The Impact of the Core's Material on the Absorption of a Quantum Dot—Metal Nanoshell Hybrid System †

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Abstract: We study the linear optical response in a hybrid nanostructure composed of a semiconductor quantum dot and a metal shell nanoparticle. We analyze the case that the nanostructure interacts with an incident electromagnetic field with polarization parallel to the symmetry axis of the nanosystem. We derive the nonlinear density matrix equations, in the rotating wave approximation, under quasistatic response of the system and use a series expansion method to obtain analytical functions for the linear susceptibility with respect to both components of the nanostructure. The imaginary part of these expressions is related to the absorption coefficient. We investigate the way in which the modification of the core's material affects the characteristics of the spectral resonance. For low values of the dielectric constant, the system exhibits an amplified gain without population inversion and a quenched absorption resonance, while for high values of the dielectric constant, we observe suppression of the gain dip and enhancement of the absorption resonance. In the first regime, the exciton lifetime is suppressed and in the second case its value is importantly increased, especially in the case of small interparticle distances, where the semiconductor quantum dot and a metal shell nanoparticle interact strongly.

Keywords: absorption; gain; hybrid nanostructure; metal nanoshell; semiconductor quantum dot

1. Introduction

During the last two decades, hybrid nanostructures fabricated by coupling semiconductor quantum dots (SQDs) with metal nanoparticles have attracted scientific interest [1–12], since they produce unique optical effects. These novel properties owe their presence to the creation of hybrid excitons originating from the long-range Coulomb coupling between excitons and plasmons and have been extensively investigated in systems where a metal nanosphere is coupled to an SQD [1–10]. However, the use of metal nanoparticles with a more complex structure may give rise to a series of interesting optical phenomena, making such systems ideal candidates for applications in the field of nanophotonics. For instance, the coupling of a metal nanoshell (MNS) with a dielectric core to an SQD provides the advantage of tunning the optical properties of the system more efficiently, by properly adjusting the size and the material of the core [11,12].

In the present work, we aim at exploring the novel characteristics that may arise on the absorption spectrum of both the SQD and the MNS, in a hybrid system where these two components are coupled together, by properly adjusting the dielectric constant of the

core material. We first derive the equations of motion, in the rotating wave approximation and expand the density matrix elements at first order with respect to the incident field. The multipolar polarizability regime is applied [4,10–12], that provides a more accurate description of the interaction between the SQD and the nanoshell. After solving the equations in the steady-state, we obtain analytical expressions for the calculation of the positions and the amplitudes of the maxima and the minima detected on the absorption spectrum, as well as of the full-width half maximum (FWHM) of the absorption resonance.

2. Methods

The hybrid nanosystem consists of a MNS structure and a SQD and is placed in a dielectric medium, as illustrated in Figure 1. The dielectric constants of the environment and the SQD are denoted by ε_{env} and ε_s, respectively. The MNS structure is composed of a dielectric core of radius r_1 and a gold metal nanoshell with outer radius r_2 and dielectric function $\varepsilon(\omega)$. The core is made of a material with dielectric constant ε_c. The center-to-center distance between the nanoparticles is R. We model the SQD as a two-level system, E_0 and E_1 being the energies of the ground state $|0\rangle$ and the excited state $|1\rangle$, respectively, with energy difference $\hbar\omega_{01} = E_1 - E_0$.
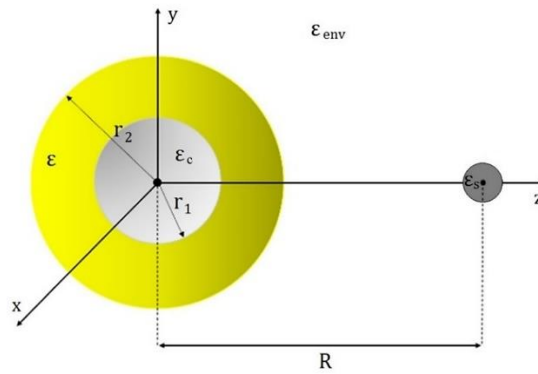

Figure 1. Schematic configuration of the hybrid system.

The entire hybrid system is subjected to an external classical electromagnetic field $E(t) = E_0 e^{-i\omega t} + c.c$, that excites the interband transition $|0\rangle \rightarrow |1\rangle$. The Hamiltonian that governs the population dynamics of the SQD, in the dipole approximation, is

$$H = \hbar\omega_{01}|1\rangle\langle 1| - \hbar[(\Omega + G\sigma_{10})e^{-i\omega t} + c.c.] (|0\rangle\langle 1| + |1\rangle\langle 0|1), \tag{1}$$

where we have also introduced the following two key parameters

$$\Omega = \frac{E_0\mu}{2\hbar\varepsilon_{effs}}\left(1 + \frac{s_{pol}f_1(\omega)r_2^3}{R^3}\right) = \Omega_R + i\Omega_I, \tag{2}$$

$$G = \frac{\mu^2}{4\pi\hbar\varepsilon_0\varepsilon_{effs}^2\varepsilon_{env}}\sum_{n=1}^{10}\frac{(n+1)^2 f_n(\omega)r_2^{2n+1}}{R^{2n+4}} = G_R + iG_I. \tag{3}$$

The first and the second terms of the Rabi frequency Ω are respectively associated to the coupling of the SQD with the probe electric field and the field emitted by the MNS, due to the induction of polarization [8]. The G parameter is related to the self-interaction of the SQD. The ε_{effs} factor accounts for the screening of the SQD [10]. The definition of the first-order polarizability of a core-shell nanoparticle is $\alpha_1(\omega) = 4\pi r_2^3 f_1(\omega)$, $f_1(\omega) = f_{1R} + if_{1I}$ being a complex factor given in Ref. [12]. In the multipole expansion approach, the polarizability factor is defined as $f_n(\omega)$ [13].

After deriving the density matrix equations and expanding the density matrix elements in first-order Taylor series, with respect to the amplitude of the weak probe field, we solve the obtained equations in the steady state and calculate the absorption coefficient

(imaginary part of the linear susceptibility of the SQD), as in Ref. [10], with the corresponding critical points

$$\text{Im}[\chi_{\text{SQD}}]_{max/min} = \mp Q \frac{M_I^2}{2(1 + T_2 G_I)\left(\sqrt{M_I^2 + M_R^2} \mp M_R\right)}, \tag{4}$$

where M_R and M_I represent the real and the imaginary parts of the complex factor $M = \frac{1}{\varepsilon_{\text{effs}}}\left(1 + \frac{s_{\text{pol}}f_{1(\omega)}r_2^3}{R^3}\right)$ and $Q = -\frac{\Gamma\mu^2 T_2}{\varepsilon_0 V\hbar}$ is a negative constant. The position and the FWHM of the absorption resonance are

$$\delta_{\text{res}} = -G_R - \frac{M_R}{M_I}\left(G_I + \frac{1}{T_2}\right), \qquad \text{FWHM} = 2\sqrt{1 + \frac{M_I^2}{M_R^2}\left(G_I + \frac{1}{T_2}\right)}. \tag{5}$$

Next, we determine the first-order optical susceptibility of the core-shell nanoparticle as in Ref. [10]. After performing calculations, we derive an analytical expression for the first-order absorption of the MNS

$$\text{Im}[\chi_{\text{MNS}}] = \frac{3\varepsilon_{\text{env}}}{\varepsilon_0}f_{1I}(\omega) + \Phi\frac{\widetilde{M}_I T_2(\delta + G_R) - \widetilde{M}_R(1 + T_2 G_I)}{T_2^2(\delta + G_R)^2 + (1 + T_2 G_I)^2}. \tag{6}$$

where, $\Phi(R) = -\frac{3s_{\text{pol}}\mu^2 T_2}{4\pi\varepsilon_0\varepsilon_{\text{effs}}R^3}$ is an R-dependent quantity and $\widetilde{M} = f_1 \cdot M = \widetilde{M}_R + i\widetilde{M}_I$ is a complex factor that is frequency-independent, within the short range of frequencies under investigation.

3. Parameters and Results

In this section, we present the profile of the absorption spectrum, as a function of the detuning energy of the applied field from resonance $\hbar\delta = \hbar(\omega - \omega_{01})$, both with regard to the SQD and the MNS. For the calculations, we assume that the MNS is made of gold. The value of the corresponding dielectric function $\varepsilon_2(\omega)$ is equal to $(-2.28 + 3.81i)$ [14], for an incident field of energy around 2.5 eV. This value corresponds to the energy that is necessary for the excitation of a localized surface plasmon on the surface of the gold metal nanoshell and is also equal to the energy band gap of the two-level quantum emitter. The dielectric constant of the environment is $\varepsilon_{\text{env}} = 1$ and the dephasing time is $T_2 = 0.3$ ns. The dielectric constant of the semiconductor quantum dot ε_s is set equal to 6 and the transition dipole moment is $\mu = 0.65q_e$, where q_e is the electron charge [10]. In the strongly confinement regime, we also take $\Gamma/V = 5 \times 10^{23}\text{m}^{-3}$ [15]. We use the multipole polarization regime and maintain terms of up to $N = 10$ order, as this approximation is sufficient to reach convergence [4]. The MNS is assumed to have a fixed size that is determined by the outer radius $r_2 = 7.5$ nm. The radius of the dielectric core r_1 may vary, since we aim at investigating in which way the value of this parameter influences the profiles of the absorption spectra. We also considered the polarization of the external field to be oriented in parallel to the symmetry axis of the nanosystem z, which means that $s_a = 2$.

In Figure 2a,b, we present the absorption spectra of the SQD and the MNS, respectively, as a function of the detuning energy of the weak probe field $\hbar\delta$, for interparticle distances $R = 12.5$ nm (turquoise solid curve), 14 nm (purple dashed curve), 17 nm (pink dotted curved) and 100 nm (green dashed-dotted curve). The radius of the dielectric core is $r_1 = 6.5$ nm and its dielectric constant is $\varepsilon_c = 1$. In Figure 3a,b, we present the spectra of the absorption coefficients, for $\varepsilon_c = 8$.
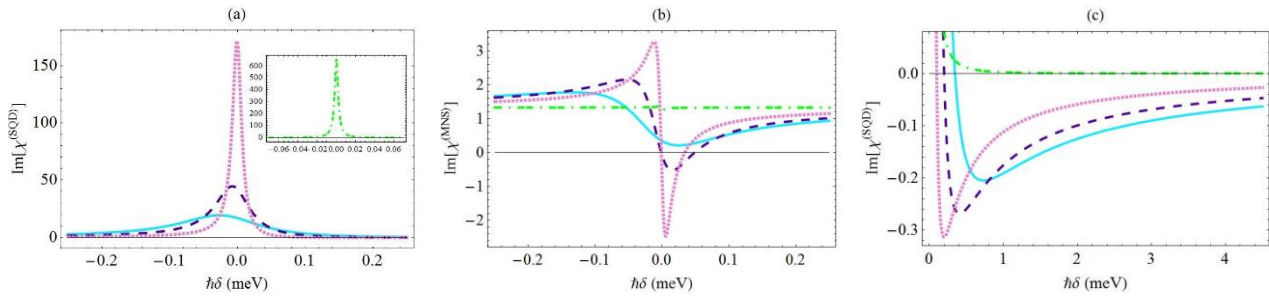
Figure 2. The imaginary part of the linear optical susceptibility of the SQD and the MNS, (**a**,**b**), as a function of the detuning energy $\hbar\delta$ of the incident field, for various center-to-center distances: $R = 12.5$ nm (turquoise solid curve), 14 nm (purple dashed curve), 17 nm (pink dotted curve) and 100 nm (green dashed-dotted curve). The rest physical parameters are $r_2 = 7.5$ nm, $r_1 = 6.5$ nm, $\mu = 0.65q_e$, $\varepsilon_s = 6$, $T_2 = 0.3$ ps and $\varepsilon_{env} = \varepsilon_c = 1$.
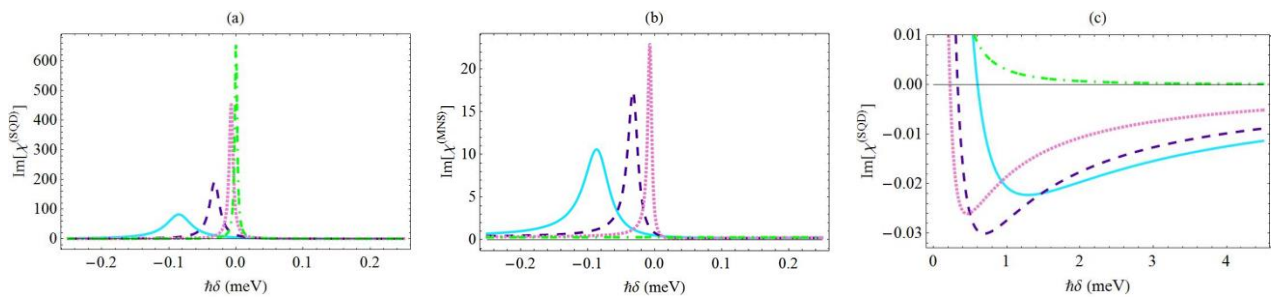

Figure 3. The linear absorption spectra of the SQD and the MNS, (**a**,**b**), for various center-to-center distances, with $\varepsilon_c = 8\varepsilon_0$. The rest physical parameters take the same values as in Figure 2.

4. Discussion and Conclusions

In Figure 2a, we note that the spectrum of $\text{Im}[\chi_{SQD}]$ manifests a Lorentzian-type absorption resonance. As the interparticle distance is reduced, we note that the FWHM of the absorption peak is substantially increased and its position is shifted towards negative values of the detuning, Equation (5), which are respectively related to shrunk lifetime of the hybrid exciton and its red shifted energy. At the same time, the magnitude of the absorption peak, Equation (4), is importantly quenched. These effects owe their presence to the decrease of the value of the parameters K_I^2/K_R^2 and G_I. The emergence of gain without population inversion within a specific range of frequencies on the profile of the SQD absorption spectrum Figure 2c, is predicted mathematically by Equation (4), according to which, for any set of the physical parameters, $\text{Im}[\chi_{SQD}]$ is always negative, due to the negative sign of the Q constant. For intermediate values of R, the magnitude of the gain is maximized, while, in the limiting case where the SQD does not practically interact with the MNS (green dotted-dashed curve: $R = 100$ nm), the profile of the absorption resonance becomes highly symmetric and the gain region extinguishes, since $M_I \rightarrow 0$. In this last case, $\text{Im}[\chi_{SQD}]_{max}$ converges to the value $-\dfrac{Q}{\varepsilon_{effs}}$ and $\text{Im}[\chi_{SQD}]_{min} \rightarrow 0$. As seen in Figure 2b, the absorption spectrum for the MNS has a Fano-type profile, for low and intermediate values of the interparticle distance. We also observe the rise of a gain region on the $\text{Im}[\chi_{MNS}]$ spectrum the magnitude of which is maximized for an intermediate value of the center-to-center distance. In addition, for high values of the interparticle distance ($R = 100$ nm), the MNS does not interact with the SQD and the second term of Equation (6) extinguishes, the reason being that the M_I variable converges to zero, since it is inversely proportional to the third order of R. Thus, the value of the imaginary part of χ_{MNS} is determined by the first term of Equation (6), which is a constant. The corresponding spectral profile is a horizontal line (green dashed-dotted curve).

By comparing Figure 2a with Figure 3a, and Figure 2c with Figure 3c, we observe that the increase of ε_C is responsible for the enhancement and the narrowing of the

absorption resonance, as well as for the gain suppression. The increase of ε_c leads to the decrease of G_I. As a result, the denominator of Equation (4) decreases, thus leading to the enhancement of the absorption peak. We also found that a substantial modification of the exciton's lifetime is governed by the dielectric constant of the core, since the increase of ε_c leads to the reduction of the FWHM of the absorption resonance. This effect can be understood in terms of Equation (5), where we note that the FWHM is proportional to the imaginary part of the self-interaction constant, G_I, the value of which decreases as we increase the dielectric constant of the core ε_c. The magnitude of the gain dip manifests a notable suppression, as the dielectric constant of the core is amplified, Figures 2c and 3c. The dielectric constant of the core's material also plays an important role in the absorption spectrum of the MNS. As we increase the value of the core's dielectric constant, the magnitude of the gain dip of the MNS absorption spectrum is suppressed and above a specific value of the dielectric constant ε_c the gain region is extinguished. The spectral profile of the MNS absorption coefficient strongly resembles the Lorentzian-type absorption spectrum of the SQD, in opposition to the case with $\varepsilon_c = 1$ presented in Figure 2b, where it exhibits a Fano-type line shape. This is due to the fact that the increase of the value of ε_c causes a substantial decrease of the $\tilde{M}_I$ factor that is introduced in the R-dependent term of Equation (6).

References

1. Sadeghi, S.M. The inhibition of optical excitations and enhancement of Rabi flopping in hybrid quantum dot–metallic nanoparticle systems. *Nanotechnology* **2009**, *20*, 225401.
2. Sadeghi, S.M. Plasmonic metaresonances: Molecular resonances in quantum dot–metallic nanoparticle conjugates. *Phys. Rev. B* **2009**, *79*, 233309.
3. Zhang, W.; Govorov, A.O.; Bryant, G.W. Semiconductor-metal nanoparticle molecules: Hybrid excitons and the nonlinear Fano effect. *Phys. Rev. Lett.* **2006**, *97*, 146804.
4. Yan, J.-Y.; Zhang, W.; Duan, S.-Q.; Zhao, X.-G.; Govorov, A.O. Optical properties of coupled metal semiconductor and metal-molecule nanocrystal complexes: Role of multipole effects. *Phys. Rev. B* **2008**, *77*, 165301.
5. Artuso, R.D.; Bryant, G.W. Strongly coupled quantum dot-metal nanoparticle systems: Exciton-induced transparency, discontinuous response, and suppression as driven quantum oscillator effects. *Phys. Rev. B* **2010**, *82*, 195419.
6. Ko, M.-C.; Kim, N.-C.; Choe, S., II; So, G.-H.; Jang, P.-R.; Kim, Y.-J.; Kim, I.-G.; Li, J.-B. Plasmonic effect on the optical properties in a hybrid V-Type three-level quantum dot-metallic nanoparticle nanosystem. *Plasmonics* **2017**, *13*, 1–8.
7. Malyshev, A.V.; Malyshev, V.A. Optical bistability and hysteresis of a hybrid metal-semiconductor nanodimer. *Phys. Rev. B* **2011**, *84*, 035314.
8. Ridolfo, A.; Di Stefano, O.; Fina, N.; Saija, R.; Savasta, S. Quantum plasmonics with quantum dot-metal nanoparticle molecules: Influence of the Fano effect on photon statistics. *Phys. Rev. Lett.* **2010**, *105*, 263601.
9. Sadeghi, S.M. Gain without inversion in hybrid quantum dot–metallic nanoparticle systems. *Nanotechnology* **2010**, *21*, 455401.
10. Kosionis, S.G.; Terzis, A.F.; Sadeghi, S.M.; Paspalakis, E. Optical response of a quantum dot-metal nanoparticle hybrid interacting with a weak probe field. J. Phys.: Condens. *Matter* **2013**, *25*, 045304.
11. Naeimi, Z.; Mohammadzadeh, A.; Miri, M. Optical response of a hybrid system composed of a quantum dot and a core-shell nanoparticle. *JOSA B* **2019**, *36*, 2317–2324.

12. Nughoro, B.S.; Iskandar, A.A.; Malyshev, V.A.; Knoester, J. Plasmon-assisted two-photon absorption in a semiconductor quantum dot-metallic nanoshell composite. *Phys. Rev. B* **2020**, *102*, 045405.
13. Huang, C.; Zhang, H.A. Simple derivation of the shell polarizability formula and investigation of the plasmonic behavior of aluminum nanoshells with the Mie theory. *Phys. Chem. Chem. Phys.* **2021**, *23*, 23501–23507.
14. Johnson, P.B.; Christy, R.W.; Optical constants of the noble metals. *Phys. Rev. B* **1972**, *6*, 4370.
15. Chang-Hasnain, C.J.; Ku, P.-C.; Kim, J.; Chuang, S.-L. Variable optical buffer using slow light in semiconductor nanostructures. *Proc. IEEE* **2003**, *91*, 1884.