Electronic structure of nanocrystal quantum-dot quantum wells

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(Received 21 December 2005; published 26 June 2006)

The electronic states of CdS/CdSe/CdS colloidal nanocrystal quantum-dot quantum wells are studied by large-scale pseudopotential local density approximation (LDA) calculations. Using this approach, we determine the effects of CdS core size, CdSe well thickness, and CdS shell thickness on the band-edge wave functions, band-gap, and electron-hole Coulomb interactions. We find the conduction-band wave function to be less confined to the CdSe well layer than predicted by $k\cdot p$ effective-mass theory, which accounts for the previous underestimation of the electron $g$ factor.

DOI: 10.1103/PhysRevB.73.245332
PACS number(s): 73.22._f, 78.67.Hc

I. INTRODUCTION

Recent synthetic advances have led to the creation of colloidal semiconductor nanocrystal quantum dots (QD) which may be individually heterostructured by the addition of one or more layers of different semiconductor materials. For example, use of large band-gap (e.g., CdS) shells on a smaller band-gap (e.g., CdSe) core improves the photoluminescence (PL) efficiency by passivating surface dangling bonds and isolating the carriers from interaction with the surrounding medium, first demonstrated with CdSe/CdS core/shell isolating the carriers from interaction with the surrounding medium, first demonstrated with CdSe/CdS core/shell,1–3 The use of multiple layers allows a gradual transition between the materials, minimizing the strain effects resulting from large differences in lattice constant between the materials, for example CdSe/CdS core/shell nanocrystals.1–3 The use of multiple layers allows a gradual transition between the materials, minimizing the strain effects resulting from large differences in lattice constant between the materials, for example CdSe/CdS core/shell nanocrystals.1–3 The use of multiple layers allows a gradual transition between the materials, minimizing the strain effects resulting from large differences in lattice constant between the materials, for example CdSe/CdS core/shell nanocrystals.1–3

Inverting the band-gap ordering of the semiconductors, by placing a shell of small band-gap material on a core of larger band-gap material, protected by an additional shell of large band-gap material, creates a quantum-well-like structure within the nanocrystal, which has been termed a quantum-dot quantum well (QDQW). Due to synthetic difficulties, early studies using CdS/HgS systems did not show distinctive well-thickness-dependent optical features and had poor PL quantum yield.7 More recently, colloidal nanocrystal QDQWs based on the highly refined CdSe, ZnSe, and ZnS chemistries, in particular CdS/CdSe/CdS core/well/shell,8 CdSe/ZnS/CdSe core/well/shell,9 ZnS/CdS/ZnS core/well/shell,10,11 and ZnSe/CdSe core/well12,13 structures, have been synthesized. In this paper, we examine the CdS/CdSe/CdS QDQWs, which have been the subject of a series of recent photoluminescence14,15 and time-resolved Faraday rotation16 experiments, and have been demonstrated to form an efficient gain medium for nanocrystal-based lasers.17 The theoretical examinations of this system have relied on the $k\cdot p$ effective-mass approximation (EMA),16,18,19 which may break down when considering the 1–4-monolayer-thick well/shell structures studied in the above experiments. Previous atomistic studies of CdS/HgS/CdS (Refs. 20 and 21) and ZnS/CdS/ZnS (Ref. 22) QDQWs relied on semiempirical tight binding. However, since these models are fit to reproduce bulk bands for a given material, they are susceptible to errors in band alignment (discussed in the context of CdSe/CdS core/shell nanocrystals by Ref. 3), and do not account for matrix element changes at the heterostructure interface. Therefore, it is desirable to use first-principles electronic-structure calculations to establish a reliable understanding of these nanostructures. In the present paper, we examine the changes in the wave function and optical properties caused by varying the core, well, and shell dimensions over an experimentally realistic range of sizes. By considering these factors separately and in combination, it is our intent to provide a better understanding for systematically designing QDQW structures and for interpreting experiments.

II. COMPUTATIONAL METHOD

The successive ion layer adsorption and reaction (SILAR)23 technique, used in the synthesis of the CdS/CdSe/CdS QDQWs,8 allows controlled monolayer-by-monolayer growth by alternately introducing the anionic and cationic precursors during the synthesis. The CdS/CdSe/CdS core/well/shell nanocrystals are constructed as a wurtzite structure, expanded from a central cation, so that the definitions of a monolayer (ML) in terms of an outward going unit cell and as an outward radial distance are the same. The structures generated in this manner are then relaxed using the valence force method.24

To solve the electronic structure, we utilize the charge patching method25 to reconstruct the nanocrystal electron density from a set of bulk and surface motifs, each determined using the ab initio pseudopotential local-density approximation (LDA) density-functional theory in a 35 Rydberg plane-wave basis. The surface passivation is modeled by hydrogen like pseudatomos of fractional charge to preserve local neutrality,26 which has recently been demonstrated to be the optimal model for removing the surface states from the band-gap and band-edge regions.27 After the electron density of the nanocrystal has been assembled, the band-edge energies and wave functions are determined by the folded-spectrum method,28 using band-corrected pseudopotentials.29 This approach has been successfully applied to quantum-dot and rod nanocrystals26,29 and core/shell nanocrystals.3 Comparisons to self-consistent LDA calculations on small systems have demonstrated that the errors of this method are on the order of 10–30 meV, comparable to the errors introduced by different pseudopotential choices in...
traditional \textit{ab initio} self-consistent plane-wave calculations.\textsuperscript{26} Using this method, we are able to treat the systems of up to 18,000 atoms studied in this paper, corresponding to a maximum total diameter of 8.6 nm, comprised of CdS cores 2.2, 2.9, and 3.6 nm in diameter surrounded by varying CdSe and CdS widths (see Fig. 1).

### III. RESULTS AND DISCUSSION

#### A. Wave-function distribution

The unique properties of QDQWs result from the additional control of quantum confinement by manipulation of core, well, and shell sizes. We first examine the role of increasing the CdS shell thickness, for a fixed 2.2-nm-diam CdS core and 1 ML CdSe well (1 ML = 0.4 nm for both materials), shown in Figs. 2(a) and 2(b). The valence-band maximum (VBM) is localized in the CdSe well region, and expands only slightly outward upon the addition of the second CdS shell monolayer, and is unchanged by further additions. As the total radius of the QDQW increases, the relatively delocalized conduction-band minimum (CBM) expands in extent. The presence of the CdSe layer distorts the CBM, leading to a reduction in the CBM density in the CdSe layer, at the same distance from the center as the VBM peak. In Figs. 2(c) and 2(d), the radially averaged $|r\psi|^2$ is examined for CdS cores of varying size, with a 1 ML CdSe well and 2 ML CdS shell. As the core size is increased, the localized VBM is moved further away from the center, and the CBM is delocalized over the larger radius of the QDQW.

The effect of increasing well width on the electronic structure of the QDQW is examined in Fig. 3. We focus on the 2.2-nm-diam core crystals, as this will let us examine the largest ranges of well and shell widths. The 2.9-nm-diam core QDQWs (not shown) differ in the position of the localized VBM, and in the spatial extent of the CBM for a given well and shell width (since the core is larger), but are otherwise qualitatively identical. Comparing Figs. 3(b), 3(d), and 3(f), we see that the VBM for the 1 and 2 ML CdSe well are unchanged by the number of CdS shell monolayers at the surface. Even for the 4 ML well case in Fig. 3(b), the discrete structure of the CdSe lattice can be seen in the VBM and CBM.

To compare the present results to the $\mathbf{k} \cdot \mathbf{p}$ effective-mass approximation (EMA) of the QDQW systems, we first examine the wave functions for the case of a 3.4-nm-diam CdS core, 2 ML CdSe well, and 1.6 nm CdS shell in Fig. 4. The results shown are based on the standard experimental band-structure and band alignment data,\textsuperscript{30} although we also examined use of LDA-derived band offsets and effective masses and found only minor changes. This particular set of dimensions was chosen to match the previous experimental and theoretical (EMA) study of Berezovsky \textit{et al}.\textsuperscript{16} The wave functions plotted in Ref. 16 [Fig. 3(c)] and Ref. 18 [Fig. 1(c)] appear to be broader than our results in Fig. 4, because a wider (3 ML) CdSe quantum-well layer is plotted in those previous figures, as compared to a 2 ML CdSe in the present case, and also $r\psi$ (rather than $|r\psi|^2$) was plotted in the former reference. The EMA CBM is strongly localized to the CdSe region, compared to the LDA result, which is delocalized across the QDQW. For comparison, a pure CdS nanocrystal CBM is plotted as the dotted line in Fig. 4. The similarity of the QDQW and pure-Cds nanocrystal CBM is consistent with a previous LDA study of CdSe/CdS core/shell nanocrystals, in which the CBM density for CdSe and CdS/CdSe nanocrystals was found to be qualitatively the same in the interior of the nanocrystal, and changed mostly at the nanocrystal surface.\textsuperscript{3} Since the EMA appears to overestimate the localization within the CdSe well, we next calculate the percentage of the CBM density $|\psi|^2$ in the CdSe region, for nanocrystals with 1–3 CdSe ML, using the core and shell dimensions above. In the EMA, this is determined by integration over the well-defined radial direction, as in Eq. (1) of Ref. 16. For the present LDA calculations, we perform the
integration over the volume of the plane-wave grid, attributing the electron density of a given voxel to the nearest anion
(either S or Se). As the CdSe well thickness is increased from 1 to 3 ML, the fraction of the CBM density in the CdSe layer predicted by LDA is 14% (38%), 28% (67%), and 32% (81%). Although the fraction of CBM density in the CdSe layer for the 3 ML case might seem large, a numerical integration of Ref. 18 gives 83%, in agreement with our calculated 81% EMA result. The reduced confinement of the CBM density to the CdSe well layer determined by the present atomistic calculations indicates that the agreement with experiment for narrow QDQWs based on the $\mathbf{k} \cdot \mathbf{p}$ CBM-density weighted $g$-factor results of Ref. 16 may not be entirely justified. It was noted previously that factors such as energy dependence of the conduction-band mass or interface terms in the $g$-factor expression may be responsible for some of the discrepancies between experiment and the EMA calculations. Although the weighted-$g$-factor approximation used previously may be satisfactory for larger systems, the treatment of these monolayer scale features may require inclusion of spin-orbit coupling and orbital angular momentum effects, and direct magnetic-field calculations. However, at present we have not implemented magnetic-field effects into our calculations and thus defer such an examination to a future work.

To explain the origin of this discrepancy between the LDA and EMA results, we examined the extent to which geometric distortions might reduce the band offsets between the materials, and therefore contribute to the reduced confinement of the CBM observed above. The combination of the valence force field relaxation and the charge-patching/LDA method reproduces the deformation potentials of the band-edge states of CdSe, but no such contribution was included in the EMA calculations. In Fig. 5, we have plotted the distribution of bond lengths for the above 3.4-nm-diam CdS core, 1.6-nm-thick CdS shell QDQW, as the CdSe well thickness is increased from 1 to 4 ML. Regardless of the well thickness, the Cd-Se bond lengths are compressed by 0.3 Å from the uncompressed 2.633 Å. From the CBM deformation potential calculated for bulk CdSe, this moves the CdSe CBM band-edge up by ~0.1 eV, from 0.32 to 0.2 eV relative to the CdS CBM. Qualitatively, this will lead to a reduction in the confinement of the CBM to the CdSe region consistent with the LDA results above. As the CdSe well becomes thicker, the initially uncompressed (2.519 Å) Cd-S bonds in the outer shell experience are lengthened by ~0.1 Å due to the underlying (larger lattice constant) CdS layer. This is evident in the increasingly

![FIG. 3. Average radial probability distribution of the conduction-band minimum (CBM) and valence-band maximum (VBM), respectively, of (a,b) 1 ML CdS shell, (c,d) 2 ML CdS shell, (e,f) 3 ML CdS shell QDQW nanocrystals, each with a 2.2-nm-diam CdS core. The CdSe well thicknesses are indicated as dotted, dash-dotted, dashed, and solid lines, for 1, 2, 3, and 4 ML thicknesses, respectively, with the boundaries indicated as in Fig. 2.](image1)

![FIG. 4. Comparison of the conduction-band minimum (CBM) wavefunction obtained using the $\mathbf{k} \cdot \mathbf{p}$ effective-mass approximation (Refs. 16 and 18) (EMA) to the present local-density approximation (LDA) results. The QDQW consists of a 3.4-nm-diam CdS core, 2 ML CdS well, and a 1.6-nm-thick CdS shell, shown schematically above the figure. The dotted line shows a pure CdS nanocrystal of the same total radius as the QDQW, indicating the delocalized nature of the LDA CBM, as compared to that of the EMA.](image2)
broadened Cd-S bond length distribution in Fig. 5. Again, based on the CBM deformation of bulk CdS, this will result in the CdS shell CBM offset being moved closer to that of CdSe by \( \sim 0.04 \) eV, or 13% of the band offset. This second contribution is consistent with the discrepancy between the EMA and experimental for the larger CdSe thickness offsets, which may lead to additional contributions. Thus, the difference between the \( k \cdot p \) EMA result and our direct atomistic calculations may result from the invalidity of the EMA in such two-layer systems or the inclusion of strain effects in our LDA calculation.

### B. Band gap

Figure 6 shows the LDA band-gaps for the QDQWs as functions of core, well, and shell thicknesses, calculated from the difference of the Kohn-Sham eigenvalues for the highest-occupied and lowest-unoccupied molecular orbitals. Due to the well-known LDA band-gap error, these values are typically lower than the experiment, but display the correct size trends for nanocrystals. This may be corrected by uniformly shifting the band gap by the difference between the LDA-calculated bulk value and the experimental bulk value. We determined shifts of +0.21 and +0.37 eV for CdSe and CdS, respectively. In the present case, since the QDQWs contain both materials, we weighted this correction by the average of the percentages of CBM and VBM densities in the CdSe/CdS regions, calculated as described in the previous section. This yields values of the energy shift between +0.27 and +0.34 eV. The band gap obtained after applying these weighted shifts is shown in Fig. 6. As observed from the steepest slope of the dotted lines, changes in the CdSe well thickness have the largest effect on the band gap, followed by the CdS core size. The exciton energy is discussed in the next section.

### C. Electron-hole Coulomb interaction and exciton energy

Using the band-edge states, the electron-hole Coulomb energy between electron state \( e \) and hole state \( h \) may be determined by

\[
E_{\text{Coul}} = \int \int \frac{|\psi_e(\mathbf{r}_1)|^2 |\psi_h(\mathbf{r}_2)|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2, \tag{1}
\]

in which the dielectric function, \( \varepsilon \), is determined using the nonlocal hybrid Thomas-Fermi-Resta/Penn model for quantum dots. Since the parameters of this dielectric model depend on measured bulk pure semiconductor values, we have examined them using either the average of the individual parameters for CdS and CdSe, or else weighting the averages by the relative number of S and Se atoms in the individual nanocrystal. In no case did the value of the Coulomb interaction calculated by these two approaches differ by more than 1 meV. The results plotted in Fig. 7(a) show a general decrease of \( E_{\text{Coul}} \) as the total size of the nanocrystal increases, resulting from the increasingly wide spatial distribution of the conduction-band electron density observed in Sec. III A.

A simple approximation for the exciton energy is to include the Coulomb interaction energy as a correction to the single-particle band gap, and ignoring the electron-hole exchange interaction, which is small in most colloidal nanostructures. This is because the exchange energy is typically an order of magnitude smaller than the Coulomb energy due to the zero overlap integral between VBM and CBM over a unit cell), which in turn is typically an order of magnitude smaller than the quantum confinement energy. Thus, the exciton energy \( E_{\text{ex}} \) may be expressed, using Eq. (1) and the results of the previous section, as \( E_{\text{ex}} = E_e - E_h - E_{\text{Coul}} \), which is plotted in Fig. 7(b). As observed in photoluminescence (PL) experiments, the largest changes occur as a result of increases in the CdSe well width. For a fixed total size and CdSe well width, changes in either the core or shell radii have roughly the same effect (\( \leq 60 \) meV) on the exciton energy, comparable to the full width at half maximum.
of the shifted gap results from the previous section gives effects.14,15

peak position as a function of temperature, which was attrib-

ute within the range of the PL peak energies observed

in Fig. 6.

Changes in core, well, and shell thickness are indicated as described

tion of the total number of radial monolayers of the nanocrystal.

property for the CdS/CdSe/CdS QDQWs, as a func-

tion of its tunable parameters is the first step toward

Acknowledgments

J.S. thanks Florian Meier for the $k \cdot p$ effective-mass cal-
culation code. This work was supported by the U.S. Depart-
ment of Energy under Contract No. DE-AC02-05CH11231

and by the DOE-SC-BES Materials Sciences and Engineer-

ing Division. The calculations were performed using the re-
sources of the National Energy Research Scientific Compu-
ting Center.

In summary, we have used $ab$ initio density-functional theory to calculate the electronic structures of CdS/CdSe/CdS quantum-dot quantum wells for sizes up to 18,000 atoms. Based on these calculations, we provide a systematic and quantitative picture for how the wave functions, eigenvalues, Coulomb interaction, and exciton energy change according to the sizes of the core, well, and shell. These results may be used in the future design of specific properties of QDQW structures, e.g., to separate electron-hole charge density or to match a particular exciton energy. Compared with a simple quantum dot, which has its size as the only tunable parameter, the QDQW structures provide more flexibility for tuning the electronic properties. Thus, a comprehensive understanding of its electronic structure as a function of its tunable parameters is the first step toward potential applications. Finally, we find that the $k \cdot p$ method, which was previously used to describe the effects of changing these parameters, is not adequate for the few monolayer quantum wells that are created experimentally, and suggest that this may result from a neglect of the strain-induced effects on the band offsets resulting from the lattice mismatch between the two different materials.

IV. CONCLUSION

ACKNOWLEDGMENTS


