Theory of dielectrically induced surface excitonic states in spherical quantum dots

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The formation of quantum dot (QD) excitonic surface states induced by dielectric mismatch is theoretically explored in spherical nanocrystals embedded in very high and in very low permittivity media. It is found that the transition from volume to surface exciton states ($V \rightarrow S$) always parallels a sudden drop of exciton brightness if the QD is embedded in low dielectric constant media. This is not the case of a QD buried in high permittivity media. In this case, the $V \rightarrow S$ transition is monitored by a reduction in exciton brightness or not depending on the m_h^*/m_e^* ratio between the effective masses of electron and hole. The presence of a hydrogenic donor impurity at the QD center can drastically reduce the electron-hole density overlap and thus the excitonic binding energy and the drop of brightness that parallels the formation of surface states.

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I. INTRODUCTION

Most of the active key components of modern information technologies rely on semiconductor devices with electronic or optoelectronic functions. It is believed that quantum bits, which are generic quantum mechanical two-level systems, will become the basic building blocks of this technology in the next future. One possible realization of these two-level systems is an exciton ground state in a quantum dot (QD).[1] The formation of QD excitons or electron-hole *e-h* pairs and *e-h* recombination leading to photoluminescence has received a great deal of attention in the literature.[2] A very interesting feature of semiconductor QDs spectra is the shift of excitonic peaks as compared to bulk values. This originates from two usually opposite contributions. On the one hand, the single-particle band gap is shifted to higher energies due to the quantum size effect. On the other hand, the Coulomb attraction between the *e-h* pair created by photoexcitation adds a redshift correction. Both corrections are size dependent and generally result in an overall blueshift of the optical band gap as compared to the bulk.[3] Since the pioneering work by Brus,[4,5] the influence of QD surface dielectric polarization on energy and density distribution of carriers has been taken into account for a proper comparison between theory and experiments. This surface polarization is especially strong for QDs in a glass matrix, liquid solution, air, or a vacuum, where the background dielectric constant of the QD and the surrounding medium are substantially different. Two contributions to the energy originate from the dielectric mismatch, namely, single-particle contributions coming from the interaction of carriers with their own induced charges (self-polarization energy) and two-particle contributions coming from the interaction of a carrier with the charge induced by the other one (polarization of the Coulomb interaction). By assuming infinitely (or very) high confinement barriers and steplike dielectric functions, the dielectric mismatch corrections on excitonic energies in spherical QDs almost totally cancel each other out.[4,6–9] However, dielectric mismatch corrections on excitonic energies no longer cancel out if finite confining barrier heights are considered.[10] Under specific conditions, the attractive self-polarization potential well originated from the dielectric mismatch is even able to confine carriers in surface states.[11–15] Dielectrically induced exciton surface states in semiconductor QDs were predicted for the first time by Bányai *et al.*[11,17] using a model where electron and hole are confined in a QD by a common low potential height barrier and have a large effective *e-h* mass ratio $m_h^*/m_e^*=10$, the QD being subject to a strong dielectric mismatch $\varepsilon_{QD}/\varepsilon_{out}=10$.

In this Brief Report, we explore the possible formation of excitonic surface states in two different situations, (i) a spherical QD in air, where the hole confining barrier height is much higher than the electron one, and (ii) a QD buried in a matrix with a higher dielectric constant (in this case, as is usual, we will assume that the confinement barrier height for holes is about 1/2 that corresponding to electrons). We will show that in both cases, a dielectric mismatch-induced transition from a volume to a surface state involving an optical band gap redshift (with respect to the case of no dielectric mismatch) can be reached under specific conditions. Relevant differences between the two cases are found. Thus, in case (i), only the electron can be confined in the self-polarization potential well, beyond the QD border. However, the hole, despite its heavier mass, as it is subject to a higher confining barrier, cannot overcome the spatial confinement and remains within the QD but close to the border due to the *e-h* attraction. The transition from volume to surface states can be monitored in this case by a sudden change in the overlap between electron and hole wave functions, i.e., by a decrease in the exciton brightness. A quite different situation holds in case (ii) because the self-polarization potential well is now located on the inner side of the QD border so that no spatial confining barrier prevents localization of particles in it. In this case, we find that the transition from volume to surface states can be monitored by a reduction in the excitonic brightness or not, depending on the m_h^*/m_e^* ratio. In addition, the influence of an on-center shallow donor impurity on the binding energy and oscillator strength of the fundamental exciton is also addressed. It results in an almost total suppression of binding and brightness.

II. THEORY AND COMPUTATIONAL DETAILS

We deal with the fundamental exciton of spherical QDs. It has been reported[2,16] that this exciton basically involves the

fundamental $1S_e$ electron and $1S_{3/2}$ hole states. Then, the hole in the fundamental exciton has a strong heavy-hole character, being well described by the one-band model. The missing small contribution of the light holes in the exciton configuration interaction (CI) expansion is expected to be negligible. This simplification on the hole description leads to a computational workable approach. Also, the electron-hole spin-exchange interaction that splits the optically active exciton ground state into a few states,[2,18,19] the lowest of which is optically passive, has been neglected in the present study. Then, to account for excitonic states, we first solve the one-particle effective-mass Schrödinger equation,

$$H = -\frac{1}{2}\nabla\left[\frac{1}{m^*(\mathbf{r})}\nabla\right] + V(\mathbf{r}) + V_s(\mathbf{r}), \tag{1}$$

where the first term is the generalized kinetic energy operator, $V(\mathbf{r})$ represents the spatial confining potential, and $V_s(\mathbf{r})$ stands for the self-polarization potential. The calculation of this potential is carried out by employing a dielectric function profile that changes smoothly within a thin interface (of the order of a lattice constant) between the semiconductor QD and its surroundings.[10,20] This approach bypasses the (unphysical) self-polarization potential divergences that arise at the interface when a steplike dielectric profile is employed[17,21] and avoids the lack of size scaling of the nondivergent regularization method.[11,17]

The radial parts of the exact single-particle eigenfunctions $\phi_{n\ell m}(\mathbf{r}_{e/h})$ are determined numerically on the grid extending far beyond the dot radius R. Hartree products of the basis functions $\phi_{n\ell m}(\mathbf{r}_e)\cdot\phi_{n'\ell'm'}(\mathbf{r}_h)$ are then used to construct CI expansions $\Psi_{LM}=\Sigma_j\Phi_j$ of the symmetry-adapted e-h configurations, where L and M are the total and z-component angular quantum numbers, respectively. The e-h Hamiltonian containing Coulomb interaction and polarization terms[10] is then diagonalized in the CI basis set. As a result, we get two-particle wave functions $\Psi_{LM}(\mathbf{r}_e,\mathbf{r}_h)$ and energies $E(L)$. We carry out full CI employing a very large orbital basis set $\phi_{n\ell m}$ including the $n=4$ lowest-lying orbitals with $\ell=0,1,2$ and the $n=3$ lowest-lying orbitals with $\ell=3,4,5,6$. The same basis set is employed for electron and holes, this basis set being by far larger than that required to achieve the accuracy shown in the figures.

From the wave function, we can define the electron *radial density* $P(r_e)$,

$$P(r_e) = \int |\Psi(\mathbf{r}_e,\mathbf{r}_h)|^2 r_e^2 r_h^2 \sin\theta_e \sin\theta_h dr_h d\theta_e d\theta_h d\phi_e d\phi_h, \tag{2}$$

the hole *radial density* $P(r_h)$ in a similar way, and the e-h overlap $S^2_{e\text{-}h}$,

$$S^2_{e\text{-}h} = \left|\int \Psi(\mathbf{r}_e=\mathbf{r}_h=\mathbf{r}) r^2 \sin\theta dr d\theta d\phi\right|^2, \tag{3}$$

which is proportional to the oscillator strength of the electron-hole state.[16,22–24]

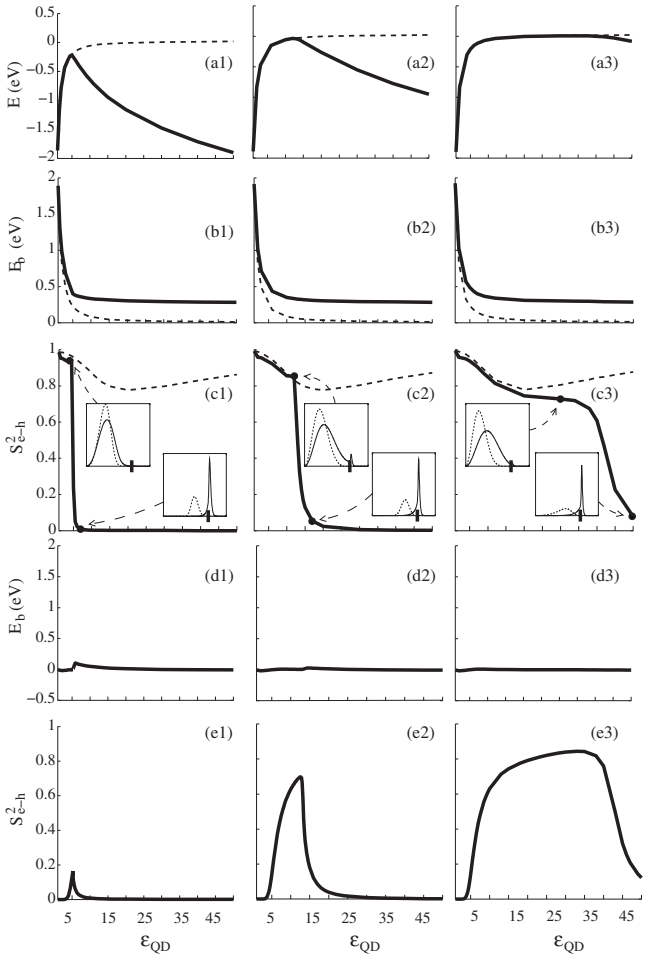

FIG. 1. Excitonic E and binding E_b energies and e-h overlap $S^2_{e\text{-}h}$ of a $R=5$ nm, $m^*_{e,QD}=0.5$, $m^*_{h,QD}=10$ freestanding QD with a confining barrier height V_e of 1 eV [(a1), (b1), and (c1)], 2 eV [(a2), (b2), (c2)], and 3 eV [(c1), (c2), (c3)], as a function of the QD dielectric constant ε_{QD}. Solid (dashed) lines include (exclude) dielectric polarization effects. Insets: electron (solid line) and hole (dotted line) radial density distributions [Eq. (2)] (the QD border is indicated by a tick in the horizontal axis). Panels (d1)–(d3) and (e1)–(e3) correspond to (b1)–(b3) and (c1)–(c3) when a hydrogenic donor impurity is located at the QD center.

III. RESULTS AND DISCUSSION

Case (i): QD in air or a vacuum. We first investigate the role of image charges on the excitonic properties of a freestanding QD. Our model consists of a spherical $R=5$ nm radius nanocrystal. We employ the following parameters:[25] $m^*_{e,QD}=0.5$, $m^*_{e,out}=m^*_{h,out}=1$, $m^*_{h,QD}=10$, and $\varepsilon_{out}=1$. Since we cannot promote holes into a vacuum, we will assume an infinite height for the spatial confining barrier of a hole when a QD is in air or a vacuum. As for electrons, we consider the QD electroaffinity as the barrier height V_e.

We have carried out three series of calculations of the overlap $S^2_{e\text{-}h}$ and excitonic E and binding E_b energies[26] vs ε_{QD} ranging from 1 up to 50, corresponding to $V_e=1$, 2, and 3 eV. The results are summarized in Fig. 1, together with partner calculations with $\varepsilon_{out}=\varepsilon_{QD}$, i.e., in the absence of

dielectric mismatch effects, that will help to analyze the obtained results.

Figures 1(c1)–1(c3) show sudden changes of *e-h* overlap $S^2_{e\text{-}h}$ that parallel the transition from volume to surface exciton states, as can be seen in the corresponding insets. This transition is also reflected as a change of sign of the slope in the excitonic energy vs ε_{QD} profile [Figs. 1(a1)–1(a3)], while it is not reflected in the binding energy plots [Figs. 1(b1)–1(b3)], whose profile vs ε_{QD} is very smooth. Differences between polarized and unpolarized excitonic energies [see Figs. 1(a1)–1(a3)] basically reflect self-polarization effects, while differences between polarized and unpolarized binding energies [see Figs. 1(b1)–1(b3)] essentially show the influence of the polarization of the Coulomb interaction, as we have verified in a series of calculations (not shown). Our results are an extreme example denying the cancellation of single- and two-particle polarization contributions to the excitonic energy. Also, they lead to the conclusion that the main effect of single-particle self-polarization is the production of a redshift in the optical band gap, while the polarization of the Coulomb interaction basically enhances the exciton binding energy. Figure 1 additionally reveals that the conditions for the QD materials to yield exciton surface states when the QD is in air or a vacuum are rather severe, namely, quite low electroaffinity χ and not very light electron effective mass m^*_e. Not many semiconductors can fulfill this requirement. We may mention SiO_2 as a possible candidate (m^*_e=0.5, χ=0.9 eV, ε=4, and m^*_h=10, see Refs. 27–30).

Next, we study the same QD doped with a hydrogenic donor impurity at its center. This impurity exerts the most relevant influence for low values of the dielectric constant by binding the electron while repelling the hole, thus leading to a drop in excitonic binding energy[31] and brightness [see panels (d1)–(d3) and (e1)–(e3) in Fig. 1]. Our calculations also reveal that the heavier the electron effective mass is, the closer its density distribution bound to the impurity site is. Accordingly, an acceptor impurity attracts the heavier hole very close to the QD center and creates an effective neutral entity that leads the electron to behave as an almost independent particle in the QD.

Case (ii): QD embedded in a medium with a larger dielectric constant. We consider, as above, a spherical 5 nm radius QD defined by the following parameters: $m^*_{e,QD}$=0.5, ε_{QD}=4, V_e=1 eV, and V_h=0.5 eV, the ratio V_e/V_h simulating typical alignments of different materials. Two different effective masses for holes have been considered, namely, $m^*_{h,QD}$=1 and 10, slightly and much heavier than $m^*_{e,QD}$, respectively. This QD is embedded in a fictitious medium with a dielectric constant ranging from $\varepsilon_{out}=\varepsilon_{QD}$ up to ε_{out}=50. The effective masses in this medium are assumed to be the same as in the QD since we have no criterion to assign them.

The key difference with respect to the previous case (i) of a QD in air is that now, the self-polarization potential has the attractive well located on the inner side of the QD border. Then, both particles can be confined in it, the heavier particle being more strongly attracted by this well due to its smaller kinetic energy. This is in contrast with the above case (i) where the hole (the heavier particle) was unable to overcome its large confining potential barrier, while the electron (the lighter particle), confined by a shorter wall, could jump to the self-polarization potential well. Indeed, in case (ii), our exploratory single-particle calculations vs ε_{out} showed a gradual localization of the carriers in the self-polarization well, facing three different phases: namely, phase 1 (low ε_{out}) corresponding to volumetrically distributed electron and hole, phase 2 (intermediate ε_{out}) where the electronic density distribution is still volumetric while the hole forms a surface state, and phase 3 (large ε_{out}) in which both electron and hole are located in the surface well. However, as the strong *e-h* attraction (ε_{QD}=4) is incorporated into the CI calculation, phase 2 drops out.[32] Thus, only two phases are encountered, in which both particles show volumetric or facial distributions simultaneously. This is shown in Fig. 2, which shows the overlap $S^2_{e\text{-}h}$, excitonic E, and binding E_b energies of the considered QD with $m^*_{h,QD}$=1 and 10 vs ε_{out} ranging from $\varepsilon_{out}=\varepsilon_{QD}$ up to ε_{out}=50. The quantitative differences in excitonic and binding energies in either case are a direct consequence of the quite different kinetic energy of the hole. Both cases show, however, similar qualitative trends (increasing band gap redshift and decreasing E_b vs an increasing dielectric mismatch), which is in turn similar to the behavior already shown for a QD in air (see Fig. 1). A relevant difference arises in the overlap vs ε_{out} profile. While Fig. 2(c1) ($m^*_{h,QD}$=10) resembles Figs. 1(c1)–1(c3), in which the transition from volume to surface excitonic states involves a sudden $S^2_{e\text{-}h}$ drop and therefore a sudden reduction in the

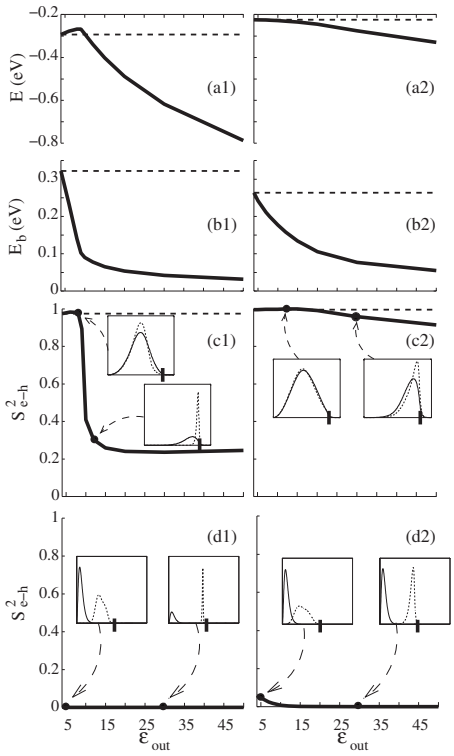

FIG. 2. Same as Fig. 1 but for a R=5 nm, ε_{QD}=4 QD with V_e=1 eV, V_h=0.5 eV, and $m^*_{e,QD}$=0.5, and two different hole effective masses, namely, $m^*_{h,QD}$=10 [(a1), (b1), and (c1)] and $m^*_{h,QD}$=1 [(a2), (b2), and (c2)], as a function of the dielectric constant of the environment ε_{out}. Panels (d1) and (d2) correspond to (c1) and (c2) when a hydrogenic donor impurity is located at the QD center.

exciton brightness, this is not the case in Fig. 2(c2) ($m^*_{h,QD}=1$). Since in the present case (ii) the transition from volume to surface state holds simultaneously for electron and hole, one may expect profiles like Fig. 2(c2), revealing an almost constant overlap vs ε_{out}. Then, the plot in Fig. 2(c1) looks like an anomaly that deserves an explanation. Indeed, the parameters $m^*_e=0.5$, $m^*_h=10$, $R=5$ nm, and $\varepsilon_{QD}=4$ yield quite a small effective Bohr radius, thus revealing that both electron and hole are in the weak confinement regime, the (volumetric) electron and hole density distributions being similar [see insets in Fig. 2(c1)]. However, once the trapping of particles in the narrow, deep self-polarization potential well occurs, both particles feel different spatial confinement. The heavier particle becomes strongly localized in the well, whereas the lighter one has a relevant leaking outside it [see insets in Fig. 2(c1)], yielding as a result a smaller overlap. In other words, in contrast to case (i) where the transition from volume to surface states always parallels a sudden decrease in brightness, in case (ii), this transition only has relevant brightness impact for QD materials with large m^*_h/m^*_e ratios.

Also, the influence of a hydrogenic donor impurity is addressed. As above, it attracts the electron toward the QD center and repels the hole [see Figs. 2(d1) and 2(d2)], resulting in a negligible binding energy and a strong reduction in oscillator strength.

In a last series of calculations, we explore the possibility of surface exciton formation in QDs built of higher dielectric constant materials. Now we set, as above, $R=5$ nm, $m^*_e=0.5$, $m^*_h=1$ and 10, $V_e=1$ eV, and $V_h=0.5$ eV. The permittivity of the external medium is set very high, $\varepsilon_{out}=100$, and we calculate the *e-h* overlap $S^2_{e\text{-}h}$ and binding energy E_b vs ε_{QD}. The results are shown in Fig. 3. As previously discussed, sudden changes in overlap reflecting transition from volume to surface exciton states only occur for large m^*_h/m^*_e ratios. As can be seen in Fig. 3(b1) (corresponding to a large m^*_h/m^*_e ratio), small (large) ε_{QD} values yield surface (volume) excitonic states with small (large) overlaps, in agreement with previous reasoning. However, intermediate ε_{QD} values are characterized by extremely small overlaps that parallel an anomalous minimum in the binding energy [Fig. 3(a1)]. This behavior occurs because, in this range of QD dielectric constants, the electron and hole single-particle densities are distributed as in the above mentioned phase 2, but now the *e-h* Coulomb attraction is not strong enough to drop phase 2 out, so we get a "broken" exciton in which the hole is localized in the self-polarization potential well, whereas the electron spreads over the whole QD volume [see insets in Fig. 3(b1)]. The small overlap and the decrease in the exciton binding energy are a direct consequence of the *e-h* spatial separation in this phase, which does not exist [see Figs. 3(a2) and 3(b2)] unless the effective masses of electron and hole are very dissimilar. Finally, Figs. 3(c1) and 3(c2) show the influence of a hydrogenic donor impurity located at the QD center. We see that the (D^+,X) exciton can approximately be described as D^0+h, i.e., a neutral electron-impurity pair and an almost independent hole, as it is revealed by the negligible binding energy calculated.

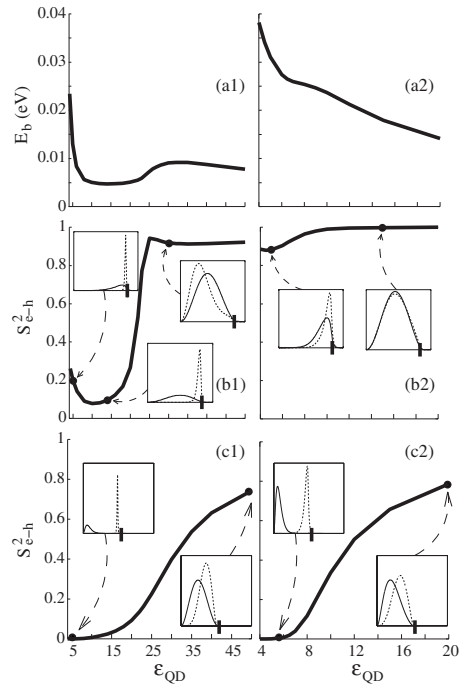

FIG. 3. Binding energy E_b and *e-h* overlap $S^2_{e\text{-}h}$ of a $R=5$ nm QD with $V_e=1$ eV, $V_h=0.5$ eV, and $m^*_{e,QD}=0.5$, and two different hole effective masses, namely, $m^*_{h,QD}=10$ [(a1) and (b1)] and $m^*_{h,QD}=1$ [(a2) and (b2)], as a function of ε_{QD} for a fixed $\varepsilon_{out}=100$. Insets: same criterion as in Fig. 1. Panels (c1) and (c2) correspond to (b1) and (b2) when a hydrogenic donor impurity is located at the QD center.

IV. CONCLUDING REMARKS

We have shown that the dielectric properties of the QD environment can strongly influence the brightness of confined excitons, as well as excitonic and binding energies, due to the formation of surface states. While a sudden decrease in exciton brightness parallels the formation of surface excitons in the case of a QD in air or a vacuum, only QD materials with a large m^*_h/m^*_e ratio present a considerable reduction in exciton brightness when the QD is buried in a large dielectric constant medium. Our calculations also reveal[33] that the conditions to reach surface exciton states in this last case are less severe than if the QD is surrounded by air or a vacuum. A shallow donor impurity located at the QD center leads to an almost total suppression of exciton binding and brightness.

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[31] We define binding energy in the presence of a hydrogenic impurity $E_b(D^+,X)$ as in W. Xie, Phys. Lett. A **270**, 343 (2000), i.e., $E_b(D^+,X)=E(D^0)+E_h-E(D^+,X)$, where $E(D^+,X)$ is the energy of the exciton in the doped QD, E_h the lowest level of a hole in the QD without impurity, and $E(D^0)$ the ground state of an electron in the doped QD.
[32] For QD dielectric constants of the order of $\varepsilon_{QD}=4$, we can only get a phase 2 or "broken" exciton if the electron is in an extremely strong confinement regime (that we may get using a very light effective mass) while the regime of confinement for the hole is weak. In such a case, the CI calculations reveal only two phases in which the electron is always volumetric and the hole is either volumetric or facial, depending on ε_{out}.
[33] A 5 nm radius QD embedded in an $\varepsilon_{out}=100$ medium presents a superficial excitonic ground state if $\varepsilon_{QD}<20$ ($m_e^*=0.5$, $m_h^*=10$), $\varepsilon_{QD}<7$ ($m_e^*=0.5$, $m_h^*=1$), and $\varepsilon_{QD}<11$ ($m_e^*=0.2$, $m_h^*=2$).