First principle study of core/shell structure quantum dots

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The electronic states of core/shell CdSe/CdS and CdSe/CdTe heterostructure quantum dots are studied by large-scale first-principles calculations. According to their natural band-offset alignments CdSe/CdS is a type-I heterostructure and CdSe/CdTe is a type-II heterostructure. We found that, the electron state changes very litte, but the hole wavefunction in CdSe/CdS quantum dots has been localized within the core, while the hole wavefunction in CdSe/CdTe quantum dots is localized within the shell. The hole state in CdSe/CdTe quantum dots has drastically different characteristics as in CdSe and CdSe/CdS quantum dots. The band alignment, strain effect, and quantum confinment are all important to determine the electronic structures of these systems.

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During the last decade, technology advances in colloid chemistry have led to fabrication of high quality size-controlled semiconductor nanocrystal quantum dots (QDs). [1] Of special interest are the wet chemical synthesis of two materials core/shell structure QDs, which extends the rich physics of 2D superlattices [2] into the area of 0D QDs. According to their band alignments, the heterostructures can be classified as type-I (the minimum of conduction band and the maximum of valence band are in the same material) or type-II, showing drastic differences in the electronic structure. In 0D heterostructure QDs, the type-I and type-II systems are also expected to show different properties. But in this case, the band alignment effects are coupled with the strong quantum confinements and strong strain effects. These make these systems physically interesting. They also make highly accurate electronic structure calculations necessary. Recently, a number of experimental groups have reported the fabrication of well controlled core/shell structure QDs, such as CdSe/CdS, [3, 4] CdSe/ZnS, [5] InAs/CdSe, [6] and CdTe/CdSe QDs [7]. Their electronic structures and optical properties are carefully studied, and in some cases [4] improved devices are developed based on these core/shell QDs.

Theoretically, a few approaches have been used to study these systems. These include the effective mass method [8], multi-band $k \cdot p$ method [9] and empirical tight-binding method [10]. But all these methods are highly approximated in nature. It has been shown that the applicabilities of the continuum effective mass and $k \cdot p$ theory to the few monolayer size QDs are questionable [11]. The empirical tight-binding method might suffer from its uncertainty of the fitting parameters and poor transferibility from bulk to QDs. Thus, it is much more desirable to do reliable first principle calculations to these systems. Here, using a recently developed charge patching method, we have carried out first principle local density approximation (LDA) calculations for the 2000 atom QDs. To model an ideal passivation, we have used pseudo-hydrogen atoms (with fractional nuclei charges and numbers of electons) on the surface of the QD. Then, atomistic valence force field (VFF) [12] is used to relax the atomic positions. After the atomic positions are relaxed, the total electronic charge density of a given system is generated by assembling of charge motifs on each atoms. These charge motifs are calculated from small prototype systems with similar atomic environments as in the nanosystem. Then the total electron potential is generated from the charge density and the band edge eigen states are solved using the folded spectrum method [13]. The resulting single particle eigen energies have a typical error of $\sim$20 meV compared to direct LDA calculations, and the eigen energy splittings within valence band and conduction band have typical errors of just $\sim$5 meV. Thus the current calculation has almost the same accuracy as a straight forward direct first principle LDA calculation. The details of this method will be reported elsewhere. We have used planewave basis sets and norm conserving pseudopotentials with a planewave cutoff of 35 Ryd. This results in a real space grid of $384 \times 360 \times 360$ to calculate the following systems. Spin-orbit interaction is included in the single particle's Schrodinger equation.

Two core/shell QDs with wurtzite (WZ) crystal structure are studied: CdSe/CdS and CdSe/CdTe. The diameter of the core is 29.03$\AA$ and the thickness of the shell is 7.6$\AA$. These core/shell system will be compared with the pure CdSe quantum dot results with a diameter of 44.23$\AA$. For the VFF parameters, we have used the experimental bulk lattice constants, for CdSe: $a = 4.3\AA$; CdS: $a = 4.11\AA$; CdTe: $a = 4.58\AA$.

There are several questions we like to answer through this study: What is the band alignment of these structures? How does the strain effect changes the band alignment? What are the qualitative difference between the type-I and type-II core/shell structures? Are the shell strong enough to confine or shield the single particale states? What are the effects on the band gap, optical transition matrix elements, and electron-hole Coulomb interactions? We have the following findings.

(1) *Band alignment of CdSe/CdS and CdSe/CdTe het-*

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