Hole levels and exciton states in CdS nanocrystals

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We have studied the hole levels and exciton states in CdS nanocrystals by using the hole effective-mass Hamiltonian for wurtzite structure. It is found that the optically passive P_x state will become the ground hole state for small CdS quantum dots of radius less than 69 Å. It suggests that the ''dark exciton'' would be more easily observed in the CdS quantum dots than that in CdSe quantum dots. The size dependence of the resonant Stokes shift is predicted for CdS quantum dots. Including the Coulomb interaction, exciton energies as functions of the dot radius are calculated and compared with experimental data.

In recent years the effect of quantum confinement on zero-dimensional structure (ZDS), such as semiconductor nanocrystals (NC's) or quantum dots (QD's), has been studied extensively both theoretically and experimentally.[1–19] The semiconductor NC's have prospective applications in optoelectronic devices due to their strongly size-dependent optical properties. Furthermore, they offer the opportunity to investigate theoretically the inherent physics in such three-dimensionally confined systems. New fabrication methods[3] have enabled the synthesis of highly monodisperse ($\sigma_R < 4\%$) CdSe NC's with radii tunable between 10 and 50 Å, which have a luminescence with high quantum yield (10%–90% at 10 K). Recently Empedocles *et al.*[4] used far-field microscopy to image and obtain ultranarrow single-dot luminescence (SDL) spectra from single CdSe NC's at 10 K. The elimination of spectral inhomogeneities reveals new spectral phenomena, including light-driven spectral diffusion, which is consistent with a Stark effect.

The semiconductor NC's of II-VI compounds are usually embedded in a large band-gap matrix, such as glasses, polymers, liquids, rock salts, or zeolites. For CdSe, CdS, and ZnS NC's the common lattice structure is hexagonal (wurtzite), as proved by high-resolution TEM and x-ray diffraction.[3] However, most theoretical models investigating the electronic structure of II-VI NCs are based on the Hamiltonian of zinc-blende structure,[5,7,15] or treat the system with single-band effective-mass approximation.[1,14] Recently Efros and co-workers[9] have considered the crystal shape asymmetry and the intrinsic crystal field (due to hexagonal structure) within the framework of a quasicubic model, and obtained optical passive (''dark exciton'') and optical active (''bright exciton'') states for CdSe QD's. The theoretical results are in agreement with the size dependence of Stokes shifts obtained in fluorescence line narrowing and photoluminescence experiments for CdSe NC's. By using the many-body expansion method, Reboredo *et al.*[16,17] reported the ''dark exciton'' due to electron-hole Coulomb or exchange interaction in Si QD's. Their calculation of splitting between dark and bright excitons agrees very well with the experimental results. In Ref. 18 we have derived the hole effective-mass Hamiltonian for the semiconductors with wurtzite structure. The energies and corresponding wave functions are calculated with the obtained effective-mass Hamiltonian for the CdSe QD's. Our numerical results are in agreement with the experiment and the ''dark exciton'' theory. Following this work, we[19] have investigated the exciton states in CdSe NCs and the numerical results are found to account for most of important features of the experimental photoluminescence excitation (PLE) spectra by Norris *et al.*[7]

CdS is a well-characterized semiconductor and widely used for the preparation of NC's growth.[1,2,11,13] The band gap in CdS NC's can be tuned between 4.5 and 2.5 eV as the size is varied from the molecular regime to the macroscopic crystal. It is well known that CdS and CdSe have the same lattice structures (wurtzite structure), and thus have very similar band structures of bulk materials. Similar to CdSe NC's the dark exciton would be observed expectantly in the small CdS NC's in experiment. However, up to now there are no experiments reporting the observation of the dark exciton in CdS NCs. Consequently the theoretical study of the electronic structure of CdS NC's in detail could prompt further interesting experiments in NC's with wurtzite structure. In addition, it offers the opportunity to compare the different properties between the CdSe and CdS NC's.

Using the $\mathbf{k}\cdot\mathbf{p}$ perturbation method, we have derived the correct effective-mass Hamiltonian for wurtzite semiconductors including the p linear term.[18,19] The CdS band structure is calculated by the empirical pseudopotential method, and the effective-mass parameters are determined by fitting the valence-band structure near the top. The parameters[20] of CdS are $\Delta_c = 0.024$ eV for the crystal-field splitting energy, and $\Delta_{SO} = 0.07$ eV for the spin-orbit splitting energy. For simplicity, in this paper we assume that the quantum sphere is surrounded by an infinitely high potential barrier represented by the matrix material, but the finite potential barrier can be taken into account conveniently in our method. The calcula-

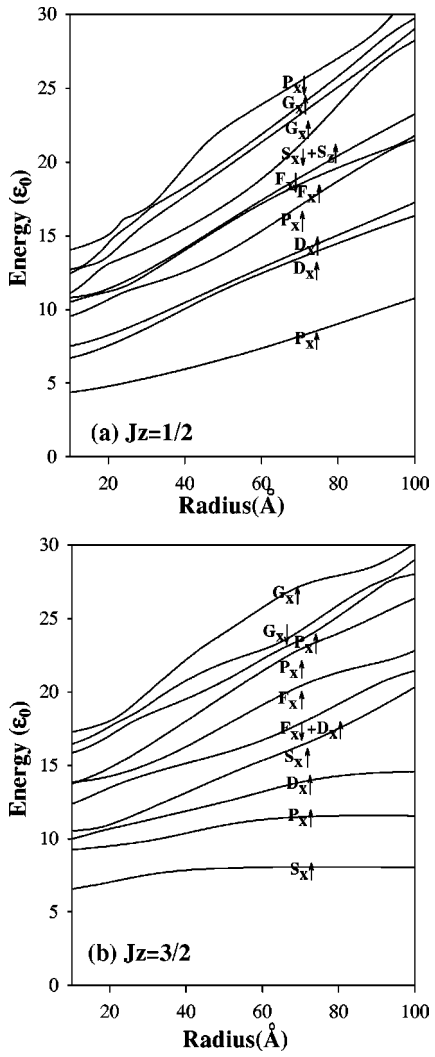

FIG. 1. Energies of hole states as functions of dot radius R (Å) for the finite SOC case. In (a) $J_z=\frac{1}{2}$ and in (b) $J_z=\frac{3}{2}$.

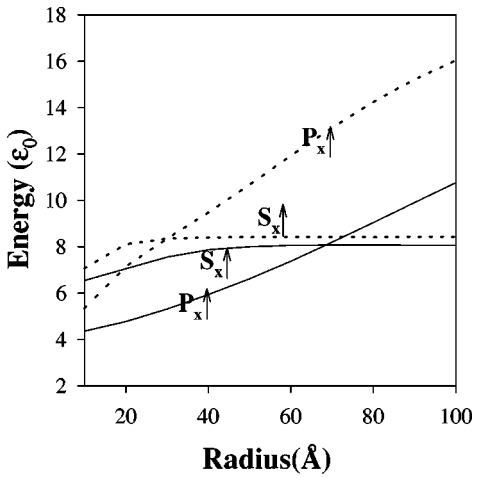

FIG. 2. The size dependence of ground hole energies of S_x and P_x states. Solid lines indicate the case of CdS, while the dotted lines show the case of CdSe.

tional scheme is described in detail in Refs. 18 and 19. We do not repeat here for the sake of conciseness.

In Fig. 1 we plot the hole energies as functions of the dot radius R (Å) for the z components of angular momentum $J_z=\frac{1}{2},\frac{3}{2}$ as shown in 1(a) and 1(b), respectively. The unit of energy in Fig. 1 is $\epsilon_0=(\gamma/2m_0)(\hbar/R)^2$, where γ is the effective-mass parameter taken from Ref. 18. In the case of cubic structure QD's the energy dependence on the dot radius R is constant in the unit of ϵ_0. However, in the case of hexagonal structure QD's the energy dependence on the dot radius R does not vary as $1/R^2$ any more as in Fig. 1. There are two major contributions to the reasons. First, the crystal-field splitting makes the $\Gamma_1(Z)$ states intersect or interact with the $\Gamma_6(X,Y)$ states. Second, the linear terms in the hole Hamiltonian will result in the mixing of even angular momentum l and odd l states. The two reasons will be easily understood if we plot the same figures of hole states with $J_z=0$, $J_z=1$, and $J_z=2$ as that shown in Ref. 18. Both Figs. 1(a) and 1(b) exhibit the hole energies in the finite spin-orbit coupling (SOC) case. In the numerical computation we find the strong SOC limit is a good approximation for the lowest hole states. But the high excited hole state is sensitive to the spin-orbit splitting energy due to its severe coupling with the spin-orbit split-off band of wurtzite semiconductors.

Comparing Fig. 1(a) with 1(b) one can find an important fact that the hole ground state is not S_x of $J_z=3/2$ for the dot radius smaller than 69 Å, but P_x of $J_z=\frac{1}{2}$. The hole S_x state is optically active, while the hole P_x is optically passive. Our theoretical model predicts the dark exciton existing in small CdS NC's. We suggest further experiments being done in the CdS NC's to verify our results.

For better visualization we plot the size dependence of ground hole energies of S_x and P_x states in Fig. 2. The hole levels of both CdS and CdSe NCs are shown in this figure. Solid lines indicate the case of CdS, while the dotted lines show the case of CdSe. From Fig. 2 it is easy to find that the P_x state would become the ground-hole state in the range of R smaller than 69 Å for CdS NC's, while for CdSe NC's the dot radius must be smaller than 30 Å. It suggests that the dark exciton would be more easily observed experimentally in CdS NC's than that in CdSe NC's.

It is the first time in experiment that Nirmal *et al.*[8] find the existence of dark exciton in small CdSe QD's. Then Efros *et al.*[9] present an eight-band model to account for it. Both Efros *et al.* and we[9,18] find that only if the inherent asymmetry of hexagonal lattice structure is taken into account for calculating the electronic structure, the dark exciton effect can be well interpreted. Furthermore, the fluorescence Stokes shift, the radiative lifetime, and the magnetic field dependence are all explained by the lowest state being a dark exciton.

The experimental plausibility of the theoretical results is an interesting problem for which Nirmal and Efros[8,9] have given a detailed discussion. However, only in the magnetic fields one can distinguish the P_x state with $J_z=\frac{1}{2}$ from the S_x state with $J_z=3/2$. In consequence the experimental work must use the external magnetic fields to identify the dark exciton state in small CdS NC's.

The other interesting results obtained from our present calculation are the resonant Stokes shift in CdS NC's. In QD's made of wurtzite structure materials the intrinsic crystal field splits the lowest exciton state into a optical passive

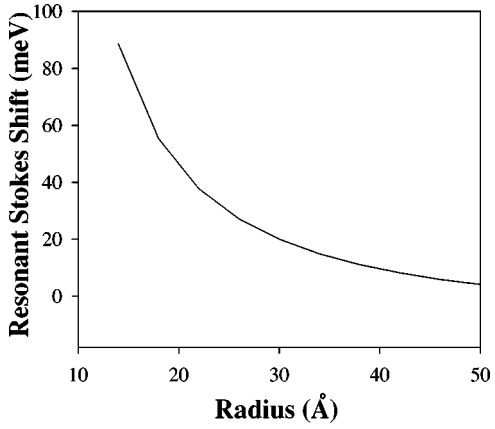

FIG. 3. The size dependence of the resonant Stokes shift. This Stokes shift is the difference in energy between $S_x(J_z=\frac{3}{2})$ and $P_x(J_z=\frac{1}{2})$ states.

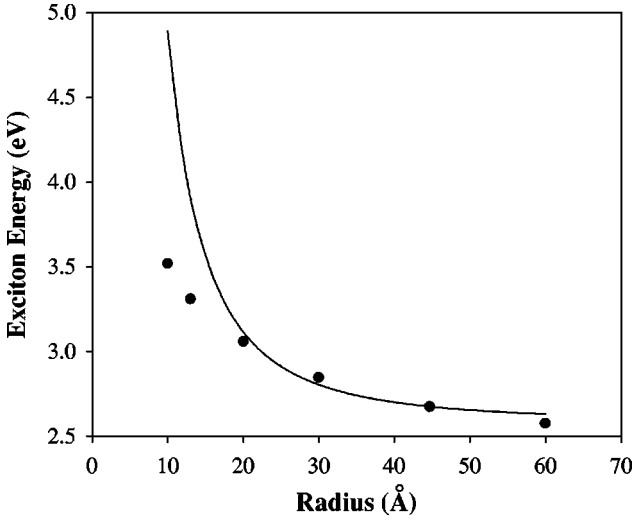

FIG. 4. Energy of the ground-exciton state as a function of the dot radius. The circle dots are experimental results of Wang *et al.* (Ref. 11) on CdS nanocrystals.

(dark) state and optical active (bright) state. This gives rise to an absorption versus emission Stokes shift in experiment. Figure 3 shows the size-dependence of the resonant Stokes shift of CdS NC's. This Stokes shift is the difference in energy between $S_x(J_z=\frac{3}{2})$ and $P_x(J_z=\frac{1}{2})$ states. Comparing with our former calculation[19] one can find that the resonant Stokes shift of CdS NC's is slightly larger than that of CdSe NC's. This prediction could be tested experimentally in the future.

Now we discuss the exciton states of the CdS NC's. In the early time, Ekimov *et al.*[1] reported the absorption spectra of CdS NC's ranging in size from 30 to 800 Å. The optical-absorption spectra of NC's have revealed that exciton energies are blueshifted compared to the value in bulk materials, and it can be understood in terms of quantum confinement of the exciton. Recently, Wang *et al.*[11] have experimentally investigated the dependence of the lowest exciton energy of CdS QDs on the cluster size. The results are in agreement with the tight-binding calculation by Lippens *et al.*,[12] and cannot be explained by models based on the single-band effective-mass approximation.

We calculate the exciton states of QD's including the Coulomb interaction between the electron and hole. The calculation formula of Coulomb interaction is presented in Ref. 19. Figure 4 plots the ground-exciton energy as a function of the dot radius. The circle-dots are experimental results given by Wang *et al.*[11] on CdS NC's. It is found that our results are in good agreement with the experimental data when the dot radius is larger than 20 Å. For the radius less than 20 Å, there are some discrepancies between our results and the experimental data. We can understand the discrepancies from the following reasons. First, major uncertainty comes from the size determination by experiment. We suggest one can measure the exciton transition energies as functions of the exciton ground-state energy, which is studied by Norris *et al.*[7] for CdSe NC's. The advantage of this method is that the energy is measured experimentally more precisely than the dot size, and one can find our theory would be more consistent with the experimental results in the strong confinement regime. Second, the model is described by the spherical dots in this paper. However, for small dots the shape is usually nonspherical and should be taken into account as an ellipsoid, which would lift the hole state degeneracy. We plan to treat the asymmetry of a nonspherical shape as a perturbation in NC's and results will be reported elsewhere. Third, an infinite potential model is used in our calculation; the energies of the ground exciton are slightly higher than those observed experimentally, especially for small QDs.[10]

In this paper we assume the dielectric constant in the dot is the same as that in the barrier material. This approximation will ignore the surface polarization effect in semiconductor NC's. Especially in small quantum dots with large surface influence, the charge and the polarization state at the interface become essential and determine the inherent electronic structure. In the early time, Brus[2] has described the dielectric contribution to the confinement of the quantum dots. Following Brus's study, Takagahara[14] analyzed the effect of dielectric confinement on the exciton states. However, Takagahara's method is within the framework of single-band effective-mass theory. Consequently, the surface polarization effect on both the electrons of the conduction band and hole-states mixing is an interesting topic that we will study in the future.

In conclusion, we have studied the hole levels and exciton states in CdS nanocrystals by using the hole effective-mass Hamiltonian for wurtzite structure. The asymmetry of crystal-field splitting and finite spin-orbit splitting energy are taken into account. It is found that the optically passive P_x state will become the ground hole state for small CdS quantum dots of radius less than 69 Å. It suggests that the dark exciton would be more easily observed in the CdS quantum dots than that in CdSe quantum dots. The size dependence of the resonant Stokes shift is predicted for CdS NC's. Including the Coulomb interaction, exciton energies for the dot radius are calculated and found to be consistent with experimental results.

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