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Nonmonotonic size dependence of the dark/bright exciton splitting in GaAs nanocrystals

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The dark/bright exciton splitting Δ_X in semiconductor nanocrystals is usually caused by electron-hole exchange interactions. Since the electron-hole wave-function overlap is enhanced by quantum confinement, it is generally assumed that Δ_X increases *monotonically* as the quantum-dot size decreases. Using atomistic pseudopotential calculations, we show that in GaAs nanocrystals Δ_X scales *nonmonotonically* with the nanocrystal size. By analyzing the nanocrystal wave functions in terms of contributions from different $\boldsymbol{k}$ points in the bulk Brillouin zone, we identify the origin of such nonmonotonic behavior in a transition of the lowest conduction-band wave function from Γ like to X like as the nanocrystal radius decreases below 19 Å. The nonmonotonicity arises because the long-range component of the electron-hole exchange interaction all but vanishes when the electron wave function becomes X like. We also show that the direct/indirect transition induced in GaAs nanocrystals by external pressure results in a sudden reduction in Δ_X.

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One of the most interesting aspects of the spectroscopy of semiconductor quantum dots is the existence of a sizable energy splitting between the lowest-energy "dark" exciton state and the lowest-energy "bright" exciton state. For example, in the well-studied case of CdSe colloidal nanocrystals (NCs), dark/bright splittings in the range of 1–20 meV (much larger than the dark/bright splitting of bulk CdSe) have been observed using fluorescence line narrowing.[1,2] Since optical transitions from the dark exciton state to the ground state are dipole forbidden, whereas transitions from the bright exciton state are dipole allowed, the radiative lifetime, photoluminescence intensity, and exciton Stokes shift of semiconductor quantum dots are largely determined by thermal population of the bright exciton states and, thus, by the magnitude of the dark/bright splitting. Furthermore, the fine structure of the band-edge exciton and, in particular, the dark/bright exciton splitting determine the dynamics of optically injected spins in semiconductor nanocrystals.[3]

In most quantum-dot systems the dark/bright exciton splitting is caused by electron-hole (e-h) exchange interactions.[1,2,4–9] This mechanism was first proposed to explain the temperature dependence of the photoluminescence lifetime of highly porous Si (Ref. 4) and later adopted to explain the dark/bright exciton splitting of many other quantum-dot systems.[1,2,9] Since e-h interactions are enhanced by quantum confinement, it is natural to assume that the dark/bright splitting Δ_X increases as the size of the quantum dot decreases. This is indeed the case for direct-gap CdSe colloidal NCs in which the dark/bright splitting was shown to increase monotonically with the NC radius R, from $\Delta_X \sim 2$ meV for $R=43$ Å to $\Delta_X \sim 18$ meV for $R=12$ Å.[1] Similarly, in the case of indirect-gap Si colloidal NCs, Δ_X increases monotonically from ~ 8 meV in large NCs (emission energy ~ 1.45 eV) to ~ 17 meV in small NCs (emission energy ~ 1.95 eV).[5]

Single-band effective-mass calculations[10] have shown that the e-h exchange interaction in quantum dots has a short-range (SR) component which scales as $1/R^3$ with the radius R of the quantum dot. The long-range (LR) component of the e-h hole exchange interaction was predicted to vanish in spherical quantum dots.[10] Atomistic pseudopotential calculations have subsequently shown[8] that in direct-gap quantum dots the LR electron-hole exchange interaction arises primarily from previously neglected monopole-monopole interactions between transition charges located in the bulklike unit cells within the quantum dot. The monopole-monopole LR interaction *does not vanish* in spherical quantum dots and scales as $\sim 1/R$ with the quantum-dot radius. In indirect-gap quantum dots, however, the transition charges, and thus the monopole-monopole interactions, do vanish. Thus, the overall scaling of Δ_X with size depends on a delicate balance between the LR and SR components, which in turn is affected by the orbital nature of the electron and hole wave functions.

In this work we show via atomistic pseudopotential many-body calculations that the dark/bright exchange splitting in GaAs NCs scales *nonmonotonically* with the NC size. We find that, as the NC radius R decreases, Δ_X initially increases until it reaches a maximum of ~ 6 meV for $R=19$ Å. For $17 < R < 19$ Å, Δ_X decreases to ~ 3 meV as the radius becomes smaller. For $R < 17$ Å, Δ_X increases again up to ~ 8 meV for $R=12$ Å. By projecting the NC band-edge states on bulk Bloch states, we demonstrate that this anomalous nonmonotonic behavior results from an electronic transition of the quantum-dot lowest unoccupied molecular orbital (LUMO) from Γ derived to X derived. This transition, which takes place when the NC radius decreases below ~ 19 Å, leads to the disappearance of the LR e-h exchange component and hence to the observed nonmonotonic size dependence of the dark/bright exciton splitting. We also show that applied hydrostatic pressure leads to a dramatic reduction in the dark/bright splitting, which occurs concomitantly with a pressure-induced Γ-X transition of the LUMO wave function. Our results point to the possibility of manipulating the dark/bright exciton splitting, and therefore excitonic lifetimes, photoluminescence quantum yields, and spin dynamics of quantum dots by altering the physical dimensions and/or the amount of external pressure.

The calculations were performed using the semiempirical pseudopotential method described in Ref. 11. This approach has two steps: (i) first, we solve the single-particle Schrödinger equation,

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$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r}) + \hat{V}_{\mathrm{SO}}\right]\psi_i(\boldsymbol{r},\sigma) = \varepsilon_i\psi_i(\boldsymbol{r},\sigma), \tag{1}$$

where m is the bare electron mass, $\hat{V}_{\mathrm{SO}}$ is the spin-orbit operator, and $V(\boldsymbol{r})$ is the local pseudopotential, given by the superposition of screened atomic potentials v_n centered at the atomic positions $\{\boldsymbol{R}_n\}$: $V(\boldsymbol{r})=\Sigma_n v_n(\boldsymbol{r}-\boldsymbol{R}_n)$. The screened atomic potentials v_n and the spin-orbit operator $\hat{V}_{\mathrm{SO}}$ were fitted to experimental transition energies, effective masses, and deformation potentials of *bulk* GaAs.[12] To mimic the effects of organic ligands, which are often used to passivate the surface of colloidally grown NCs, we surround the nanocrystals by a fictitious lattice-matched barrier material having a large band gap and large type-I band offsets with respect to GaAs. Equation (1) is solved by expanding the wave functions $\psi_i(\boldsymbol{r},\sigma)$ in a plane-wave basis set and selectively calculating the band-edge eigenstates via the folded-spectrum method.[13] The atomistic pseudopotential method used here fully includes intervalley coupling and intraband coupling, which are brought about by the lack of translational symmetry. The wave functions of Eq. (1) can be analyzed in reciprocal space by projecting them on the bulk GaAs wave functions, i.e., $\psi_i(\boldsymbol{r},\sigma)=\Sigma_{n,k}c_i(n,\boldsymbol{k})\phi_{n,k}(\boldsymbol{r},\sigma)$, and summing over the coefficients $c_i(n,\boldsymbol{k})$ to obtain the projection of the quantum-dot wave function i on each $\boldsymbol{k}$ point in the bulk Brillouin zone as follows:

$$P_i(\boldsymbol{k}) = \sum_n |c_i(n,\boldsymbol{k})|^2. \tag{2}$$

(ii) In the second step, the excitonic energies and wave functions are calculated in the framework of the configuration-interaction (CI) scheme.[11] In this approach, the excitonic wave functions $\Psi^{(i)}$ are expanded in terms of single-substitution Slater determinants $\Phi_{v,c}$ constructed by promoting an electron from the occupied single-particle state v to the unoccupied single-particle state c,

$$\Psi^{(i)} = \sum_{v=1}^{N_v}\sum_{c=1}^{N_c} C_{v,c}^{(i)}\Phi_{v,c}. \tag{3}$$

The coefficients $C_{v,c}^{(i)}$ of the CI expansion are calculated by diagonalizing the CI Hamiltonian for a single exciton,

$$\begin{aligned} H_{vc,v'c'} &\equiv \langle\Phi_{v,c}|H_{CI}|\Phi_{v',c'}\rangle \\ &= (\varepsilon_c - \varepsilon_v)\delta_{v,v'}\delta_{c,c'} - J_{vc,v'c'} + K_{vc,v'c'}, \end{aligned} \tag{4}$$

where the Coulomb and exchange integrals $J_{vc,v'c'}$ and $K_{vc,v'c'}$ are given by

$$J_{vc,v'c'} = e^2\sum_{\sigma,\sigma'}\int\int \frac{\psi_v^*(\boldsymbol{r},\sigma)\psi_c^*(\boldsymbol{r}',\sigma')\psi_{v'}(\boldsymbol{r},\sigma)\psi_{c'}(\boldsymbol{r}',\sigma')}{\bar{\varepsilon}(\boldsymbol{r},\boldsymbol{r}')|\boldsymbol{r}-\boldsymbol{r}'|} \times\theta(S-|\boldsymbol{r}-\boldsymbol{r}'|)d\boldsymbol{r}d\boldsymbol{r}', \tag{5a}$$

$$K_{vc,v'c'} = e^2\sum_{\sigma,\sigma'}\int\int \frac{\psi_v^*(\boldsymbol{r},\sigma)\psi_c^*(\boldsymbol{r}',\sigma')\psi_{c'}(\boldsymbol{r},\sigma)\psi_{v'}(\boldsymbol{r}',\sigma')}{\bar{\varepsilon}(\boldsymbol{r},\boldsymbol{r}')|\boldsymbol{r}-\boldsymbol{r}'|} \times\theta(S-|\boldsymbol{r}-\boldsymbol{r}'|)d\boldsymbol{r}d\boldsymbol{r}'. \tag{5b}$$

The Coulomb potential in Eqs. (5a) and (5b) is screened using a position-dependent and size-dependent screening function $\bar{\varepsilon}(\boldsymbol{r},\boldsymbol{r}')$.[11] To determine the SR and LR components of the e-h interaction, we multiply the Coulomb potential in Eqs. (5a) and (5b) by the cutoff function $\theta(S-|\boldsymbol{r}-\boldsymbol{r}'|)$, which vanishes when $|\boldsymbol{r}-\boldsymbol{r}'|>S$. The converged values of $J_{vc,v'c'}$ and $K_{vc,v'c'}$ are recovered in the limit $S\to\infty$. The Slater determinants of Eq. (3) are built using $N_v=8$ valence states and $N_c=14$ conduction states (including spin), corresponding to a CI basis set of 112 configurations. The dark/bright splitting Δ_X is obtained from the difference between the lowest-energy optically forbidden exciton state and the lowest-energy optically allowed exciton state, as determined by the magnitude of their dipole matrix element from the electronic ground state. We find that Δ_X is converged to within 1 meV with the CI basis set used in the present calculations.

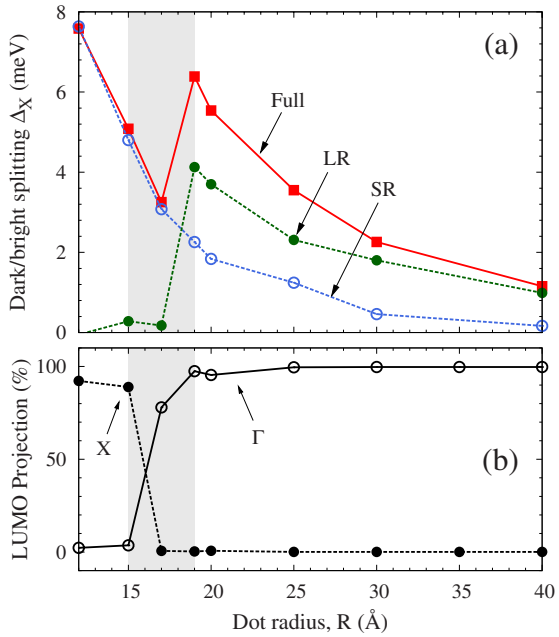

FIG. 1. (Color online) The solid line in (a) shows the total dark/bright splitting Δ_X of the lowest exciton state of GaAs NCs as a function of the nanocrystal radius R. The dashed lines show the breakdown of Δ_X into SR and LR components. Part (b) shows the projection of the LUMO wave function around the Γ and X points of the Brillouin zone of bulk GaAs. The shaded area indicates the Γ-X crossover range.

Figure 1(a) shows the calculated dark/bright splitting Δ_X for a series of spherical GaAs NCs ranging in radius from 12 to 40 Å. The figure clearly shows the nonmonotonic behavior of Δ_X (solid line) for NC sizes in the 15–19 Å range. To understand the origin of this nonmonotonicity, we show in Fig. 1(b) the $\boldsymbol{k}$-space projection of the LUMO wave function for several NC sizes, calculated according to Eq. (2) and integrated over spheres centered at $\boldsymbol{k}=\Gamma$ and $\boldsymbol{k}=X$. We see from Fig. 1(b) that the LUMO changes its character from Γ derived to X derived as the NC radius decreases from 19 to 15 Å. As previously shown,[12] this electronic "phase transition" is caused by quantum-confinement effects pushing the small-effective-mass, Γ-derived conduction-band states higher in energy than the large-effective-mass, X-derived states as the size of the NC decreases. In semiconductor NCs

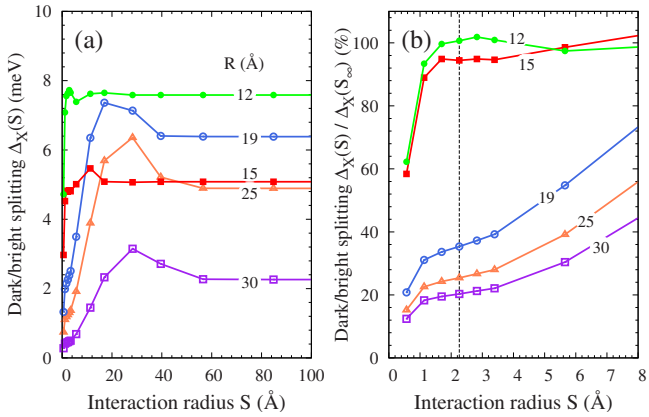

FIG. 2. (Color online) Part (a) shows the dark/bright splitting $\Delta_X(S)$ as a function of the Coulomb cutoff radius S for several NC sizes. Part (b) shows the ratio $\Delta_X(S)/\Delta_X(\infty)$, illustrating the relative importance of the SR and LR contributions to Δ_X. The vertical dashed line in (b) denotes the Wigner-Seitz radius of bulk GaAs (R_{WS}=2.21 Å).

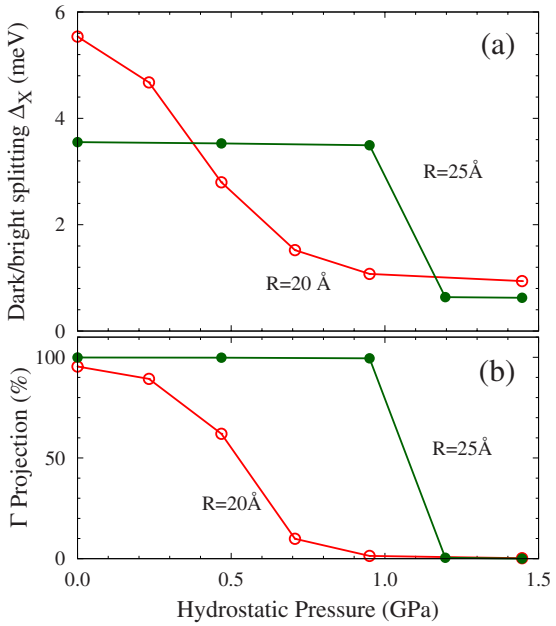

FIG. 3. (Color online) The dependence of the dark/bright splitting Δ_X on hydrostatic pressure is shown in (a) for two GaAs NCs. Part (b) shows the pressure dependence of the Γ projection of the LUMO wave function.

with the T_d point-group symmetry, Γ-derived states belong to the a_1 irreducible representation, while X-derived states can belong to the a_1, e, or t_2 irreducible representations.[14,15] In all the GaAs NCs considered here the LUMO has the a_1 symmetry, except the R=15 Å NC, where the X-derived LUMO has the t_2 symmetry.

To clarify the causality effect between the Γ-X electronic transition of the LUMO and the nonmonotonic behavior of the exchange splitting, we calculated Δ_X as a function of the electron-hole interaction radius S [see Eqs. (5a) and (5b)]. Figure 2(a) shows $\Delta_X(S)$ for several NC sizes, suggesting a qualitatively different behavior of Δ_X in small NCs (R=12 and 15 Å) compared to large NCs (R=19, 25, and 30 Å). This is demonstrated more clearly in Fig. 2(b), which shows the ratio $\Delta_X(S)/\Delta_X(\infty)$, where $\Delta_X(\infty)$ is the converged value of $\Delta_X(S)$.

Figure 2(b) shows that the GaAs NCs can be classified into two groups: large NCs ($R>18$ Å) have a significant LR component to the dark/bright splitting Δ_X, whereas small NCs ($R<18$ Å) have a negligible LR component. This can be gleaned from the fact that in large NCs the quantity $\Delta_X(R_{WS})$, i.e., the value of $\Delta_X(S)$ calculated at the Wigner-Seitz radius R_{WS}, is only ~20–35 % of $\Delta_X(\infty)$, whereas in small NCs $\Delta_X(R_{WS})$ is ~100% of $\Delta_X(\infty)$ [see Fig. 2(b)]. Thus, the Γ-X electronic transition is responsible for the disappearance of the LR component of the e-h exchange interaction in small GaAs NCs and for the nonmonotonic behavior of Δ_X as a function of size. This is illustrated in Fig. 1(a), which shows the decomposition of Δ_X into the SR component $\Delta_X^{SR}=\Delta_X(R_{WS})$ and the LR component $\Delta_X^{LR}=\Delta_X(\infty)-\Delta_X(R_{WS})$. Whereas Δ_X^{LR} is the dominant contribution to the dark/bright splitting for $R>18$ Å, Δ_X^{SR} becomes the dominant contributions for $R<18$ Å.

The *qualitative* reason why the LR exchange component becomes negligible when the LUMO is X derived can be understood using a simplified effective-mass model. As shown in Ref. 8, the LR component of the e-h exchange interaction originates primarily from monopole-monopole interactions between the highest occupied molecular orbital (HOMO)-LUMO transition charges q_n located in the Wigner-Seitz primitive cells Ω_n,

$$q_n = \int_{\Omega_n} \psi^*_{\mathrm{HOMO}}(\boldsymbol{r})\psi_{\mathrm{LUMO}}(\boldsymbol{r})d\boldsymbol{r}, \tag{6}$$

where a sum over the spin degrees of freedom is assumed. In the spirit of the single-band envelope function approximation, one can express the NC HOMO and LUMO wave functions as products of the bulk wave functions from which they derive and the NC envelope functions: $\psi_{\mathrm{HOMO}}(\boldsymbol{r}) \approx \varphi_V(\boldsymbol{r})F_{\mathrm{HOMO}}(\boldsymbol{r})$ and $\psi_{\mathrm{LUMO}}(\boldsymbol{r}) \approx \varphi_C(\boldsymbol{r})F_{\mathrm{LUMO}}(\boldsymbol{r})$.

By Taylor expanding the envelope functions $F_{\mathrm{HOMO}}(\boldsymbol{r})$ and $F_{\mathrm{LUMO}}(\boldsymbol{r})$ in each unit cell Ω_n (centered at the lattice position $\boldsymbol{R}_n$), we obtain $q_n \approx \langle\varphi_V|\boldsymbol{r}|\varphi_C\rangle \cdot [F_{\mathrm{HOMO}}(\boldsymbol{R}_n)\nabla F_{\mathrm{LUMO}}(\boldsymbol{R}_n) + F_{\mathrm{LUMO}}(\boldsymbol{R}_n)\nabla F_{\mathrm{HOMO}}(\boldsymbol{R}_n)]$, which shows that the transition charges q_n vanish when $\langle\varphi_V|\boldsymbol{r}|\varphi_C\rangle=0$, as is the case when the bulk wave functions φ_V and φ_C originate from different points of the Brillouin zone. In small GaAs NCs the HOMO originates from the Γ point of the bulk Brillouin zone, while the LUMO originates from the X point. Thus, the LR component of the e-h exchange interaction becomes small due to the absence of a monopole-monopole component.

Direct-gap quantum dots can undergo a direct-to-indirect transition of the LUMO wave function as external pressure is applied.[16] In fact, because of quantum-confinement effects, such transition tends to occur at lower pressure in quantum dots than it does in the corresponding bulk semiconductor. Our pseudopotential calculations suggest that such pressure-induced direct/indirect transition will also be accompanied by the disappearance of the LR component of the e-h ex-

change interaction. Figure 3 shows in (a) the pressure dependence of Δ_X for two GaAs NCs of radius $R=20$ Å and $R=25$ Å, and in (b) the pressure dependence of the projection of the LUMO wave functions on the Γ point of the Brillouin zone. In these calculations, the effects of external pressure are described by uniformly rescaling the Ga-As bond lengths and by determining the corresponding pressure via the Murnaghan equation for bulk GaAs.[17] We see from Fig. 3(a) that when the external pressure exceeds a critical value, the dark/bright splitting decreases. This transition correlates with a reduction in the Γ component of the LUMO wave function, as shown in Fig. 3(b). The pressure-induced Γ-X transition and the ensuing decrease in the dark/bright splitting are very sharp in the case of the 25 Å GaAs NC, for which we find a critical pressure of ~1 GPa and a concomitant reduction in Δ_X from ~3.6 to ~0.6 meV. In the case of the 20 Å NC, the Γ-X transition and the reduction in the dark/bright splitting occur over a pressure range from ~0 to ~1 GPa, reflecting the increased intervalley and interband couplings in smaller NCs.

In conclusion, we have shown that the size dependence of the dark/bright exciton splitting in GaAs NCs is characterized by a peculiar nonmonotonic behavior. This nonmonotonicity is the result of an electronic transition that changes the character of the LUMO wave function from Γ derived to X derived when the NC becomes smaller than 19 Å in radius. We also find that applied pressure leads to a dramatic reduction in the dark/bright exciton splitting because the LUMO wave function changes from Γ like to X like when pressure is applied. A similar behavior is expected to occur in other semiconductor nanostructures that display such direct/indirect transition as a function of size or pressure, for example, InP quantum dots.

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