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Hybrid Quantum Dot–Metal Nanoparticle Systems: Connecting the Dots

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Hybrid molecules formed by coupling semiconductor quantum dots to metal nanoparticle nanoantennas provide a new paradigm for directed nanoscale transfer of quantum information. To assess this possibility, we study theoretically the response of these hybrid molecules to applied optical fields. Quantum-coherent time-evolution of the semiconductor quantum dots in the hybrid molecule is found by solving the semiconductor quantum dot density matrix equations. We study hybrid molecules in the weak and strong coupling regimes. In strongly driven, strongly dipole-coupled semiconductor quantum dot–metal nanoparticle hybrids with spherical metal nanoparticles, interference, dispersion near resonance and self interaction define the metal nanoparticle/semiconductor quantum dot coupling and lead to the Fano resonances, exciton induced transparency, suppressed semiconductor quantum dot response and bistability. More complicated response can be tailored by using metal nanoparticle shape and the placement of semiconductor quantum dots to control the local near-fields that couple the metal nanoparticles and semiconductor quantum dots. We describe how coupling to metal nanoparticle dark modes and higher order multipolar modes impact interference and self-interaction effects. The physics of the metal nanoparticle/semiconductor quantum dot coupling is outlined.

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1. Introduction

Transmission of quantum information between qubits for quantum communication, quantum computing and quantum measurement must maintain the quantum character of the information. Diffraction limited waveguiding of light (flying qubits) only gives wavelength scale resolution, which will not be adequate for site-to-site nanoscale transmission. Directed transmission is needed. One paradigm for directed nanoscale information transfer couples qubits, for example in quantum dots, to plasmonic structures. This can be done for transfer over long distances with dielectric nanoguides [1] and over nanoscale distances with nanoantennas or nanoguides made from metallic nanowires and nanoparticles [2].

To exploit this paradigm for quantum, nanoscale communication, one must understand how metallic nanoparticles act as nanoantennas and nanoguides. One must understand the coupling between the dots and the plasmons in metallic nanoparticles. One must also understand how dot-to-dot quantum communication is modified by transfer via plasmons. Finally, one must understand how transfer is further modified if the metal nanoparticles are small and quantum effects can influence their response. Here we focus on the response of strongly coupled quantum dot/metal nanoparticle, hybrid molecule systems to understand the exciton–plasmon coupling that connects the dots to the nanoparticles. We also consider how MNP shape can impact the exciton–plasmon coupling and the response of the hybrid molecule.

We discuss here, theoretically, the response of hybrid nanostructure molecules made from semiconductor quantum dots (SQD) and metal nanoparticles (MNP) subject to an optical driving field (see Fig. 1). This system has been studied in the weak coupling regime [3, 4] and in the strong coupling regime [5–11].

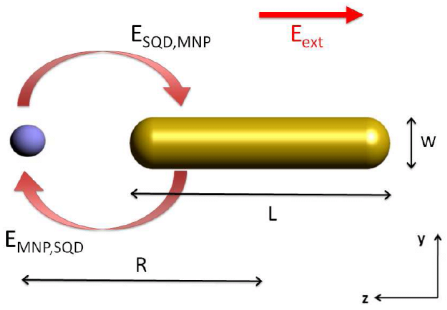

Fig. 1. An applied field polarizes both the MNP and SQD which in turn allows for a dipole–dipole coupling.

The optical excitations of SQDs are excitons, with a sharp, discrete response. The excitons act as quantum emitters. The strong, local, plasmonic excitations of the MNP provide a continuous spectrum of response. En-

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hanced local fields in the vicinity of the MNP provide strong coupling to neighboring SQDs. There is no direct tunneling between the MNP and SQD. However, due to the long-range Coulomb interaction, there is a dipole–dipole interaction that allows them to couple and leads to excitation transfer. The discrete excitons coupled with the broad response of the plasmons give rise to exotic hybrid states with clear signatures for their optical response. As a damped driven oscillator, the SQD response to driving fields changes rapidly from in-phase to out-of-phase near an SQD resonance. Rapid variations in hybrid response are expected near the SQD resonances. Effects depending on the interference between applied and induced fields are sensitive to this phase change in SQD response, providing dramatic signatures in the hybrid response.

In Sect. 2, we discuss the model that we study. We use a density matrix approach to treat the SQD, while the MNP is taken as a classical dielectric. In Sect. 3 we discuss the behavior of the system in the strong coupling regime to identify the key effects that determine the hybrid response [3, 5, 6]. In Sect. 4, we describe how MNP shape can be used to tune the SQD/MNP coupling [12]. We conclude in Sect. 5.

2. Modeling SQD/MNP hybrid molecules

We consider a spherical SQD with radius r interacting with an MNP, separated by a distance R [3, 5, 6]. The MNP could be a nanorod of length L and width w (as shown in Fig. 1) or a nanosphere of radius a. The entire system is subject to an applied optical field $E = E_0\cos(\omega t)$. We assume that all distances are small enough that retardation effects can be ignored. We assume that the applied field is large enough to be considered a classical field. We treat the SQD quantum mechanically in the density matrix formalism as a two-level system with exciton energy $\hbar\omega_0$, dipole moment μ and dielectric constant ϵ_S. In the dipole limit, three bright excitons (one for each optical axis) could participate in the interaction. By choosing the applied field to be either perpendicular or parallel to the axis of the molecule, only one of the three excitons is excited. Dark excitons contribute to the exciton lifetime. We treat the MNP as a classical spherical dielectric particle with dielectric function $\epsilon_{\mathrm{M}}(\omega)$.

The Hamiltonian for the two level SQD, $\mathcal{H}_{\mathrm{SQD}}$, is

$$\mathcal{H}_{\mathrm{SQD}} = \hbar\omega_0\hat{a}^\dagger\hat{a} - \mu E_{\mathrm{SQD}}(\hat{a}+\hat{a}^\dagger), \tag{1}$$

where $\hat{a}$ and $\hat{a}^\dagger$ are the atomic, two-level operators representing exciton creation and annihilation. For a spherical MNP, the fields can be determined explicitly. E_{SQD} is the total electric field felt by the SQD and consists of the applied, external field, E, and the induced, internal field, produced by the polarization of the MNP, $E_{\mathrm{MNP,SQD}}$. In the dipole limit, E_{SQD} is

$$E_{\mathrm{SQD}} = \frac{1}{\epsilon_{\mathrm{effS}}}\left(E + \frac{1}{4\pi\epsilon_{\mathrm{B}}}\frac{s_\alpha P_{\mathrm{MNP}}}{R^3}\right), \tag{2}$$

where $\epsilon_{\mathrm{effS}} = \frac{2\epsilon_{\mathrm{B}}+\epsilon_S}{3\epsilon_{\mathrm{B}}}$ and $s_\alpha = 2$ (-1) when the applied field is parallel (perpendicular) to the axis of the system. ϵ_{B} is a background dielectric constant which would correspond to the substrate on which the system is placed. Separating out the negative and positive frequency contributions, the polarization of the MNP is [13]

$$P_{\mathrm{MNP}} = (4\pi\epsilon_{\mathrm{B}})a^3\left[\gamma\widetilde{E}^{(+)}_{\mathrm{MNP}}\mathrm{e}^{-\mathrm{i}\omega t} + \gamma^*\widetilde{E}^{(-)}_{\mathrm{MNP}}\mathrm{e}^{\mathrm{i}\omega t}\right].$$

$\widetilde{E}^{(+)}_{\mathrm{MNP}}$ and $\widetilde{E}^{(-)}_{\mathrm{MNP}}$ are the positive and negative frequency parts of the electric field felt by the MNP. Note that our choice of the sign convention is such that $\mathrm{Im}(\epsilon_m(\omega)) > 0$ for $\omega > 0$. The total field acting on the MNP, E_{MNP}, is

$$E_{\mathrm{MNP}} = \left(E + \frac{1}{4\pi\epsilon_{\mathrm{B}}}\frac{s_\alpha P_{\mathrm{SQD}}}{\epsilon_{\mathrm{effS}}R^3}\right), \tag{3}$$

and $\gamma = \frac{\epsilon_{\mathrm{M}}(\omega)-\epsilon_{\mathrm{B}}}{2\epsilon_{\mathrm{B}}+\epsilon_{\mathrm{M}}(\omega)}$. We make use of the density matrix ρ to calculate the polarization of the SQD. We label the ground state of the SQD (no exciton) as level 1 and the excited state (one exciton) as level 2. Then, the SQD polarization is $P_{\mathrm{SQD}} = \mu(\rho_{12}+\rho_{21})$ (see [14]). Factoring out the high-frequency time dependence of the off-diagonal terms of the density matrix, we write

$$\rho_{12} = \widetilde{\rho}_{12}\mathrm{e}^{\mathrm{i}\omega t}, \quad \rho_{21} = \widetilde{\rho}_{21}\mathrm{e}^{-\mathrm{i}\omega t}. \tag{4}$$

The field acting on the SQD is

$$E_{\mathrm{SQD}} = \frac{\hbar}{\mu}\left[(\Omega + G\widetilde{\rho}_{21})\mathrm{e}^{-\mathrm{i}\omega t} + (\Omega^* + G^*\widetilde{\rho}_{12})\mathrm{e}^{\mathrm{i}\omega t}\right], \tag{5}$$

where

$$G = \frac{s_\alpha^2\gamma a^3\mu^2}{4\pi\epsilon_{\mathrm{B}}\hbar\epsilon_{\mathrm{effS}}^2R^6}, \quad \Omega = \frac{E_0\mu}{2\hbar\epsilon_{\mathrm{effS}}}\left(1 + \frac{\gamma a^3\ s_\alpha}{R^3}\right).$$

G arises when the applied field polarizes the SQD, which in turn polarizes the MNP and then produces a field to interact with the SQD. Thus, this can be thought of as the self-interaction of the SQD because this coupling to the SQD depends on the polarization of the SQD. The first term in Ω is just the direct coupling to the applied field and the second term is the field from the MNP that is induced by the applied field. When the MNP is nonspherical, we use the boundary element method to determine numerically these response fields [12].

We solve the master equation

$$\dot{\rho} = \frac{\mathrm{i}}{\hbar}[\rho, \mathcal{H}_{\mathrm{SQD}}] - \Gamma(\rho), \tag{6}$$

where $\Gamma(\rho)$ is the relaxation matrix with $\Gamma_{11} = \frac{\rho_{11}-1}{\tau_0}$, $\Gamma_{12} = \Gamma_{21}^* = \frac{\rho_{12}}{T_{20}}$ and $\Gamma_{22} = \frac{\rho_{22}}{\tau_0}$. The relaxation time τ_0 contains a contribution from nonradiative decay to dark states. We write the density matrix elements in terms of

$$\widetilde{\rho}_{12} = A + \mathrm{i}B, \quad \widetilde{\rho}_{21} = A - \mathrm{i}B, \quad \Delta = \rho_{11} - \rho_{22},$$

where Δ is the population difference between the excited and ground states. To solve (6), we make the rotating wave approximation. When changing the Hamiltonian to

the interaction picture we keep terms that oscillate like $e^{i(\omega-\omega_0)t}$ and neglect terms that oscillate like $e^{i(\omega+\omega_0)t}$. Making use of our definitions and the rotating wave approximation, we obtain the set of coupled differential equations,

$$\dot{A} = -\frac{A}{T_{20}} + (\omega-\omega_0)B - \Big(\Omega_I + G_I A - G_R B\Big)\Delta,$$

$$\dot{B} = -\frac{B}{T_{20}} - (\omega-\omega_0)A - \Big(\Omega_R + G_R A + G_I B\Big)\Delta,$$

$$\dot{\Delta} = \frac{1-\Delta}{\tau_0} + 4\Omega_I A + 4\Omega_R B + 4G_I(A^2+B^2), \qquad (7)$$

where G_R, G_I, Ω_R and Ω_I are the real and imaginary parts of G and Ω, respectively. These equations can be solved for the steady-state limit, where the time derivatives of A, B, and Δ vanish, or by explicitly evolving the equations in time.

3. Exciton–plasmon coupling: what matters

To understand exciton–plasmon coupling in optically driven hybrid molecules, one must understand what matters. The coupling is defined by the fields that act on each particle. This includes the external field. This includes any field induced at a particle arising from polarization induced at other particles. The induced polarizations lead to the self-interaction G: the SQD is polarized, this polarization induces image charges in the MNP, and the image charges then polarize the SQD. The induced image charge depends on the polarization of the dot, so the dot polarization couples to itself.

How these fields interfere at each particle defines the total strength of the polarizing field at each particle. The MNP resonance is broad. Near this dipolar resonance, the spectral dispersion is weak and the phase of its response changes slowly near resonance. In comparison, an SQD has sharp resonances, with rapid spectral dispersion and large phase changes near resonance. Below the SQD resonance, the SQD polarization and the fields it generates are in phase with the external driving field. Above the SQD resonance, the external field and the field due to the SQD polarization are out of phase. This change in phase drastically alters the response at the MNP and at the SQD.

Finally, the relative strength of the external field and the induced fields is important. We assume in the model that each of the particles responds linearly to the field acting on it. For the SQD, the strength of this response changes rapidly near the sharp SQD resonance. The polarization of the SQD, $P_{\rm SQD}$, depends on the coherence, ρ_{12}, induced on the SQD. From Eq. (7), the level excitation and coherence build up when strong coupling to the driving and induced fields compensates for decay due to decoherence. Far from resonance and in weak fields, the excitation is weak and the decoherence prevents a buildup of ρ_{12}. In this limit, the external field and the polarization of the MNP by the external field are the significant fields. Close to the SQD resonance and for large driving fields, the coherence can be maintained, despite any decoherence, and the fields induced by the polarization of the SQD become important as well.

The exciton–plasmon coupling is defined by what happens in the weak and strong field limits [3, 5, 6]. To understand these limits we consider a hybrid molecule with a single SQD coupled to an Au MNP. We discuss the case where the external field is along the molecule axis. We use an empirical dielectric function to describe the bulk Au response [15]. For the SQD, we consider a resonance at 2.5 eV and decay times $\tau_0 = 0.8$ ns and $T_{20} = 0.3$ ns [5, 6]. For weak driving fields (intensities $I \approx 1$ W/cm^2) [3], the polarization of the SQD is insignificant and the main effect of the coupling is an enhancement and broadening of the SQD response for larger SQD/MNP separations R and a quenching of the SQD for small R.

For strong fields (i.e. fields that drive the SQD strong enough to maintain the SQD coherence in steady state, typically $I \approx 1000$ W/cm^2, as shown in Fig. 2) the field induced by the SQD polarization becomes important. As a result, there is a Fano resonance in the steady-state response of the MNP, with the external field and the field from the SQD constructively interfering below the SQD resonance and destructively interfering above the SQD resonance [3]. As the SQD transition dipole moment, μ, is increased or R is decreased, the field at the MNP due to the SQD polarization can become comparable to the driving field. Above resonance, the field acting on the MNP can be completely cancelled by the destructive interference. At the frequency where this cancellation occurs there is an exciton induced transparency (EXIT) in the response of the MNP.

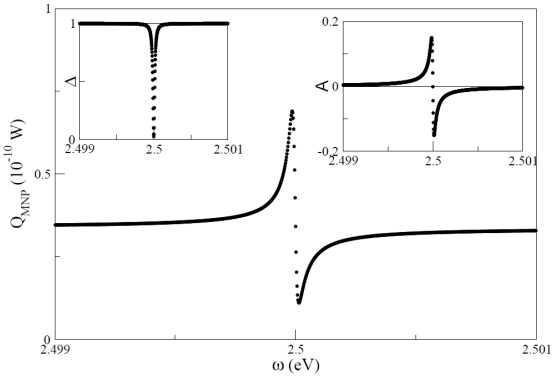

Fig. 2. Steady-state Fano resonance: $R = 13$ nm, $a = 3$ nm, $\mu = 0.25$ e nm. Steady-state MNP absorption rate, $Q_{\rm MNP}$, shows a Fano lineshape due to the phase change in dipole moment of the SQD. This phase change is shown in the real part of the SQD dipole moment in the right inset. Left inset shows the sharp dip in the population difference at resonance. See Ref. [6].

When the coupling between the SQD and MNP is large (i.e. for large SQD transition dipole moments, small R,

or large MNP radius a), the SQD self-interaction due to the image charge it induces on the MNP can also become significant [6]. In this limit, the field on the SQD due to the image charges can be comparable to the external driving field and the field directly from the MNP induced when the MNP is polarized by the external field. These two direct fields have the same phase. The phase of the field due to the self-interaction changes rapidly at the SQD resonance. As with the Fano resonance in the MNP response, the SQD response can be dramatically different above and below resonance when the coupling is strong enough. Below resonance, the self-interaction G acts in phase with the direct fields Ω, leading to an even stronger polarization of the SQD. Above resonance, destructive interference weakens the field acting on the SQD and the excitation of the SQD is turned off. This suppression of the above resonance SQD response is shown in Fig. 3. For strong coupling, Δ has an asymmetric line shape with reduced SQD excitation above resonance (compare with Fig. 2).

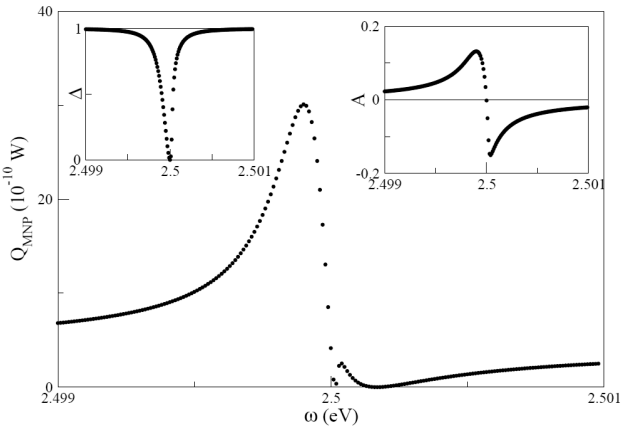

Fig. 3. Weak suppression. $R = 13$ nm, $a = 7$ nm, $\mu = 1$ e nm. The onset of suppression of the SQD response is apparent in the asymmetry of Δ. See Ref. [6].

For larger coupling the suppression can lead to a discontinuous response, as shown in Fig. 4. Below resonance, where a strong field acts on the SQD, the SQD response is broadened. Above resonance, the SQD response is suppressed and drastically narrows. As a result of the non-linear self-interaction, the SQD response can switch between these dramatically different limits. Below resonance, the SQD responds as a broad resonance in a strong field, strong coupling regime. Above resonance, the SQD responds as if it were a sharp line in the weak field limit.

Everything discussed so far pertains to the steady state response of the hybrid molecule. This dramatic, discontinuous change in SQD response is the first hint of the bistable response that arises, due to the nonlinear self-interaction, for further increases in interparticle coupling [5, 6, 16]. In the bistable regime, there is no unique steady-state. Rather, the evolution of the hybrid

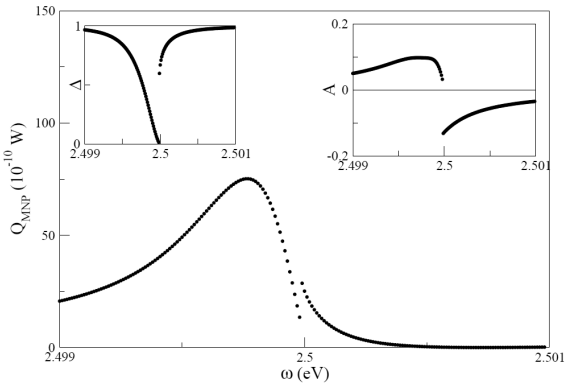

Fig. 4. Strong suppression. $R = 13$ nm, $a = 7$ nm, $\mu = 2$ e nm. See Ref. [6].

molecule depends on the initial state of the SQD. When the SQD starts in a weakly excited state, it evolves to a state that remains weakly excited, even near resonance, because the suppression dominates the near-resonance response. However, if the SQD starts strongly excited, then it can remain strongly excited below but near to the resonance but switches to the weakly excited state above resonance. This state-dependent optical bistability is the basis for possible applications to nanoscale optical switching [16].

4. Effect of MNP shape

So far, we have discussed exciton–plasmon coupling in optically driven SQD/MNP hybrids when the MNP is a spherical particle with dipolar plasmonic response. When the MNP has a more complicated geometry, for example a nanorod, there is greater flexibility to tailor the SQD/MNP response [12]. Local fields are more enhanced at the ends of long, narrow nanorods than near the surface of a spherical MNP. This feature alone can significantly enhance the local coupling, making strong-field/strong-coupling effects accessible for a broader range of particle sizes, separations and transition dipole moments. More importantly, a nanorod can have a variety of higher order modes that could contribute to the SQD/MNP coupling. These modes can be higher order bright modes that, like the dipolar mode, respond both to the external field and to any local fields from other particles. However, these higher-order MNP modes can also be dark modes, which do not respond to the external field but do respond to the local fields from the other particles. Near the dark-mode resonance, the external field cannot polarize the MNP so there are no directly induced polarization fields from the MNP acting on the SQD. Ω includes only the external field. The MNP couples to the SQD only via the induced self-interaction. At these modes, the relative contribution of Ω and the self-interaction G on the SQD is changed, leading to significantly stronger self-interaction effects [12]. The choice of MNP shape provides a flexibility to tune the MNP resonance frequency to better

match the SQD resonance, to enhance the local fields, and to change the character of the SQD/MNP coupling that defines the response of optically driven hybrids.

5. Concluding remarks

We study hybrid semiconductor quantum dot/metal nanoparticle molecules in the weak and strong coupling regimes to understand better how to connect SQDs to MNPs in structures intended for nanoscale coherent information transfer. In strongly driven, strongly dipole--coupled SQD–MNP hybrids with spherical MNPs, interference, dispersion near resonance and self interaction define the MNP/SQD coupling and lead to the Fano resonances, exciton induced transparency, suppressed SQD response and bistability. SQD dispersion plays a key role, providing constructive interference of the fields below the SQD resonance and destructive interference above the SQD resonance. This can lead to suppressed, weak MNP and SQD response above resonance even when the MNP and SQD are strongly coupled and strongly driven by an external field. More complicated response can be tailored by using MNP shape and the placement of SQDs to control the local near-fields that couple the MNPs and SQDs. MNPs that support dark modes will provide a coupling that enhances the relative importance of the self-interaction effects, providing a means to tailor the character as well as the strength of the coupling.

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