Plasmon–exciton coupling in a dimer cavity revisited: effect of excitonic dipole orientation

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We revisit plasmon–exciton coupling of a single emitter in a dimer cavity, featuring the analysis of how the excitonic dipole orientation influences the coupling behaviour from both the spectral and temporal aspects. Results demonstrate that the dipolar mode could be suppressed to vanish while the magnitude of the pseudomode could only be suppressed to half of the maximum value. The temporal analysis gives further evidence of this effect on the dipolar mode and pseudomode. The analysis might have potential significance on the experimental community as the excitonic dipole orientation could be precisely measured and has a rather important impact on the experiments.

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Plasmon–exciton coupling is a fundamental process in quantum optics. It also plays an important role in an emerging field named polariton chemistry. Plexciton, equivalently the plasmon–exciton–Polariton (PEP), the hybrid state formed by plasmon–exciton strong coupling, with profound significance in nanoscale science has been a physical phenomenon extensively investigated in past decades. Well-developed theoretical descriptions can be generally categorized based on how (classical or quantum) light and matter are treated although the feasibility of some quantum concepts utilized in PEP strong coupling is still worth further clarifying. Meanwhile, transformation optics (TO) as a convenient auxiliary tool to simplify the cavity geometry and reduce the computation scale, has merged into plasmonics and quantum optics and helped establish quasi-analytical descriptions on the strong coupling of a single quantum emitter (QE) in a dimer cavity. On the other side, quantum effects at short distances (around and below 10 nm) between QEs and cavity surfaces. Recently established treatment has incorporated these nonclassical effects within the framework of mesoscopic electrodynamics.

Experimentally, due to advances in nanoscale fabrication and characterization, plasmon–exciton strong coupling has been achieved from emitter ensembles up to single emitter level. Notably, Baumberg et al. have implemented plasmon–exciton strong coupling at the single emitter level and later obtained multilayers of WSe$_2$ strongly coupled to plasmonic modes. If we look into the detailed analysis of the above two experiments, both considered the orientation of excitons. Reference 20 exhibits the obvious differences in scattering spectra of single NPoM (Nano-Particle-on-Mirror) cavities inside which the transition dipole moments (TDM) are vertically and horizontally orientated. The origin of the coordinate system is set at the centre of the lower sphere. As mentioned above, the TO approach helps acquire concentric spherical geometry. We skip the algebraic derivation of the geometric parameters. For this part, we suggest readers to refer to Refs. 16 and 17 and the results there will be directly used in this article for the avoidance of repetition. We only write down the inversion coordinate mapping $\mathbf{r}' = \mathbf{r}([-\mathbf{r} - \mathbf{r}_0])$. Here, $\mathbf{r}_0$ is a scaling constant. $\mathbf{r}([-\mathbf{r}'])$ and $\mathbf{r}_0([-\mathbf{r}_0])$ are the position vector and the inversion point of the physical (transformed) space, respectively. From now on, all the variables in the transformed space are denoted with an apostrophe.

The general methodology is a celebrated matrix formulation linking the current study. In the quasi-static approximation, the electric field could be described by the scalar potential. In the transformed space [Fig. 1(b)], the scalar potential $\Phi'$ could be elegantly expanded with spherical harmonics $Y_{lm}(\theta, \phi)$ as $|\mathbf{r}' - \mathbf{r}_0|^3 \Phi'$ satisfies...
Laplace's equation under the inversion coordinate transformation:26b

\[ \Phi' = \left| r' - R'_0 \right| \sum_{j=0}^{\infty} \sum_{m=-\infty}^{\infty} \left[ a^+_{\ell,m}(r'/R_0) + a^-_{\ell,m}(r'/R_0)^{-\ell+1} \right] Y_m(\vartheta, \phi) \] (1)

Note the difference between Eq. (1) with Eq. (2) in Ref. 16. In this work, the orientation of the TDM is the degree of freedom to be investigated. The incline of the TDM denoted by angles \( \theta \) and \( \varphi \) [Fig. 1(c)] would destroy the rotational symmetry and leads to the inclusion of spherical harmonics with \( m \neq 0 \).

We firstly determine the expansion coefficients \( a^+_{\ell,m} \) and \( a^-_{\ell,m} \) of source potential \( \Phi'_E(r') = \Phi_E(r'(r')) \). In the original space, the TDM-induced potential is \( \Phi_E = \frac{1}{4\pi\varepsilon_0c^2} \left| r - R_E \right|^2 \) [26]. Applying the coordinate mapping leads to the source (a point dipole) potential distribution in the transformed space:

\[ \Phi'_E(r') = \frac{\mathbf{p} \cdot (r(r') - R_E)}{4\pi\varepsilon_0c^2 \left| r(r') - R_E \right|^3} \] (2)

Here, \( \mathbf{p} = |\mathbf{p}|(\cos \theta_E \hat{z} + \sin \theta_E \cos \varphi_E \hat{x} + \sin \theta_E \sin \varphi_E \hat{y}) \) is the arbitrarily oriented TDM of the QE [Fig. 1(c)]. Expanding \( \Phi'_E(r') \) is purely algebraic. Finally, the expansion comprises spherical harmonics with index \( m \in \{-1, 1\} \). For \( m = 0 \), \( a^0_{\ell,0} = a^E_{\ell,0} \), where \( a^E_{\ell,0} \) is defined by Eq. (3) of Ref. 16. For \( m = \pm 1 \),

\[ a^E_{\ell, \pm 1} = \pm \frac{\pi}{2l + 1} \frac{\sin \theta_E e^{\pm i\varphi_E}}{(l+1)!} R_0^2 \frac{R_E^3}{\zeta(R_0 - R_E)^3} \xi^{-(l+1)}, \] (3a)

Here, \( \zeta = R'_E/R'_0 \), \( \xi = R'_E R'_0 \). To facilitate the numerical calculations, we further express \( R'_E \) and \( R'_0 \) with geometric parameters only in the original space:

\[ R'_E = R'_0 + R_0^2/(R_0 - R_0) \] and \( R'_0 = R_0^2 \left[ (R_0 - R_0 + \delta)^{-1} + (2R_0 + \delta - R_0)^{-1} \right] \). Based on the derived source expansion coefficients, three matrix equations are solved, each of which is for a different index \( m \in \{-1, 1\} \) independently. The summation of the solutions of the matrix equations gives rise to the scattered potential field \( \Phi'_S(r') \). Through the inverse coordinate mapping, the scattered field in the original space is retrieved as \( \Phi_S(r'(r)) = \Phi'_S(r') \). The total scalar potential can be denoted as \( \Phi(r) = \Phi_S(r) + \Phi_E(r) \).

The spectral density \( J(\omega) \) is the quantity describing the spectrum of QE-cavity coupling strength: \( J(\omega) = \rho(\omega) |g(\omega)|^2 \). In this definition, \( \rho(\omega) \) is the density of modes of the system while \( g(\omega) \) denotes the coupling strength. In macroscopic quantum electrodynamics, \( J(\omega) \) is formally expressed with the dyadic Green function \( \mathbf{G}(\mathbf{r}, \mathbf{r}_0, \omega) \) of the system:27

\[ J(\omega) = \frac{\omega^2 |\mathbf{p}|^2}{\pi \varepsilon_0 c^2} \mathbf{n}_p \cdot \text{Im}[\mathbf{G} (\mathbf{R}_E, \mathbf{R}_E, \omega)] \cdot \mathbf{n}_p. \] (4)

Here, \( \varepsilon_0 \) is the permittivity in vacuum, \( c \) is the light speed in free space, and \( \mathbf{R}_E \) is the position of the QE. \( \mathbf{G} (\mathbf{R}_E, \mathbf{R}_E, \omega) \) is the dyadic Green function evaluated at the source point. Note Eq. (4) could not be simplified to Eq. (4) in Ref. 16 due to...
to the arbitrary orientation of the TDM: 
\[ \mathbf{n}_p = (\sin \theta_E \cos \varphi_E, \sin \theta_E \sin \varphi_E, \cos \theta_E). \]
Employing the definition of the Green function: 
\[ \mathbf{E}(\mathbf{r}, \mathbf{r}_0, \omega) = \omega^2 \epsilon_0 \mu_0 G(\mathbf{r}, \mathbf{r}_0, \omega) \cdot \mathbf{p}. \]
Eq. (4) can be expressed as 
\[ J(\omega) = \frac{1}{2} \text{Im}[\mathbf{p} \cdot \nabla \Phi(\mathbf{r})]_{\mathbf{r} = \mathbf{R}_E}. \]
Here we have set relative permeability to unity as the system works in the optical regime. Substituting the electric field with the scalar potential, the expression is further connected directly to the potential field evaluated at the source point: 
\[ J(\omega) = \frac{1}{2} \text{Im}[\mathbf{p} \cdot \nabla \Phi(\mathbf{r})]_{\mathbf{r} = \mathbf{R}_E}. \]

In the numerical calculations, the diameter of the nanospheres are set to \( R_1 = R_2 = 20 \text{ nm}. \) The background is set to vacuum. The gap between the nanospheres is set to \( \delta = 1 \text{ nm}. \) The TDM is set to \( |p| = 1.5 e \cdot \text{ nm}. \) It should be noted that we set \( \varphi_E = 0 \) in the following for simplicity. The contour plot in Fig. 2(a) explicitly exhibits the relation between the TDM orientation and the spectral density. It can be observed that the amplitude of the lowest mode (in the dashed black rectangle) is suppressed as the orientation of TDM switches from vertical (\( \theta_E = 0 \)) to horizontal (\( \theta_E = \pi/2 \)) direction. It has been demonstrated with an electric field map that the lowest mode is the electric dipolar mode [see Fig. 1 of Ref. 17]. Importantly, the dipolar mode vanishes at \( \theta_E = \pi/2 \). It is also obvious that the so-called pseudomode, which is intrinsically the superposition of spectrally overlapping high-order modes, decreases in amplitude through this process. To observe the comparison of different TDM orientations more clearly, three cases are plotted in Fig. 3(b). The amplitude of the dipolar mode vanishes and the pseudomode decreases to half the magnitude of the vertical case when the TDM is horizontally orientated.

From the other aspect, we could get a more intuitive view from the temporal dynamics. The Wigner–Weiskopf theory links the spectral information to the temporal behaviour of the emitter-cavity system.\(^{28}\) The population dynamics of the emitter-cavity system could be described well with a well-known integro-differential equation. For a more obvious comparison without loss of generality, the gap is set to \( \delta = 2 \text{ nm}. \) Firstly, we set the natural frequency of the QE to be close to the resonance frequency of the dipolar mode. We can observe from Fig. 3(a) that for \( \theta_E = 0 \), strong reversible dynamics occurs which indicates the intense energy exchange between the QE and the plasmonic cavity modes in a timescale much smaller than the decaying lifetime of the QE. However, with \( \theta_E \) increases, the reversible dynamics becomes much weaker and the oscillation frequency also decreases. However, when the natural frequency of the QE is set to be close to the resonance frequency of the pseudomode, the reversible dynamics is so strong that the system enters the strong coupling regime. The decrease of the magnitude of the pseudomode only leads to a small decrease in the Rabi oscillation frequency. The difference between Figs. 3(a) and 3(b) shows the different effect the TDM orientation has on different modes. For the dipolar mode, switching the TDM orientation could let the mode magnitude decrease and finally vanish. For the pseudomode, the magnitude could only decrease to half the value of the vertical case.

**Fig. 2.** (Color online) (a) Contour map of the spectral density in logscale versus TDM orientation denoted by \( \theta_E \). Inside the dashed rectangle is the dipolar mode which attenuates with the increasing \( \theta_E \). (b) Three selected cases \([\theta_E = 0 \text{ (blue solid line)}, \theta_E = \pi/4 \text{ (red solid line)}, \theta_E = \pi/2 \text{ (green solid line)}]\) clearly demonstrate the vanishing of the dipolar mode at \( \theta_E = \pi/2 \) and the decreasing of the pseudomode.
In conclusion, based on the inversion coordinate mapping, we investigated how the TDM orientation of the QE influences the plasmon–exciton coupling in a dimer cavity. It has been observed that the dipolar mode could be suppressed to vanish when the TDM switches from the vertical to the horizontal direction. But the pseudomode could only be suppressed to half of the magnitude of the vertical case. This gives rise to the different control of the population dynamics when the emitter frequency is close to the resonance frequencies of the dipolar and the pseudomode. Further investigations would possibly be to give analytical analysis which could give a deeper physical insight into the evolution process of both the dipolar mode and the pseudomode when the TDM orientation varies.

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