Optical properties of coupled metal-semiconductor and metal-molecule nanocrystal complexes: the role of multipole effects

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We investigate theoretically the effects of interaction between an optical dipole (semiconductor quantum dot or molecule) and metal nanoparticles. The calculated absorption spectra of hybrid structures demonstrate strong effects of interference coming from the exciton-plasmon coupling. In particular, the absorption spectra acquire characteristic asymmetric lineshapes and strong anti-resonances. We present here an exact solution of the problem beyond the dipole approximation and find that the multipole treatment of the interaction is crucial for the understanding of strongly-interacting exciton-plasmon nano-systems. Interestingly, the visibility of the exciton resonance becomes greatly enhanced for small inter-particle distances due to the interference phenomenon, multipole effects, and electromagnetic enhancement. We find that the destructive interference is particularly strong. Using our exact theory, we show that the interference effects can be observed experimentally even in the exciting systems at room temperature.

I. INTRODUCTION

Nanomaterials incorporating semiconductor quantum dots (SQDs), metal nanoparticles (MNPs), metal surfaces, and dye molecules have been studied intensively 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11a, 12, 13. Such hybrid structures take advantage of physical properties of different material systems and demonstrate useful sensor and light-harvesting properties. In a complex made of emitter (SQD or dye) and MNPs, excitons and plasmons interact via the Coulomb forces. Emission of SQD (dye) in the presence of MNPs can be suppressed or enhanced depending on the size and organization of nano-assembly 2, 5, 11. This occurs due to the following physical factors: (1) modified density of states of photons, (2) amplified absorption in the presence of plasmon resonance in the MNPs, and (3) shortening of exciton lifetime due to an increased radiation rate and energy transfer to the MNPs. Theoretically, an emitting dipole in the vicinity of metal objects has been studied in many publications 3, 5, 11, 12, 13, 14. The exciton-plasmon interaction between an emitting dipole and metal objects leads to energy transfer, a shift of energy of quantum emitter, and vacuum Rabi oscillations 11, 12, 13, 14. The energy transfer mechanism is similar to Förster transfer between two dye molecules 13. In most theoretical publications, the energy transfer in nanoscale systems was treated as uni-directional flow of energy from a donor to acceptor using the rate equations. This rate-equation approach describes non-coherent interactions at elevated temperatures. Very recently, several theoretical studies were performed for the quantum regime of exciton-plasmon interaction between a SQD/dye and MNP 16, 17a, 18a, 19a. These studies revealed a novel feature of strongly-interacting hybrid nanocrystals - interference effects. The absorption spectra of coupled SQD and MNP acquire characteristic asymmetry due to the interference of external and induced electric fields. At low temperatures and small exciton broadening, the absorption line shapes are described by the Fano formula 20. However, previous theoretical results 16, 17a, 18a, 19a were based on the dipole approximation. The dipole approximation is valid when an exciton-MNP distance is large, compared to the sizes of components, and the exciton-plasmon interaction is relatively weak. But, the most interesting regime of strong exciton-plasmon interaction appears when a exciton-MNP distance is small and the dipole approximation is not valid anymore. Therefore, to describe the regime of strong exciton-plasmon coupling, one should treat the Coulomb interaction exactly, including electric multipole effects. In this paper we obtain an exact solution for the problem of interacting dipole and MNP.

Here we present a theory of strong exciton-plasmon interaction and show that the multipole effects are of crucial importance for the understanding of the exciton-plasmon interaction in the most interesting regime of small exciton-MNP separations. A strong interaction between excitons and plasmons at small exciton-MNP distances reveals itself in absorption spectra as asymmetric lineshapes and anti-resonances (deep minima). Moreover, we consider two types of nanoscale hybrid complexes (SQD-MNP and dye-MNP) and show that, for small exciton-MNP distances, the interference effects can appear in room-temperature experiments. For the multipole regime of Coulomb interaction, the visibility of exciton resonance grows dramatically due to both the interference effect and the plasmon-induced electromagnetic enhancement. For large inter-particle distances, the absorptions by SQD and MNP add up constructively. For the hybrid structures of small dimensions, the spectra exhibit very strong effects of constructive and destructive interference. We think that these interference effects can be observed experimentally using presently available
material systems. In this paper, we discuss three material systems: colloidal nanocrystals, self-assembled dots, and dye molecules. Most of the current experiments on metal-semiconductor and metal-dye assemblies employ colloidal nanoparticles \[\text{and nano-wires} \] and nanowires \[\text{nano-wires} \]. To observe the effects described in this paper, single colloidal nanocrystal complexes can be deposited on a surface or buried in a polymer film. Assemble measurements of colloidal complexes in a solution can also be suitable. Presently, there are attempts to fabricate metal nanoparticles inside epitaxial structures \[\text{potential: colloidal and epitaxial nanocrystals can be combined in one structure} \]. For example, an epitaxial dot can be buried close to the surface \[\text{and a MNP can be attached to the surface} \].

The paper is organized as follows. In Section II, we give a description of the electric field inside the system. The optical properties of a nanocrystal molecule are presented in Section III. Section IV discusses the absorption line shape. The numerical results for SQD-MNP molecules and dye molecule-MNP nanocrystals are given in Section V. Finally, a brief conclusion is presented.

II. ELECTRIC FIELDS INSIDE THE SYSTEM

Now we consider the hybrid nanocrystal molecule composed of a spherical MNP of radius \(R_0\) and a spherical SQD of radius \(R_s\) in the environment with dielectric constant \(\varepsilon_e\) (see Fig. 1a). The center-to-center distance for the nanocrystals is denoted as \(R_d\). In the following, we will assume that a SQD has small dimensions \(R_s \ll R_d\), whereas the size of MNP can be arbitrary, i.e. \(R_0 \sim R_d\). In the case of a dye molecule-MNP complex, the size \(R_d\) becomes irrelevant and we have only the obvious condition: the molecule-MNP distance \(R_d\) should be larger than the MNP radius, i.e. \(R_d > R_0\).

When the hybrid molecule (SQD-MNP or dye-MNP) is radiated with a laser, the oscillating electric field excites both the interband transition in a SQD and the plasmon in a MNP. The interband transition (exciton) in a SQD (dye) has an oscillating dipole moment and, therefore, creates an oscillating electric field that acts on a MNP and excites the plasmons. The plasmons excited in a MNP in turn influence the exciton. In this way, the exciton and plasmon form a new collective excitation - a hybrid exciton. The origin of this hybrid exciton is in the Coulomb interaction between a SQD and MNP Fig. 1(b).

Since a nanoscale structure has small dimensions, we assume that the electric field of the laser is spatial uniform and use the quasistatic approximation. Also, we describe the MNP with the local dynamic dielectric function \(\varepsilon_m(\omega)\). By carefully solving the Laplace’s equations \(\nabla^2 \varphi = 0\), we can get the electric potential \(\varphi\) and so the electric field \(\mathbf{E} = -\nabla \varphi\). As for the dipole in SQD, we take it as a perfect dipole, labeled as \(\mathbf{p}\), because the radius of SQD \(R_s\) is much smaller in contrast with \(R_0\) usually.

We now consider the laser electric field in the form \(\mathbf{E}_0(t) = \mathbf{E}_0 \cos \omega t\). We first discuss the part with positive frequency, \(\mathbf{E}_0 e^{-i\omega t}/2\). The electric field inside SQD could be split in three parts: \(\mathbf{E}_{\text{SQD}}(\omega) = (\mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3)e^{-i\omega t}\). \(\mathbf{E}_1 e^{-i\omega t}\) is the electric field induced by \(\mathbf{E}_0\) inside a SQD in the absence of a MNP:

\[
\mathbf{E}_1 = \frac{\varepsilon_e}{\varepsilon_{\text{eff1}}} \frac{\mathbf{E}_0}{2},
\]

where \(\varepsilon_{\text{eff1}} = (\varepsilon_s + 2\varepsilon_e)/3\) is the effective dielectric constant of the SQD and \(\varepsilon_s\) is the background dielectric constant of semiconductor.

The second part \(\mathbf{E}_2 e^{-i\omega t}\) comes from surface charges of MNP induced only by the external optical electric field \(\mathbf{E}_0 e^{-i\omega t}/2\):

\[
\mathbf{E}_2 = s_\alpha \varepsilon_e \gamma_1 R_0^3 \frac{\mathbf{E}_0}{\varepsilon_{\text{eff1}} R_d^3},
\]

where \(\gamma_1 = [\varepsilon_m(\omega) - \varepsilon_e]/[\varepsilon_m(\omega) + 2\varepsilon_e]\) and \(s_\alpha = 2(-1)\) for electric field polarization \(\mathbf{E}_0\) is parallel to the \(z(x)\) axis. The choice of a sign of imaginary part of dielectric constant should be the following: \(\text{Im}[\varepsilon_m(\omega)] > 0\) if \(\omega > 0\).

The last part \(\mathbf{E}_3 e^{-i\omega t}\) is the SQD-felt effective electric field produced by the multipole polarization in MNP induced by the effective dipole of SQD \(\mathbf{p} = (\varepsilon_e/\varepsilon_{\text{eff1}})\mathbf{E}_0 e^{-i\omega t}\). This part is the most important one, underlying the interaction of the MNP and SQD. We finally find this part of electric field is

\[
\mathbf{E}_3 = \sum_{n=1}^{\infty} \frac{s_n \varepsilon_e \alpha \gamma_2 R_0^{2n+1}}{\epsilon_2^2 \varepsilon_{\text{eff1}} R_d^{2n+1}} \mathbf{p}.
\]
where
\[ \gamma_n = \frac{\varepsilon_m(\omega) - \varepsilon_e}{\varepsilon_m(\omega) + \frac{n+1}{n} \varepsilon_e}, \]
and the coefficients \( s_n = (n+1)^2 \) or \( P'_n(1) \) for the polarization \( p \) is parallel to the \( z \) or \( x \) axis respectively. Here \( P_n \) is the Legendre function and \( P'_n(1) \) is the differential of Legendre function at the argument of 1.

When \( n = 1 \), the electric field \( \tilde{E}_3 \) becomes
\[ \tilde{E}_3 = s_1 \frac{\gamma_1 \varepsilon_e P'_1}{\varepsilon_{\text{eff1}}} \hat{R}_d \mathbf{p}, \]
which is the very result under the dipole approximation: the SQD dipole-induced electric field everywhere inside the MNP is uniform and equals to the value at the center of MNP. This dipole approximation is used in Ref.\[10\], which is reasonable when the distance \( R_d \) is relatively large because the factor \( 1/R^{2n+4} \) makes other terms negligible. However, when the distance is comparable to the radius of MNP, i.e. \( R_0 \sim R_d \), which is always the case in such molecules, the items \( n > 1 \) become important and may even have a bigger contribution than the leading terms. Actually the items with different \( n \) are related to different order multipole polarization in MNP: \( n = 1 \) is dipole, \( n = 2 \) quadrupole, \( n = 3 \) octopole and so on. The function of \( \gamma_n \), Eqn.\[4\], also reflects the characteristics of the multipole polarization as tells by the Mie theory \[24 \[25\]. But it should notice that the multipole effect in Mie theory is caused by the comparable radius of MNP with wavelength of the light. Here the radius is small enough to neglect the effect and hence the multipole effect totally comes from the induced polarization by the SQD when the the interparticle distance is relatively small.

The electric field inside MNP \( \tilde{E}_{\text{MNP}}, \text{tot} \) can also be solved, and the corresponding positive frequency part is \( \tilde{E}_{\text{MNP}}, \text{tot} e^{-i\omega t} = (\frac{\varepsilon_e}{\varepsilon_{\text{eff1}}} \tilde{E}_{\text{MNP}}) e^{-i\omega t} \), where \( \varepsilon_{\text{eff1}} = [\varepsilon_m(\omega) + 2\varepsilon_e]/3 \) and \( \tilde{E}_{\text{MNP}} \) is
\[ \tilde{E}_{\text{MNP}}|_{E} = \sum_{n=1}^{\infty} \frac{n+1}{n} \frac{\beta_n R^{n-1}}{\varepsilon_{\text{eff1}}} \hat{R}_d \mathbf{p} \]
\[ \times \left\{ -\frac{x^2}{R} P'_{n-1}(z/R) + n P_{n-1}(z/R) \hat{x} \right\}, \]
\[ \tilde{E}_{\text{MNP}}|_{E} = \sum_{n=1}^{\infty} \frac{\beta_n R^{n-1}}{\varepsilon_{\text{eff1}}} \hat{R}_d \mathbf{p} \]
\[ = \sum_{n=1}^{\infty} \frac{\beta_n R^{n-1}}{\varepsilon_{\text{eff1}}} \hat{R}_d \mathbf{p} \]
\[ = \frac{x^2}{R} P'_{n-1}(z/R) + n R P_{n-1}(z/R) \hat{x} \]
\[ + \frac{xy}{R^2} P''_{n-1}(z/R) \hat{y} - (n + 1) \frac{x}{R} P'_{n-1}(z/R) \hat{z} \]}

(7)

where
\[ \beta_n = \frac{2n+1}{n} \frac{\varepsilon_e}{\varepsilon_m(\omega) + \frac{n+1}{n} \varepsilon_e}. \]

When \( n = 1 \), the electric field inside the MNP,
\[ \tilde{E}_{\text{MNP}} = s_0 \frac{1}{\varepsilon_{\text{eff2}}} \left( \frac{\varepsilon_e}{\varepsilon_{\text{eff1}}} \hat{p} \right), \]
is just the electric field produced by the dipole inside the SQD at the point of MNP’s spherical center, the dipole approximation.

III. DENSITY MATRIX OF THE SYSTEM

In the SQD, we use a two-level exciton model to describe the optical process. The exciting laser field is now taken in the form: \( E_0(t) = E_0 \cos(\omega t) \). Under these conditions, the Hamiltonian is
\[ H = \hbar \omega a_2^\dagger a_2 - \chi(t)(a_1^\dagger a_1 + a_1^\dagger a_2), \]
where \( a_i \) and \( a_i^\dagger \) is the annihilation and creation operator of level \( i \) \( (i = 1, 2) \), corresponding to the vacuum ground state and the exciton state respectively (see Fig.\[1(b)\]). Note that the energy of level 1 is taken as zero. 

These matrix elements satisfy the well-known optical Bloch equations:
\[ \partial_t \rho_{22} = \frac{i}{\hbar} \chi(t) [\rho_{21} - \rho_{22}] - \frac{1}{T_1} \rho_{22}, \]
\[ \partial_t \rho_{21} = -i \omega_0 \rho_{21} + i \chi(t) (1 - 2 \rho_{22}) - \frac{1}{T_20} \rho_{21}. \]

Also, \( \rho_{11} + \rho_{22} = 1 \). \( T_1 \) and \( T_20 \) are the longitudinal and transverse dephasing times. The dipole of the SQD relates to the interband polarization by \( p = \mu_\parallel (\rho_{21}^* + \rho_{22}) \), \( \rho_{21} = (a_1^\dagger a_2) \). In the rotating wave and steady state approximation, \( p = \tilde{p} e^{-i\omega t} + \tilde{p}^* e^{i\omega t} \), where \( \tilde{p} \) is time-independent. Then the equations give:
\[ \rho_{22} = \frac{2T_1}{\hbar} \text{Im}[\chi^* \rho_{21}], \quad \tilde{p}_{21} = \frac{-\Omega \Delta}{(\omega - \omega_0 + G \Delta + i/T_20)} \]

(13)

where
\[ \Omega = \frac{\mu \cdot (\hat{E}_1 + \hat{E}_2)}{\hbar}, \]
\[ G = \sum_{n=1}^{\infty} s_n \varepsilon_m R_0^{2n+1} \mu^2 = G_R + iG_I, \]

(14)

and \( G_R \) and \( G_I \) are the real and imaginary part of \( G \), \( \Delta = \rho_{21} - \rho_{22} \). While \( \Omega \) is determined by the electric field of \( \hat{E}_1 \) and \( \hat{E}_2 \), \( G \) comes totally from the contribution of the electric field \( \hat{E}_3 \), responsible for the interaction between MNP and SQD. Therefore the plasmon-exciton interaction leads to the formation of a hybrid exciton.
with shifted exciton frequency and decreased lifetime determined by \( G_R \) and \( G_I \) respectively.

For a weak external field, \( \Delta = \rho_{11} - \rho_{22} = 1 - 2\rho_{22} \approx 1 \) (since \( \rho_{22} \ll 1 \)) and Eqn. (13) and Eqn. (15) yield the solution of the problem. For a strong driving field, the problem is reduced to the nonlinear equation (Eqn. (14)) investigated in [16]. Since the quantity \( G_R \) includes multipole polarization in MNP, the energy shift is determined by the multipole effect rather than a simple dipole effect. In Fig 2, we plot the \( G = \sum_{\omega=1}^{N} (\cdots) \) with the change of frequency \( \omega \). The MNP is made of gold and dielectric constant is taken from Ref. [26]. Other parameters are chosen as: \( \varepsilon_s = 6, R_0=15 \text{ nm}, R_d=20 \text{ nm} \). The chosen SQD parameters are typical for the CdSe and CdTe colloidal quantum-dot systems. It shows that the excitonic frequency shift \( G_R \) enhances with \( N \) increasing and finally converges. Due to the factor \( 1/R_d^{2n+4} \), the terms of higher order have smaller contribution. However, in finite range, the contribution from terms of \( n > 1 \) is more than that of \( n = 1 \). The shift when \( N = 10 \) is almost seven times than that of \( N = 1 \). As for the lifetime of the exciton, it decreases with \( N \) increasing due to \( G_I \). More close the distance of the molecule, more multipole contribution should be considered. In some case such as the frequency \( \omega \) locates at the value making \( Re[\varepsilon_m(\omega)] + 3/2\varepsilon_s = 0 \), the quadrupole effect becomes the leading one. As for the lifetime of exciton, the interaction makes it shorter and multipole interaction boosts up this effect. For Au MNP, the lifetime is almost unchanged when \( \omega \) below 2 eV while the exciton frequency shift is still outstanding, which may have important applications.

The multipole effects can also be seen in the energy absorption spectrum. Under the radiation of laser, both SQD and MNP absorb energy, which will eventually transformed into heat by all kinds of scattering mechanics. The energy absorption rate is actually the time-average of power dissipation density. In SQD, the energy absorption rate \( Q_{\text{SQD}} \) is \( Q_{\text{SQD}} = \hbar \omega_0/\tau_1 \).

As for the MNP, the optical transmission property is more measured by the quantity of extinction, which has two main parts: absorption and scattering. The relative contribution of scattering to the extinction for metal particles of radius less than about 30 nm can be negligible. In the MNP-SQD molecules fabricated in recent experiments, the size of MNP is within the range to discount the scattering. For example, the Rayleigh scattering has been calculated and found about three order of magnitude smaller than the energy absorption rate [10]. The energy absorption rate in MNP \( Q_{\text{MNP}} \) is expressed as \( Q_{\text{MNP}} = \int \text{Im}[\varepsilon_m(\omega)]|E_{\text{MNP, tot}}|^2 dV \), where \( E_{\text{MNP, tot}}^2 = \frac{\varepsilon_{m2}}{\varepsilon_{m2}} + E_{\text{MNP}}^2 \) and \( E_{\text{MNP}} \) is given by Eqns (14) and (15). The total rate of absorption is therefore:

\[
Q_{\text{tot}} = Q_{\text{MNP}} + Q_{\text{SQD}}.
\] (16)

A typical energy absorption spectrum is shown in the insert of Fig 2 (Bottom). Here the energy absorption rate including multipole effect for a typical value \( R_d=20 \text{ nm} \) is plotted in contrast with the result in dipole approximation in the inset. The interaction of the discrete state in SQD and the continuous states in MNP gives birth to the Fano lineshape. The laser intensity is \( I_0 = 1 \text{ W/cm}^2 \). The original excitonic energy is \( h\omega_0 = 2.5 \text{ eV} \), the plasmon peak of Au. Fig 2 also plots peak shift of energy absorption rate with different interparticle distances in logarithmic coordinate. The solid (Red) line and circle is the one including multipole effect (\( N = 10 \)), while the dash (Black) line and square is only in dipole approximation (\( N = 1 \)). Inset is contrast of energy absorption rate for a typical interparticle distances \( R_d=20 \text{ nm} \), with peak value emphasized.

![Image](image-url)
FIG. 3: The different shift caused by the multipole effect in contrast with dipole approximation. The Ag MNP and SQD is emerged in water ($\varepsilon_0 = 1.8$). Other parameters are $R_d = 22$ nm, $R_0 = 15$ nm and $h\omega_0 = 3.34$ eV.

change in the relation of $G$ and $R_d$ and leads to larger shift of peak. Especially when the value of $R_d/R_0$ is small, the shift increases almost by one order of magnitude, which makes it more possible to be observed experimentally. As the interdistance of the molecule can be adjusted through biolinker by temperature, the shift is temperature-controlled, which may have important application in sensor and detector. The broadening of spectra is related to the incoherent energy transfer rate. The incoherent energy transfer in the hybrid molecule is via the Forster mechanism with energy transfer rate $G_I$. As the multipole effect increase the value of $G_I$ in the vicinity of the plasmon peak, see Fig. 2, the energy transfer time changes remarkably.

Multipole effects not only lead to quantitative changes (which is important for experiments), but also qualitative difference. For example, we consider the Ag MNP and SQD composed molecule emerged in water solution. As shown in Fig. 3 in dipole approximation, the peak of absorption rate has blue shift. With multipole effect, the peak’s shift of energy absorption rate changes to the red direction and the broadening increases a lot.

The total energy absorption versus interparticle distances for a fixed frequency is presented in Fig. 4, which shows that with decreasing the interparticle distance, the energy absorption first increases, then decreases. That means there exists an optimal distance for energy absorption. Here the dipole approximation fails to provide the correct picture. The energy absorption of MNP and SQD versus interparticle distance show the similar results (not shown here). The existence of optimal distance for SQD energy absorption can be understood in the following way. The energy absorption of SQD depends on the competition of two factors: the local field enhancement and transfer the energy to MNP. With decreasing interparticle distance, local field becomes larger and energy transfer rate increases also. At short distance, the factor from fast energy transfer wins over the factor from local field enhancement. In fact Forster transfer (FT) rate is $1/\delta^3$, here $\delta$ is the distance between the exciton and MNP surface ($\delta = R_d - R_0$). When $\delta \to 0$, the FT rate $\to \infty$.

**IV. ABSORPTION LINE SHAPES**

Using Eqn. (13), Eqn. (16), we can write the absorption rate as

$$Q_{tot} = Q_{MNP}^0 + \frac{A\Gamma_{12}}{(\omega - \omega_0)^2 + \Gamma_{12}^2} + \frac{B(\omega - \omega_0)}{(\omega - \omega_0)^2 + \Gamma_{12}^2},$$

where $\Gamma_{12} = 1/T_{20} + G_I$ and $\omega_0 = \omega_0 + G_R$ are the renormalized off-diagonal broadening and the modified absorption frequency, respectively. The absorption by an isolated MNP is given by $Q_{MNP}^0 = \frac{\hbar}{\pi} \Im \{\varepsilon_m(\omega)\} \frac{\varepsilon_m E_m^2}{\varepsilon_{eff}^2} V_{MNP}$, where $V_{MNP}$ is the MNP volume. In the general case, the coefficients $A$ and $B$ are given by rather complex expressions. Here it is instructive for us to give these coefficients in the dipole limit. Then the key function $G$ takes the form: $G = \frac{s_{12} \gamma \varepsilon_m R_0^3}{\varepsilon_{eff}^2 R_d^2 \hbar^2}$. Note that $G_I > 0$. For the limit $\Gamma_{12} \to 0$, we can obtain the Fano resonance [21],

$$Q_{tot} = Q_{MNP}^0 \frac{(\omega - \omega_0 - q_{Fano}\Delta_{int})^2}{(\omega - \omega_0)^2 + \Delta_{int}^2},$$

where $\Delta_{int} = G_I$ is the interaction-induced broadening and $q_{Fano}(\omega_0, R_d) = \frac{R_d^3}{\hbar \Im \{\varepsilon_m(\omega_0)\}}$ is the Fano factor. The line is strongly asymmetric if $q_{Fano}(\omega_0, R_d) \sim 1$. In the
limit \( q_{\text{asym}}(\omega_0, R_d) \gg 1 \), the absorption line becomes close to a Lorentzian. For molecular systems and systems at room temperature, the off-diagonal decoherence is typically strong: \( \Gamma_{12} \gg |G| \). In this limit, the coefficients in the lineshape become:

\[
A = \frac{\omega}{2\hbar} \left( \frac{\varepsilon_e \tilde{E}_0 \mu}{\varepsilon_{\text{eff}1}} \right)^2 \left( 1 + \frac{s_{\alpha} \gamma_1 R_0^3}{R_d^3} \right) \\
B = \frac{s_{\alpha} \mu^2 \varepsilon_e \tilde{E}_0^2 \omega R_0^3}{3\hbar \varepsilon_{\text{eff}2} R_d^3} \left| \varepsilon_e \varepsilon_{\text{eff}2} \right|^2 \left| \text{Im}[\varepsilon_m(\omega)] \right|^2
\]

(19)

In the strong decoherence regime, it is convenient to introduce an asymmetry factor:

\[
q_{\text{asym}} = \frac{A}{B}
\]

\[
q_{\text{asym}} = \frac{\varepsilon_e}{\varepsilon_{\text{eff}2}} \left( 1 + \frac{s_{\alpha} \gamma_1 R_0^3}{R_d^3} \right)^2 \left( 1 + \frac{s_{\alpha} \text{Re}[\gamma_1] R_0^3}{R_d^3} \right) \left| \text{Im}[\varepsilon_m(\omega)] \right| \\
\]

(20)

If \( |Q_{\text{asym}}| \sim 1 \), the lineshape is asymmetric and the interference effect is strong. We also should note that the interference effect may appear as a symmetric line with a deep. Such "antiresonance" may appear if \( A < 0 \) and \( |q_{\text{asym}}| \gg 1 \). The visibility of the antiresonance can be described by the ratio \( |A|/\Gamma_{12} Q_{\text{asym}}(\omega_0) \). Our numerical simulations show that anti-resonances appear for small inter-particle distances (see the graphs in the next section).

V. NUMERICAL RESULTS

In this section, we show the results of numerical calculations of energy absorptions for various systems. We pay special attention to the short interparticle distance regime, where the multipole effects are crucial. We emphasize the important role of the environment, that is essential to describe and understand experiments. One of the effects of environment is the dephasing time. Another is the dielectric constant of a matrix. These parameters have a significant impact on the asymmetric lineshapes of an absorption spectrum.

In Fig. 5, we show the absorption spectrum of colloidal SQD-MNP(Au) for different interparticle distances. The parameters are \( 1/T_{20} = 1 \, \text{meV}, \, T_1 = 10 \, \text{ns}, \, R_0 = 10 \, \text{nm}, \, \varepsilon_e = 1.8 \) (water), \( \hbar \omega_0 = 2.356 \, \text{eV} \). The chosen dephasing times correspond to the low-temperature regime when the exciton broadening \( 1/T_{20} = 1 \, \text{meV} \) is relatively small. One can see that the energy absorption

FIG. 5: The absorption spectrum of SQD-MNP(Au). (a) Polarization is along z direction. (b) Polarization is along x direction. (c) The peak and valley intensity versus distance corresponding to (a).
The parameters are 1ial SQD-MNP(Au) for different interparticle distances. The laser light polarization is taken as \( \mathbf{E}_0 \parallel \mathbf{x}(y) \). In this case, we see lineshapes with quite different Fano parameters, compared to those for the colloidal SQD-MNP molecule. The minimum becomes very deep for two reasons: 1) Large background dielectric constant and, therefore, strong enhancement of electric fields inside the system and 2) the intrinsic exciton linewidth \( 1/T_{20} \) is relativley small and, therefore, the exciton-plasmon interaction becomes "concentrated" in a narrow energy interval. The above reasons (1 and 2) lead to a strong interference effect for the case shown in Fig. 6.

It is interesting that the visibility of the exciton in SQD-MNP molecules becomes greatly increased for small \( R_d \) (Figs. 5 and 6). This appears due to both the interference effect and plasmon enhancement. The plasmon enhancement effect is basically an increase of actual electric fields inside the system in the regime of exciton-plasmon and photon-plasmon resonances \( \omega_0 \approx \omega_{\text{plasmon}} \). Mathematically, the plasmon enhancement appears in our equations through the factor \( \epsilon_c \). The typical enhancement factors for A-QM molecules with small \( R_d \) are about 10. The increased visibility of the exciton resonance in a SQD-MNP molecule was also found for the dipole regime of interaction in Ref. [16]. However our present theory provides us with an exact solution for the electric fields and allows us to describe this effect for the most important regime of the multipole interaction. For example, the strong anti-resonance in Fig. 5 is described by the factors: \( A/Q_0 \approx 0.005 \) and 0.02 for \( R_d = 100 \text{nm} \) and 12 nm, respectively.

In Fig. 5 we show the absorption spectrum of epitaxial SQD-MNP(Au) for different interparticle distances. The parameters are \( 1/T_{20}=2 \text{ meV}, T_1 = T_{20}/2, R_0 = 10 \text{ nm}, \epsilon_c = \epsilon_s = 12, \) the interband dipole matrix element

\[ \mu = c r_0, \quad r_0 = 0.6 \text{ nm}, \quad \hbar \omega_0=1.546 \text{eV}. \]

Again, the above parameters correspond to the low-temperature regime. The laser light polarization is taken as \( \mathbf{E}_0 \parallel \mathbf{x}(y) \). In this case, we see lineshapes with quite different Fano parameters, compared to those for the colloidal SQD-MNP molecule. The minimum becomes very deep for two reasons: 1) Large background dielectric constant and, therefore, strong enhancement of electric fields inside the system and 2) the intrinsic exciton linewidth \( 1/T_{20} \) is relativley small and, therefore, the exciton-plasmon interaction becomes "concentrated" in a narrow energy interval. The above reasons (1 and 2) lead to a strong interference effect for the case shown in Fig. 6.

It is interesting that the visibility of the exciton in SQD-MNP molecules becomes greatly increased for small \( R_d \) (Figs. 5 and 6). This appears due to both the interference effect and plasmon enhancement. The plasmon enhancement effect is basically an increase of actual electric fields inside the system in the regime of exciton-plasmon and photon-plasmon resonances \( \omega_0 \approx \omega_{\text{plasmon}} \). Mathematically, the plasmon enhancement appears in our equations through the factor \( \epsilon_c \). The typical enhancement factors for A-QM molecules with small \( R_d \) are about 10. The increased visibility of the exciton resonance in a SQD-MNP molecule was also found for the dipole regime of interaction in Ref. [16]. However our present theory provides us with an exact solution for the electric fields and allows us to describe this effect for the most important regime of the multipole interaction. For example, the strong anti-resonance in Fig. 5 is described by the factors: \( A/Q_0 \approx 0.005 \) and 0.02 for \( R_d = 100 \text{nm} \) and 12 nm, respectively.

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eral or many dye molecules can be attached to a single MNP, and therefore, the interference effect can become much stronger $\ddagger$. Fig. 7 shows the absorption spectrum of dye-MNP(Au) for different interparticle distances. The parameters correspond to the room temperature regime and water environment: $1/T_{20}=23$ meV, $T_1=5$ ns, $\varepsilon_c=1.8\varepsilon_0$ (water). Other parameters are $R_0=10$ nm, $\mu=\varepsilon_0$, $r_0=0.6$ nm, $\hbar\omega_0=2.345\varepsilon_0$. Here we see that the environment has an important impact on the energy absorption. The very large off-diagonal decoherence leads again to quite different absorption line shapes. Importantly, even for the large room-temperature broadening (23 meV), we see the anti-resonance. If a few or many dye molecules are attached, the depth of the anti-resonance will increase. Neglecting the interaction between dye molecules and the dipole orientation, we can write $A_N=N\varepsilon$, where $A_N$ is the anti-resonance coefficient for the $N$-molecule complex, $\varepsilon$ is the coefficient for a single dye molecule, and $N$ is the number of attached dye molecules. From Fig. 7 we see that the effect of the single exciton anti-resonance on the total absorption spectrum $|\Delta Q|/Q_{\text{MNP}}^0 \approx 0.035$ or 3.5%. If we now assume a structure with $N=10$, we obtain $|\Delta Q_N|/Q_{\text{MNP}}^0 \approx 35\%$. This tells us that the change in the total absorption spectrum due to the exciton-plasmon anti-resonance can be seen experimentally.

VI. CONCLUSION

We investigate the optical properties of hybrid molecules composed of SQD, dye, and MNPs. The main focus of the paper is the regime of strong exciton-plasmon interaction and multipole effects. First we derive an exact analytical solution for electric fields and absorption spectra. Then, we show that the multipole effects play the crucial role for the strong interaction regime. When the interparticle distance is relatively small, the multipole effect gives significantly larger peak shifts and broadenings for the energy absorption rate and the dipole approximation fails. The results obtained in this paper can be used to analyze optical experiments on hybrid systems with a strong exciton-plasmon interaction.

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