actual value of Γ_0. However, in this case the dynamics shows no population trapping for the largest Γ_0 value, as the light-matter coupling between the QE and the WSe_2 layer, which is directly proportional to the corresponding directional Purcell factor at this distance between QE and layer, is about two orders of magnitude smaller than the corresponding Purcell factor at $D = 2$ nm, as shown in the right panel of Figure 1.

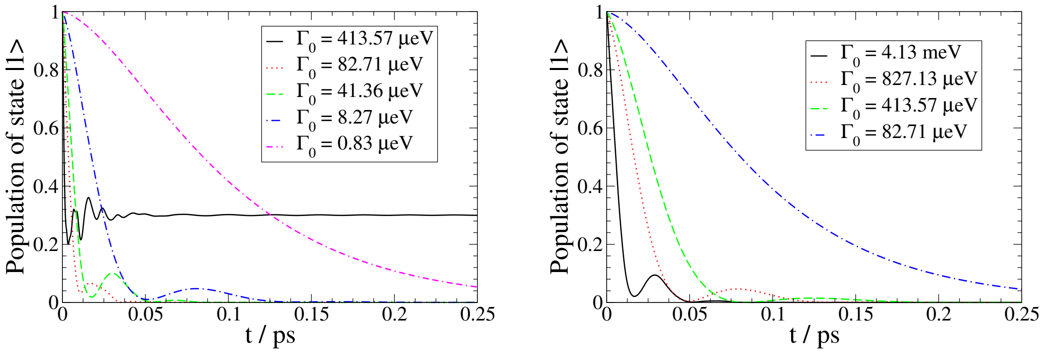

Figure 2. (color online) SE dynamics of a QE with z-oriented transition dipole moment located at $D = 2$ nm (**left**) and $D = 10$ nm (**right**), with $\omega_0 = 1.6625$ eV and $\omega_0 = 1.6585$ eV respectively, from a WSe_2 layer for various free-space decay rates Γ_0.

We further investigate the non-Markovian behavior of the SE dynamics in presence of the WSe_2 atomically-thin layer by using the non-Makovianity BLP measure $\mathcal{N}$, which quantifies the non-Markovianity of a quantum dynamical process with respect to the flow of information between the quantum system and the environment using the trace distance between two states, given by $\mathcal{N} = -\int_{\gamma(t)<0} \gamma(t)F(t)dt$, with

$$\gamma(t) = -2\Re\left(\frac{\dot{c}_1(t)}{c_1(t)}\right) = -\frac{2}{c_1(t)}\frac{d}{dt}|c_1(t)|, \quad F(t) = \frac{a^2 e^{-\frac{3}{2}\Gamma(t)} + \frac{1}{2}|b|^2 e^{-\frac{1}{2}\Gamma(t)}}{\sqrt{a^2 e^{-\Gamma(t)} + |b|^2}}, \tag{7}$$

where $\Gamma(t) = \int_0^t dt' \gamma(t')$ [6,15]. Here, $a = \langle 1|\rho_1(0)|1\rangle - \langle 1|\rho_2(0)|1\rangle$ is the difference of the populations and $b = \langle 1|\rho_1(0)|0\rangle - \langle 1|\rho_2(0)|0\rangle$ the difference of the coherences between the two initial states.

In Table 1, we present the values for the above measures in cases of a WSe_2 layer located at $D = 2$ nm and $D = 10$ nm. Apparently, the more the underlying population dynamics of the QE is non-Markovian, as shown in the left panel in Figure 2, the larger than one are the above non-Markovianity measure values. We also note that for the non-Markovianity measure $\mathcal{N}$ given in Table 1, we consider the cases with parameters $\{a, b\}$, as defined above, equal to $\{1, 0\}$.

Table 1. The BLP non-Markovianity measure $\mathcal{N}$ [6] of a QE with z-oriented transition dipole moment located at $D = 2$ nm and $D = 10$ nm, with $\omega_0 = 1.6625$ eV and $\omega_0 = 1.6585$ eV, respectively, from a WSe_2 atomically-thin layer. The values are obtained in case $\{a, b\} = \{1, 0\}$, as defined in Ref. [15]

	$D = 2$ nm					**$D = 10$ nm**			
Γ_0/μeV	413.57	82.71	41.36	8.27	0.83	4135.7	827.13	413.47	82.71
$\mathcal{N}$	0.36	0.04	0.09	0.04	0	0.08	0.04	0.01	0

4. Conclusions

In conclusion, we investigated the SE dynamics of a two-level QE in proximity to an atomically-thin tungsten diselenide layer at various distances of the emitter from the layer and various free-space decay rates of the emitter. By varying the distance and the decay rate value, our studies covered the range of weak to (ultra)strong coupling regime of the light-matter interaction between the QE and the electromagnetic continuum modified by the WSe_2 layer. We found that the decay dynamics is Markovian under weak coupling conditions, and it becomes strongly non-Markovian, characterized by oscillatory population emitter dynamics, on the top of the overall population decay. We also quantified the non-Markovianity of the dynamics by using the BLP measure. Most interestingly, when the ultrastrong coupling regime for the interaction between the QE and the WSe_2 layer is reached, we observed population trapping in the emitter, which is the signature of the formation of a hybrid bound state between the QE and the WSe_2 exciton-polaritons.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

QE	quantum emitter
SE	spontaneous emission

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