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# Quantum confinement in CdSe nanocrystallites

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## Abstract

Quantum confinement increases the spacing between energy levels as the nanocrystallite size is decreased. Its qualitative features hold both for states localized near the center of a nanocrystallite and those near the surface, such as states due primarily to dangling bonds. However, different quantitative features are expected because of the different size constraints on each of these states. Since the majority of atoms in a typical nanocrystallite are on the surface, contrasting confinement effects between these two types may prove useful in predicting how surface state dependent properties, such as optical absorption, change with the size of the nanocrystallite. By applying first principles pseudopotential methods to indium doped, uncapped CdSe nanocrystallites containing 17 and 34 atoms, we identify center and surface localized states. Using the lowest occupied energy state as a reference, the energy of a state localized near the center is found to increase 24 mRy from the 34 to 17 atom nanocrystallite. An equivalent surface state within the two cases studied is not found, but the energy level spacing is speculated to increase on the order of 100 mRy between the 34 and 17 atom cases based on states that are highly local to the surface, but not equivalent. Furthermore, we find that it is necessary for the impurity to sit at the center of the nanocrystallite in order for the impurity states to be electrically active. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The origin of quantum confinement in so-called zero-dimensional nanocrystallites, such as quantum dots (QDs), is understood to arise from the spatial confinement of electrons within the crystallite boundary. It leads to a larger spacing between energy levels as the size of the nanocrystallite is decreased. Qualitatively this effect is analogous to the problem of a particle in a box, and efforts to quantify confinement effects have been the topic of considerable research [1]. In CdSe semiconductor QDs, an important conse-

quence of quantum confinement is the increase in the band gap as the QD size is decreased. Since this is observed as an increase in the energy of the lowest exciton peak as the radius of the QD is decreased [2,3], research in this area has focussed almost exclusively on understanding the energy spectrum of an exciton as a function of QD radius [1,4,5] in order to predict the optical properties of CdSe QDs of an arbitrary size. However, in principle, quantum confinement should affect every electronic state within the QD, but *not* equally. For instance, electrons within a nanocrystallite can be confined in different spatial regions, such as near the center or surface, and these different regions should lead to discernible differences in how the spacing between energy levels changes with respect to the size of the QD.

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Using first principles self-consistent pseudopotential methods, we quantify these differences for the electronic states within small, uncapped CdSe QDs containing 17 and 34 atoms ( $\sim 1$  nm diameter). Doped CdSe QDs are examined, with indium (a donor) substituted for cadmium, allowing distinct impurity states to be identified. We contrast confinement effects for impurity states confined near the center of the QD to those confined near the surface. Furthermore, we find that placing the impurity at the center of the QD is necessary for these impurity states to be electrically active.

Contrasting confinement effects between states localized near the center to those localized near the surface is important, since the majority of atoms within a QD are located on the surface. Quantifying quantum confinement in nanocrystallites, such as QDs, requires refinement of the particle in a box picture to incorporate the different ‘boxes’ available within a nanocrystallite; in particular the difference between the surface and center.

## 2. Models

Two sizes of CdSe QDs containing 17 and 34 atoms were modeled (Fig. 1). These were constructed using the cubic zincblende crystal structure up to a cutoff radius of 8.35 and 11.81 a.u., for the 17 and 34 atom cases, respectively, from a central Cd atom. This structure was then surrounded within a supercell of 30.0 and 40.0 a.u., respectively, on each side. No relaxation of the ionic positions was done, since such relaxation can itself be a formidable task and the effect we are studying should not depend strongly on it.

These models represent uncapped, non-interacting colloidal CdSe quantum dots with diameters of roughly 1 nm. To make the confining region at the surface similar between the two cases, an atom was removed from the 34 atom QD to make the bonding environment at the selected surface site more like that of the 17 atom case (shown in Fig. 1). Without this atom, both the 17 and 34 atom cases have a site on the surface that is missing three bonds. Indium was then substituted for cadmium at either this site or the center.

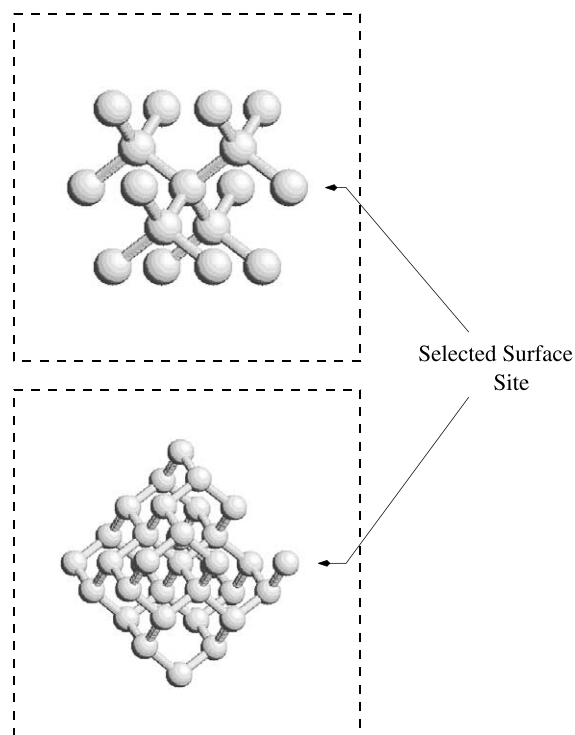


Fig. 1. Models of CdSe quantum dots containing 17 (top) and 34 (bottom) atoms. (Not to scale.) Both quantum dots have a diameter of approximately 1 nm and are centered around a cadmium atom. The dashed line illustrates schematically the 30.0 and 40.0 a.u. supercell, for the 17 atom and 34 atom cases, respectively. Indium is substituted for cadmium at either the center or the surface site shown.

## 3. Methods

### 3.1. Electronic properties

Norm-conserving pseudopotentials of the Hamann form [6] were used in conjunction with the local density approximation of density functional theory [7,8] to calculate all electronic properties. The wave function was expanded in a plane wave basis with a 50.0 Ry energy cutoff, using approximately 150 000 and 375 000 plane waves for the 17 and 34 atom cases, respectively.

### 3.2. Identifying states

The added electron associated with the indium atom introduces a unique impurity state that,

when substituted at either the center or a surface site, provides a way to identify a particular state between QDs of different size that will be localized either near the center or surface. By calculating self-consistently the wave function and energy spectrum using the local density approximation of density functional theory it is possible to (1) identify these impurity states by analyzing the projected density of states local to an atom and (2) quantify the confinement effect on these states, using the lowest energy state as a reference.

The projected density of the  $n$ th state  $D_n(\epsilon, r, \vec{\tau})$  local to an atom at the location  $\vec{\tau}$  is used to identify states.

$$\begin{aligned} D_n(\epsilon, r, \vec{\tau}) &= \frac{1}{V} \sum_{l=0}^{\infty} \sum_{m=-l}^l |\langle lm | \psi_n(\vec{r} - \vec{\tau}) \rangle_{\text{ang}}|^2 \delta(\epsilon - \epsilon_n) \\ &= \frac{1}{V} \sum_{l=0}^{\infty} \sum_{m=-l}^l |4\pi \sum_{\vec{G}} a_{\vec{G},n} e^{-i\vec{G}\cdot\vec{\tau}} j_l(Gr) \\ &\quad \times Y_{lm}^*(\theta_{\vec{G}}, \phi_{\vec{G}})|^2 \delta(\epsilon - \epsilon_n). \end{aligned} \quad (1)$$

Here  $\psi_n$  and  $\epsilon_n$  are the wave function and energy of the  $n$ th state, and  $V$  is the volume of the unit cell.  $\psi_n(\vec{r} - \vec{\tau}) = \sum_{\vec{G}} a_{\vec{G},n} e^{i\vec{G}\cdot(\vec{r}-\vec{\tau})}$  is projected onto the spherical harmonic basis  $|lm\rangle$ . Based on the magnitude of the  $s$  ( $l=0$ ),  $p$  ( $l=1$ ), and  $d$  ( $l=2$ )

components it is possible to identify the states associated with an atom, in particular, the impurity.

#### 4. Results

The lowest energy state is used as a reference to compare energies between QDs of different size and impurity location. This state, which can be thought of as originating from the 4s state of the interior shell of Se atoms, was selected because it is expected to be the most inert and therefore least affected by the addition of the impurity atom. Fig. 2 shows the projected density, as defined in Eq. (1), of the lowest energy state for the cases considered. The projection origin  $\vec{\tau}$  is the center of the QD, which corresponds to either a Cd or In atom. With the projection oriented as such, the  $s$  character shown is a result of a symmetric combination of orbitals on each of the four neighboring, tetrahedrally positioned Se atoms. No substantial  $p$  or  $d$  components are present for this state. For the case of In at the center of the QD (the middle column of graphs), the more attractive In pseudopotential (compared to Cd) distorts these orbitals leading to an increase in the peak between the In and Se atoms at approximately 2 a.u.

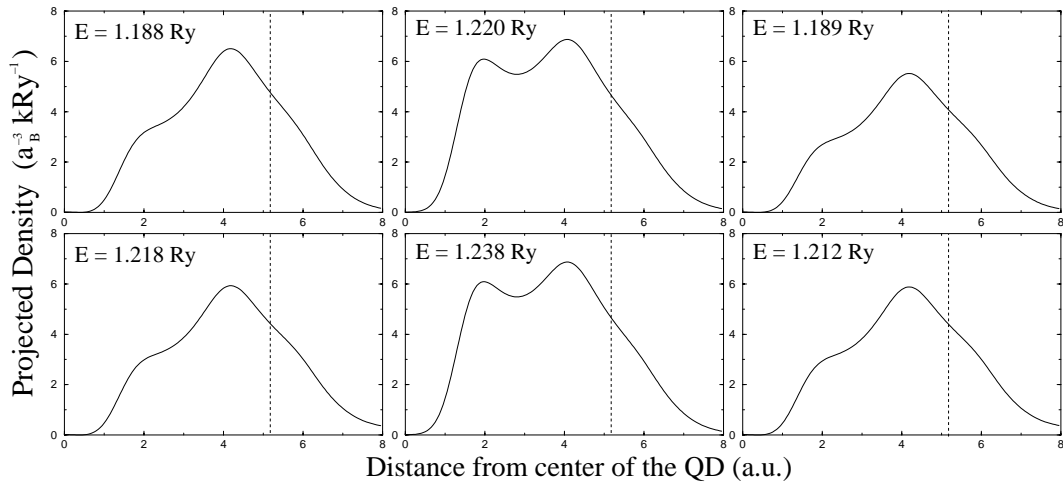


Fig. 2. Projected density for the lowest energy state, with the projection origin at the center of the QD. The columns, from left to right, are for the case with no impurity, the impurity at the center, and the impurity at the surface for the 17 atom QD (graphs along the top row) and 34 atom QD (bottom row). The location of the neighboring Se atom is shown by a line at 5.11 a.u. The energy of the state is labeled.

The assumption of the lowest energy state being inert holds for the case of the impurity at the surface of the QD, which only differs in energy from the lowest energy state with no impurity by 0.7 and 5.7 mRy for the 17 and 34 atom cases. Within the accuracy of our calculations, which are on the order of 1 mRy, these two states are essentially identical in energy.

However, the assumption does not hold when the impurity is at the center. The energy difference between the lowest energy state with the impurity at the center and the lowest energy state with no impurity is 31.7 mRy for the 17 atom case and 20.2 mRy for the 34 atom case. We attribute this non-constant shift in energy of the lowest energy state between QDs of different size to quantum confinement on the lowest state. For the impurity at the surface, the effect of quantum confinement is negligible; however, when the impurity is at the center of the QD there is a 11.5 mRy discrepancy in the shift of the lowest energy state.

With the impurity at either the center or a surface site, the projected density is analyzed to identify an analogous state between 17 and 34 atom quantum dots. The 34 atom case, because it has more electrons, necessarily has more electronic states. However, if a state is found within its energy spectrum that is similar in character to a state in the energy spectrum of the 17 atom QD, then these states can be considered to be physically the same. Comparing the energies of such a state with respect to a suitable reference will then quantify the effect due to confinement.

## 5. Discussion

For the case of the impurity at the center (Fig. 3), it was possible to identify a unique state between the two sizes of QDs. For the 17 atom case, this state was the lowest unoccupied energy state and is 1.0038 Ry above the lowest energy state of the 17 atom QD. For the 34 atom case, it was the highest occupied energy state at an energy of 0.9685 Ry above the lowest state. Naïvely, this suggests that quantum confinement has increased the energy level spacing for this state by 35 mRy as the size of the QD was reduced from 34 to 17

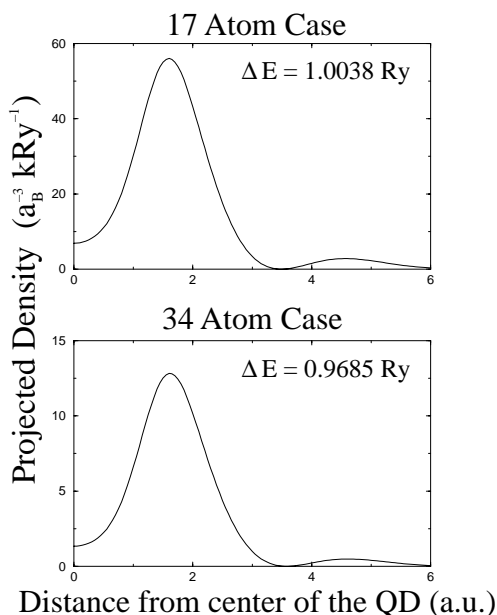


Fig. 3. The projected density for two equivalent states in the 17 (top) and 34 (bottom) CdSe quantum dot models. These states, at the lowest unoccupied (17 atom case) and highest occupied (34 atom case) energy states, are localized spatially near the center of the quantum dot. The relative energy of the state is given with respect to the lowest occupied energy level of the system.

atoms. However, because the lowest energy state of the 17 atom case has itself been affected by confinement this value should instead be 24 mRy.

With the impurity at the surface, finding a similar state between the two sizes of QDs is complicated by the surface; even *with* the removal of one atom from the surface to make the impurity sites similar, as discussed in Section 2 and shown in Fig. 1. In contrast to the case of the impurity at the center, no states near the highest occupied energy state were significantly localized near the impurity atom. However, there were significantly localized states below this energy level. An example of two such states is shown in Fig. 4. Physically, the impurity state at the surface is more bound than the corresponding impurity state at the center. At the center the bonding with the nearest neighbor layer of Se is complete with Cd. Substituting In for Cd introduces an extra electron that is relatively unlocalized. This is supported by the predominantly s projected density seen in Fig. 3. At the surface,

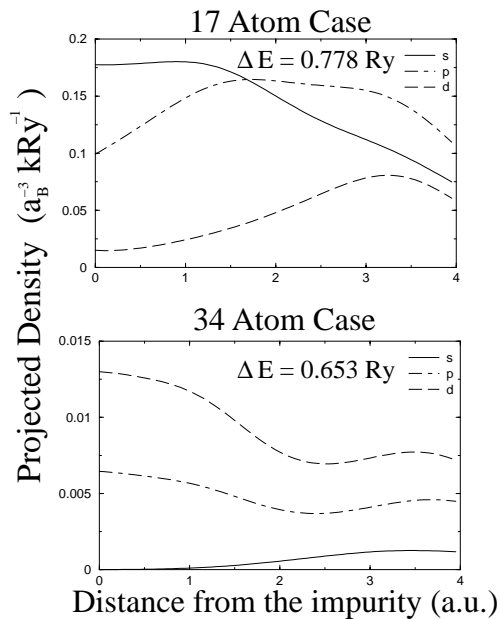


Fig. 4. Projected density for states that are localized near the impurity atom (In) at the surface of the 17 (top) and 34 (bottom) atom QDs. Both of these states are lower in energy than the highest occupied energy level. The relative energy of the state is given with respect to the lowest occupied energy level of the system.

however, the nearest neighbor layer of Se has only three neighboring Cd atoms, instead of four. The extra electron introduced when In is substituted for Cd therefore participates in bonding, resulting in a lower energy for that state.

Since the identification of a unique impurity related surface state for both sizes of QD is not possible, we proceed by comparing two states which are localized near the impurity atom, but not equivalent. The projected density of the chosen states is in Fig. 4. Other states were also found to be localized around the impurity. The selected states were chosen because they were the most localized states near the highest occupied energy state. For the 17 atom case the chosen state is at an energy of 0.778 Ry above the lowest occupied energy state. Within the energy spectrum of the 34 atom case, the chosen state is at an energy of 0.6530 Ry above the lowest occupied energy state of that system. To compare, the spacing between the energy level of the chosen state and the lowest

occupied energy state has increased on the order of 100 mRy between 34 and 17 atom QDs.

The observation that confinement effects at the surface are more pronounced than in the center of the QD is suggestive, but hardly convincing based on the ad hoc assumption made that the localized states chosen could be compared between the two sizes of QDs. In ongoing research we are investigating the charge density of these states to see if a more certain identification can be made. In addition, we are looking at a 71 atom QD model (essentially another layer of Se and Cd) that mimics the surface bonding environment of the 17 atom case much more closely, with the hope of eliminating this ambiguity.

## 6. Conclusion

In identifying a reference energy, which is a necessary prerequisite of any quantitative analysis of quantum confinement, we encountered the complication that the most suitable energy level, the lowest occupied energy state, was itself affected by quantum confinement. By making a comparison to the case with no impurity, it was possible to quantify this discrepancy to find that the energy level spacing for states localized near the center of the QD increased 24 mRy between the 34 and 17 atom cases. For states localized near the surface, although identifying a suitable reference state was straightforward, unambiguously identifying a state near the surface in both the 17 and 34 atom cases was impossible due to complications at the surface. Our results suggest that the energy level spacing of such a state would increase on the order of 100 mRy in going from 34 to 17 atom QD. Furthermore, in identifying impurity states we found that doping at the center was necessary to introduce electrically active impurity states. Such states, either at or just above the highest occupied energy level, would be expected to contribute to transport and optical properties within these systems.

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