RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 24 15 DECEMBER 1995-II

Theory for quantum-dot quantum wells: Pair correlation and internal quantum confinement in nanoheterostructures

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(Received 25 August 1995; revised manuscript received 10 October 1995)

Spherical quantum-dot–quantum-well nanocrystallites, with internal radial quantum-well band profiles, can now be fabricated. Pair states in these nanoheterostructures are determined by electron-hole attraction, global confinement in the dot, and local confinement within the well. Configuration-interaction calculations using effective-mass models with screened pair interaction give accurate exciton energies for CdS/HgS quantum-dot quantum wells. Binding energy and pair correlation are suppressed but pair-oscillator strengths are enhanced by adding a HgS quantum well to a CdS quantum dot.

Quantum dots (QD's) are semiconductor nanostructures quantum confined in three dimensions to provide discrete electronic states that can be tailored to enhance optical properties. Quantum dots so far have been homogeneous with no internal structure; II-VI nanocrystallites in glass or solution, and narrow-gap III-V semiconductors confined by lithographically defined wide-gap regions. Recently, a new class of quantum dots, called quantum-dot quantum wells (QDQW's), have been fabricated and studied.[1–4] QDQW's have an internal *nanoheterostructure*, with a quantum-well region contained *inside* the quantum dot. Spherical nanocrystallite QDQW's have been fabricated by chemically controlling the composition of each layer in the QDQW as the dot is grown layer by layer. For example, CdS/HgS QDQW's (see Fig. 1; HgS, with the lower band gap, provides a quantum well for both electrons and holes) are grown in the following steps:[1] first, a CdS QD is grown in solution; next, the outer monolayer of Cd is chemically replaced with Hg to form the well; finally, S is added to the solution and an additional monolayer of CdS is deposited on the dot as a cladding layer. The last two steps are repeated to increase the well width. Controlling the size and composition of the well provides additional flexibility to tailor the electronic structure of the QD and the new possibility of altering where charge is located inside the QD, to keep the charge away from surface traps, or to enhance electron-hole overlap.

A complete theory for the electronic states and optical properties of QDQW nanoheterostructures must account for global quantum confinement within the quantum dot, local quantum confinement within the internal well, and valence-band mixing and electron-hole correlation in this complicated spatial potential. Initial calculations for QDQW's, based on effective-mass models for the electronic structure, have demonstrated the effect of the internal well on single-particle electron and hole energies and pair overlaps in a QDQW (Refs. 1, 2, and 5) and have determined the ground-state energy, including the Hartree energy, of an uncorrelated electron-hole pair.[1,2] In this paper I describe calculations of pair states in QDQW's that includes pair correlations. I examine how the internal well affects pair correlation in a QDQW. I show that pair correlation must be included to give a qualitatively accurate model for QDQW's and that effective-mass models with screened pair interaction give quantitatively accurate exciton ground-state energies in QDQW's provided the effects of complex geometry on quantum confinement and pair correlation are accounted for. I explain how the competing effects of global and internal confinement influence pair-correlation and pair-oscillator strengths. I illustrate these results by considering CdS/HgS QDQW's that have been characterized experimentally.[1,2]

Large-scale configuration-interaction (CI) calculations,[6,7] previously used to study multielectrons in QD's and excitons in QD's, have been extended to spherical QDQW's (as shown in Fig. 1) to study the effect of the internal well on the correlated electron-hole pair states. Basis states used in the CI calculations for QDQW's were uncorrelated pair states constructed from states for independent electrons and holes in the QDQW. These single-particle states were found by solving the single-particle radial Schrödinger equation for each angular momentum using a transfer matrix approach. Following Schooss, Mews, Eychmuller, and Weller,[2] I model a QDQW in solution as a four-layer structure that includes the core region, the well, a cladding region, and water surrounding the QDQW. The radial potential is given by the band-edge profile of the QDQW. Tunneling out of the dot into the water is included. An isotropic, independent-band, effective-mass model is used to simply describe single-particle states. Effects of valence-band mixing will be considered elsewhere. I use the material parameters given in Ref. 2 for CdS and HgS. The effective masses are $m_{e,\mathrm{CdS}}=0.2$, $m_{h,\mathrm{CdS}}=0.7$, $m_{e,\mathrm{HgS}}=0.036$, $m_{h,\mathrm{HgS}}=0.044$, and $m_{e,\mathrm{H_2O}}=m_{h,\mathrm{H_2O}}=1$. Band gaps are $E_{g,\mathrm{HgS}}=0.5$ eV and $E_{g,\mathrm{CdS}}=2.5$ eV with the CdS conduction-band edge 1.35 eV above the HgS conduction-band edge. The barriers for tunneling into water are 3 eV above the CdS band edges. Fabricated CdS/HgS QDQW's have quantum wells that are 1–3 ML thick. Results presented here show that the effective-

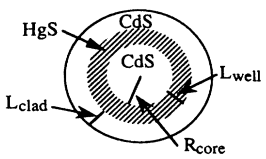

FIG. 1. Cross section of a CdS/HgS quantum-dot quantum well. The layer dimensions are indicated.

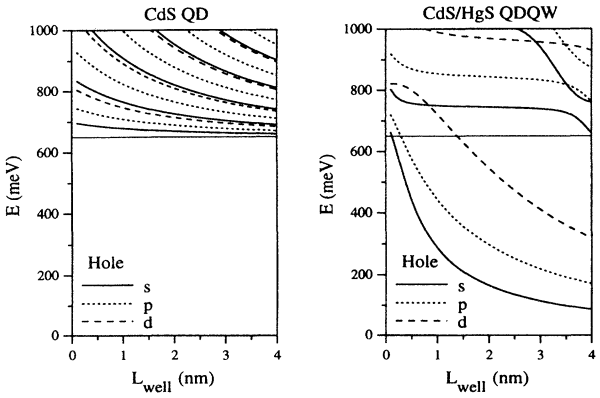

FIG. 2. Hole energies in a CdS quantum dot and a CdS/HgS quantum-dot quantum well. $R_{\text{CdS core}}=2.35$ nm and $L_{\text{CdS clad}}=0.8$ nm. The well is CdS (HgS) in the first (second) case. States with angular momentum $l_h=0,1,2$ are shown. The HgS (CdS) hole band edge is 0 (0.65) eV.

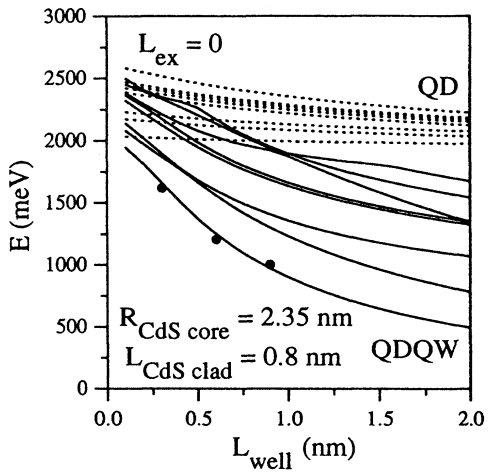

FIG. 3. Energies for the lowest eight optically active exciton states ($L_{\text{ex}}=0$) in a CdS/HgS quantum-dot quantum well (solid curves) and in a CdS quantum dot with the same dimensions (dotted curves). Energies are relative to the HgS band gap. The points are experimental absorbance data for QDQW with 1-, 2-, and 3-ML HgS internal wells.

mass model gives reasonable agreement with experiment even for such small structures.

In principle, the electron-hole interaction in the QDQW should include the screened electron-hole Coulomb attraction plus the interaction with polarization charges at the dielectric interfaces[8,9] in the QDQW. The full potential that includes the polarization of four different dielectric regions is very complicated. Therefore, I use instead a simple Coulomb potential screened with an average dielectric constant. The high-frequency dielectric constants[2] for the different regions are $\varepsilon_{\text{CdS}}=5.5$, $\varepsilon_{\text{HgS}}=11.36$, and $\varepsilon_{\text{H}_2\text{O}}=1.78$. For an average, effective high-frequency dielectric constant, I use $\varepsilon_{\text{ave}}=6$. This simple model provides results in good agreement with experiment. Surface trapping by surface-polarization instabilities[9] is not included when this simple interaction is used. However, surface trapping should not be important in a QDQW because the internal well inhibits charge localization at the dot surface.

A key characteristic of CdS/HgS QDQW's is that the HgS electron and hole masses are light and nearly the same while both CdS masses are much heavier. Since electron and hole masses are similar, electron and hole states are similar. Both states become trapped in the internal well at similar well thicknesses. Hole energies in CdS/HgS QDQW's and CdS QD's with the same dimensions are shown in Fig. 2. In each case, the inner CdS core radius is 2.35 nm and the outer CdS cladding layer is 0.8 nm wide.[1,2] The well region is HgS (CdS) for the QDQW (QD). QD energies decrease approximately quadratically with no level crossing as the total dot size increases. In contrast, hole energies in QDQW's display other distinct features. The energies decrease rapidly when a state is trapped in the well. The decrease depends quadratically on well thickness L_{well} rather than total dot size. Higher-energy states, which must be orthogonal to states trapped in the well, cannot extend effectively beyond the core. These states have energies that depend on L_{core} but only weakly on L_{well}. Crossings (anticrossings) occur between states with different (the same) angular momentum. Also, level splittings are much greater in CdS/HgS QDQW's than in CdS QD's. In QD's the level energies and splittings can be adjusted. In a QDQW, the trapped states can be adjusted without altering much the low-energy delocalized states. For QDQW's this gives added flexibility to tailor the ordering, degeneracy, and coupling between trapped and delocalized states that should provide more capability to modify level occupancies, relaxation dynamics, pair correlation, and oscillator strengths that determine optical properties.

Energies for the eight lowest, optically active (angular momentum $L_{\text{ex}}=0$), correlated-pair (exciton) states of CdS/HgS QDQW's and uniform CdS QD's with the same dimensions are compared in Fig. 3. Calculated and experimental energies for the QDQW exciton ground state agree well, even though the theory uses a simple effective-mass model and a simple pair interaction. When a HgS internal well is added to a QDQW, exciton energies redshift significantly, exhibiting the same flexibility to adjust by an eV as shown in Fig. 2 for single-particle states. The dominant contribution to the QD and QDQW exciton ground state is made by the noninteracting pair state with the electron and hole in their lowest s states. The dominant contribution to the first (second) excited QD exciton state comes from the pair state with the hole in its first excited s state (both the electron and hole in their lowest p states). There is significant mixing of all three noninteracting-pair states in each of these exciton states. There is less mixing in a QDQW, because the different single-particle states are more strongly localized to different regions in a QDQW. These three noninteracting pair states are well split in energy in QD's, so no low-energy QD exciton-level crossings occur. In QDQW's these two noninteracting-pair excited states cross when the well is thick enough to strongly trap the lowest electron and hole p states. The corresponding QDQW exciton states have a narrow anticrossing because the pair states are weakly Coulomb

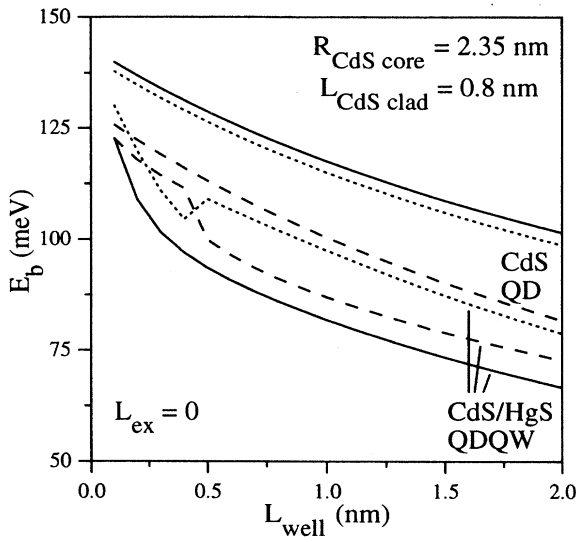

FIG. 4. Binding energies for the $L_{ex}=0$ exciton ground state (solid curves) and first (dotted curves) and second (dashed curves) excited state in a CdS/HgS quantum-dot quantum well and a CdS quantum dot. The sharpness of the kinks due to the anticrossing between excited states in the QDQW is an artifact caused by doing the calculations at discrete values for L_{well}.

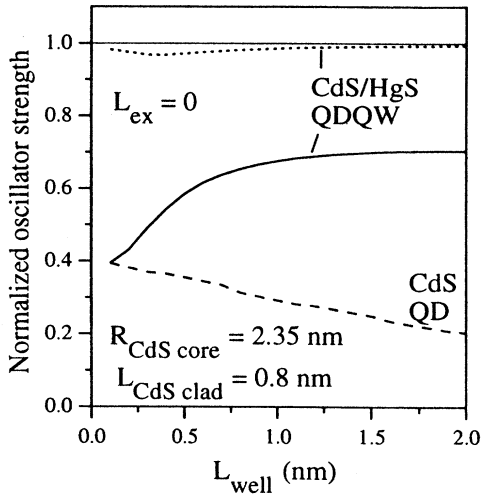

FIG. 5. Normalized oscillator strengths for the exciton ground state in a CdS/HgS quantum-dot quantum well (solid curve) and a CdS quantum dot (dashed curve), and for the uncorrelated pair state in the quantum-dot quantum well (dotted curve).

coupled. Similar QDQW exciton-level anticrossings occur at higher energies when other states are localized to the well.

Binding energies (energy difference between corresponding interacting- and noninteracting-pair states) for QDQW and QD ground and first- and second-excited optically active exciton states are shown in Fig. 4. As total dot size increases and global confinement decreases, the ground-state binding energy decreases. Binding energies in the QDQW are less than in the QD: adding the internal well to the dot draws the charge away from the dot center, reducing the pair attraction. The QD exciton excited-state binding energies are less than the QD exciton ground-state binding energy because the ground state is more localized to the core. Conversely, the QDQW exciton *ground*-state binding energy is less than the QDQW exciton excited-state binding energies because the exciton ground state, which is more strongly trapped in the well, has larger pair separation. Strong confinement of the QDQW exciton ground state to the internal well also inhibits correlation, further lowering the binding energy. There is less correlation energy in the QDQW exciton ground state than in the QD exciton ground state. Moreover, the correlation energy *decreases* in QDQW's as the well size increases but increases in QD's as the dot size increases. Correlation is enhanced by increasing dot size but suppressed by increasing well thickness and trapping.

The electron-hole pair overlap that determines the normalized pair ground-state oscillator strength is shown in Fig. 5. For a noninteracting pair in a CdS/HgS QDQW, pair overlap is nearly unity for all well sizes, indicating that single-particle electron and hole ground states are nearly identical. The overlap falls slightly below unity for L_{well} near 0.4 nm, because the hole is more easily trapped in the well. In the correlated-pair ground state of a small CdS QD, the hole, which is heavier than the electron, is localized in the center of the electron cloud by the electron-hole interaction, while the electron distribution is determined by quantum confinement. This strong hole localization reduces electron-hole overlap, so the pair ground-state oscillator strength for a small QD is less for a correlated pair than for an uncorrelated, noninteracting pair. Correlated-pair overlap decreases in a QD as dot size increases, so long as the electron is quantum confined. The pair ground-state oscillator strength is enhanced when the internal well is added, because global confinement of the electron and interaction-induced hole localization are suppressed, allowing the electron and hole to localize to the same region. The correlated-pair ground-state overlap for QDQW's increases toward the overlap for a noninteracting pair as well thickness increases.

In summary, effective-mass models with screened pair interaction give reasonable ground-state energies for excitons in CdS/HgS quantum-dot–quantum-well nanoheterostructures provided the effects of complex geometry on quantum confinement and pair correlation are accounted for. Pair correlation must be included to correctly model the effects of adding an internal well to a quantum dot. In small CdS quantum dots, the pair is strongly correlated with the hole localized to the center of the electron distribution. When a HgS well is added to a CdS quantum dot, the pair behaves more like an independent electron and hole. Binding energy and pair correlation in a CdS/HgS QDQW are *reduced* because pair separation is increased and there is less flexibility to correlate the pair when the pair is quantum confined to the same narrow spherical-shell quantum-well region away from the dot center. The exciton oscillator strength is *enhanced* when the internal well is introduced, because the electron and hole are strongly confined to the same region and neither can be localized to the center of the other charge distribution.

Quantum-dot–quantum-well nanoheterostructures are a class of quantum-dot systems which can be tailored to con-

trol energy levels, spacings and occupancies, relaxation dynamics, pair correlations, and oscillator strengths. Each quantum-dot–quantum-well system must be considered separately, because the competing effects of global confinement, internal confinement, and pair correlation will depend sensitively on particle masses, interaction strengths, and band offsets. Other systems will be considered in future publications.

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