**Ab initio** study of ZnSe and CdTe semiconductor quantum dots

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**A B S T R A C T**

We apply first principles density functional and time dependent density functional computational methods to study the structures, densities of states, absorption spectra, and optical gaps of spherical ZnSe and CdTe semiconductor quantum dots in the size range 0.3–2.2 nm. Our calculations are performed in real space without an explicit basis. The surfaces of the quantum dots are passivated with partially charged hydrogen atoms. We find that this passivation technique effectively removes the electronic states associated with the surface atoms from the gaps of ZnSe and CdTe nanocrystals, but does not affect the energies of the quantum-confined electronic states. Our study shows that the absorption gaps of ZnSe and CdTe quantum dots decrease with increasing dot diameter. The size-dependent variations of the computed optical gaps in surface-passivated ZnSe and CdTe quantum dots are found to be consistent with the effects of quantum confinement observed in group IV and group III–V semiconductor nanocrystals.

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1. Introduction

Semiconductor quantum dots exhibit a variety of unique physical properties resulting from the interplay of quantum confinement and electronic correlations. Spatial confinement of electronic wave functions in semiconductor nanocrystals strongly affects the spectral characteristics and recombination dynamics of single- and multi-exciton states [1]. Understanding these effects is important for the development of practical technologies, such as lasing, photogeneration, carrier multiplication, and photovoltaics. Studies of the effects of quantum confinement in porous and nanocrystalline semiconductors have become one of the focal points of materials research [2–22]. Over the last two decades, surface-passivated nanocrystals in the form of spherical quantum dots have been the subject of intensive experimental and theoretical investigations. The studies of semiconductor quantum dots made of Si [2–19], Ge [18–20], GaAs [23], CdS [24,25], ZnS [26,27], ZnSe [24,28,29], CdSe [30–35], CdTe [36–38], and ZnTe [39] have confirmed an important role of quantum confinement in these systems. It has been demonstrated that quantum confinement increases the size of the optical gap and enhanced the intensity of photoluminescence in semiconductor quantum dots [1,40].

Inorganic and organic composites containing luminescent group II–VI semiconductor quantum dots have emerged as a promising new class of photovoltaic materials [41]. These materials represent an attractive alternative to traditional light harvesting assemblies made from bulk semiconductors. Colloidal quantum dots composed of group II–VI semiconductors are photochemically stable and can be easily incorporated into polymer matrices and substrates [42]. The variation of the absorption gaps in semiconductor nanocrystals due to the effects of quantum confinement makes it possible to design photovoltaic systems that can capture a wider portion of the solar spectrum than bulk semiconductors. In experimental studies, colloidal group II-VI semiconductor quantum dots are commonly synthesized in the presence of organic surface ligands, such as thioglycolic acid (TGA), trioctylphosphine (TOP), trioctylphosphine oxide (TOPO), dodecylamine (DDA), or hexadecylamine (HDA) [38,43–46]. Organic ligands passivate the surfaces of nanocrystals by saturating dangling bonds and removing surface trap states from the gap edges.

To reproduce the experimental chemical environment, the surfaces of semiconductor quantum dots modeled in theoretical studies are usually passivated with atoms or simple chemical groups. Many previous computational studies of group IV semiconductor quantum dots have used hydrogen as a passivating agent [5–8,12,13,20]. The main advantage of this approach is a relatively low computational cost of adding hydrogen atoms to the surface of the studied nanocrystals. Unfortunately, while the hydrogen surface passivation works relatively well for group IV semiconductor quantum dots, this method tends to produce localized surface states situated within the optical gaps of nanocrystals composed of group III–V and group II–VI binary compound semiconductors. The presence of localized surface states within the gaps makes the standard hydrogen...
passivation scheme unsuitable for theoretical studies of the quantum confinement effects in group III–V and group II–VI semiconductor quantum dots.

A simple but an efficient surface passivation scheme for group III–V and group II–VI semiconductor quantum dots can be constructed using fictitious partially charged hydrogen atoms [23,47]. Within this scheme, the value of fractional charge for the surface-passivating hydrogen atoms is selected according to the type of covalent bond. Fractional charges simulate the differences in the heteropolar bonding between the atoms with a different number of valence electrons. This passivation technique has been successfully applied to GaAs nanocrystals [23] and ZnSe/ZnS core–shell quantum dots [48]. Our paper presents a systematic first principles density functional study of the electronic and optical properties of ZnSe and CdTe semiconductor quantum dots passivated with fractionally charged hydrogen atoms. The computed densities of states, absorption spectra, and optical gaps of ZnSe and CdTe quantum dots are compared with the available experimental data and with the results of previous theoretical studies for group IV and group III–V semiconductor nanocrystals.

2. Computational methods

Our calculations were performed in the framework of an *ab initio* pseudopotential computational method based on density functional theory (DFT) [49,50]. Within the pseudopotential approximation, the quantum mechanical equation for the electronic states was solved explicitly only for the valence electrons [51]. The functional formalism transforms the many-body Schrödinger equation into a set of single-electron Kohn–Sham equations [49]

\[
\left( \frac{-\hbar^2}{2m} \nabla^2 + \sum_{\sigma} v_{\text{ion}}(\mathbf{r} - \mathbf{r}_\sigma) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right) \psi_\sigma(\mathbf{r}) = \varepsilon_\sigma \psi_\sigma(\mathbf{r}),
\]

(1)

where the ionic pseudopotential, \(v_{\text{ion}}(\mathbf{r} - \mathbf{r}_\sigma)\), accounts for the interactions of the valence electrons with the core electrons and nuclei, the Hartree potential, \(v_{\text{H}}(\mathbf{r})\), describes the electrostatic interactions among valence electrons, and the exchange–correlation potential, \(v_{\text{xc}}(\mathbf{r})\), represents the non-classical part of the Hamiltonian. The exchange–correlation potential was evaluated as a function of the core-corrected charge density [52]:

\[
\rho(\mathbf{r}) = \rho_s(\mathbf{r}) + \sum_{\sigma} \rho_v(\mathbf{r} - \mathbf{r}_\sigma),
\]

\[
\rho_v(\mathbf{r}) = \sum_{\sigma} n_\sigma |\psi_\sigma(\mathbf{r})|^2,
\]

(2)

where \(\rho_v(\mathbf{r} - \mathbf{r}_\sigma)\) is a fixed partial correction for the core charge density and \(\rho_s(\mathbf{r})\) is the valence-electron charge density obtained from the Kohn–Sham wave functions, \(\psi_\sigma(\mathbf{r})\), and the occupation numbers, \(n_\sigma\).

The *ab initio* DFT computational technique was applied to calculate the structures, densities of electronic states, and energy gaps of surface-passivated ZnSe and CdTe nanocrystals. The calculations were performed using a parallel version of the PARSEC (Pseudopotential Algorithms for Real Space Energy Calculations) electronic structure code [53]. Within the PARSEC code, the system of Kohn–Sham equations for electronic states was set up and solved on a three-dimensional Cartesian grid inside a spherical boundary domain [54]. Outside the boundary sphere, wave functions were required to vanish. The kinetic energy term of the Hamiltonian was approximated by a higher-order finite-difference expansion for the Laplacian operator, which replaced spatial derivatives with a weighted sum of the wave function values at the neighboring grid points. The atomic pseudopotentials for Zn, Se, Cd, Te, and fractionally charged H atoms were constructed using the Troullier–Martins pseudopotential generation scheme [51]. The pseudopotentials for Cd and Te were generated using the relativistic correction. The exchange–correlation energy was computed within the generalized gradient approximation (GGA) implemented in the form developed by Perdew et al. [55]. The Hartree potential was obtained by setting up and solving the Poisson equation for the charge density using the conjugate-gradient method [56].

The structures of ZnSe and CdTe semiconductor quantum dots were obtained by starting with spherical fragments of bulk zinc selenide and cadmium telluride. The fragments were centered at the midpoints of the Zn–Se and Cd–Te interatomic bonds to ensure that the ZnSe and CdTe nanocrystals had the same number of group II and group VI atoms. By construction, the initial configurations of ZnSe and CdTe quantum dots were based on the zincblende lattice symmetry of bulk zinc selenide and cadmium telluride. Fictitious H atoms with a nuclear charge of 1.5 e and 0.5 e were used to passivate the dangling bonds originating from group II (Zn, Cd) and group VI (Se, Te) surface atoms, respectively. The fractional charges of the passivating H atoms accounted for the differences in the heteropolar bonding between group II and group VI elements. The geometries of surface-passivated ZnSe and CdTe nanocrystals were optimized using the Broyden–Fletcher–Goldfarb–Shanno algorithm [57]. The residual interatomic forces were required to be less than \(5 \times 10^{-3}\) a.u. The calculated ground-state energies and equilibrium structures of ZnSe and CdTe quantum dots were tested for convergence with respect to the grid spacing and the size of the boundary domain. The final structural optimization was performed using a grid spacing of 0.6 a.u. A separation of at least 8 a.u. was required between the position of any atom and the domain boundary. These parameters ensured the convergence of the computed energies and interatomic distances to within 0.05 eV and 0.01 a.u., respectively.

The absorption spectra and optical gaps of surface-passivated ZnSe and CdTe quantum dots were computed using a linear response method based on time-dependent density functional theory (TDDFT) [58]. The linear response formalism was used to construct a density-functional expression for the dynamic polarizability [59,60]. The excitation energies, \(\Omega_\beta\), which corresponded to the poles of the dynamic polarizability, were obtained from the solution of the eigenvalue problem [60]:

\[
\mathbf{Q} \mathbf{F}_\beta = \Omega_\beta^2 \mathbf{F}_\beta,
\]

(3)

where the matrix \(\mathbf{Q}\) is given by

\[
Q_{ij,kl} = \delta_{ik} \delta_{j,l} \alpha_{\beta}^2 \alpha_{\beta} + 2 \sqrt{\delta_{ij} \delta_{kl} \lambda_{\beta}^2} \alpha_{\beta}^2 - \delta_{kl} \delta_{ij} \alpha_{\beta}^2 \lambda_{\beta}^2.
\]

(4)

The indices \(i, j\) and \(k, l\) in Eq. (4) referred to the space and spin components of the unperturbed static Kohn–Sham wave functions \(\psi_\beta(\mathbf{r})\). \(\alpha_{\beta} = \epsilon_{ij} - \epsilon_{kl}\) were the differences between the eigenvalues of the single-electron states, and \(\lambda_{\beta} = n_{ij} - n_{kl}\) were the difference between their occupation numbers. The coupling matrix \(\mathbf{K}\) in the adiabatic approximation was given by

\[
K_{ij,kl} = \int \psi^*(\mathbf{r}) \psi_j(\mathbf{r}) \psi_i(\mathbf{r}) \psi_k(\mathbf{r}) \left( \frac{1}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta_{ij} \delta_{kl} \alpha_{\beta}^2 \lambda_{\beta}^2}{\delta_{ij} \delta_{kl} \alpha_{\beta}^2 \lambda_{\beta}^2} \right) d\mathbf{r} d\mathbf{r}',
\]

(5)

where \(E_{\text{xc}}\) is the exchange–correlation energy of the system. The oscillator strengths \(f_\beta\), which corresponded to the residues of the dynamic polarizability, were calculated as

\[
f_\beta = \frac{2}{3} \sum_{x,y,z} \beta \left| \mathbf{R}^z |\mathbf{F}_\beta|^2 \right|^2,
\]

(6)

where \(\mathbf{F}_\beta\) are the eigenvectors of Eq. (3), \(\mathbf{R}^z|\mathbf{F}_\beta\rangle = \delta_{ik} \delta_{j,l} \alpha_{\beta}^2 \alpha_{\beta}^2 \lambda_{\beta}^2 \alpha_{\beta}^2 \lambda_{\beta}^2\), and \(\beta\) are the dipole matrix elements, \(\beta_{ij,kl} = \int \psi^*_i(\mathbf{r}) \psi_j(\mathbf{r}) \psi_k(\mathbf{r}) \psi_l(\mathbf{r}) d\mathbf{r} d\mathbf{r}'\). The time-independent Kohn–Sham wave functions \(\psi_i(\mathbf{r})\) and eigenvalues \(\epsilon_i\) used in Eqs. (3)–(6) were obtained from the solution of Eq. (1).
The linear response TDDFT algorithm was implemented within the PARSEC electronic structure code [13]. To improve the accuracy of the computed excitation energies, the TDDFT calculations were carried out using an asymptotically corrected exchange–correlation functional developed by Casida and Salahub [61]. The calculated absorption spectra of ZnSe and CdTe quantum dots were tested for convergence with respect to the number of occupied and unoccupied electronic states included in the coupling matrix $K$. The tests demonstrated that the computed TDDFT transition energies were converged to within 0.1 eV in the spectral range up to 10 eV.

3. Results and discussion

The optimized structures of surface-passivated ZnSe and CdTe semiconductor quantum dots are shown in Figs. 1 and 2, respectively.

![Fig. 1. Structures of ZnSe quantum dots passivated with partially charged hydrogen atoms.](image1)

![Fig. 2. Structures of CdTe quantum dots passivated with partially charged hydrogen atoms.](image2)
The relaxed geometries of ZnSe and CdTe nanocrystals were found to be similar to each other. The equilibrium distances between nearest-neighbor atoms in ZnSe and CdTe quantum dots were almost identical to those in bulk zinc selenide and cadmium telluride. Due to the difference in the Zn–Se and Cd–Te interatomic distances, the diameters of CdTe dots were approximately 12–14% larger than the diameters of ZnSe dots containing the same number of atoms.

To test the influence of different types of surface passivation on the electronic properties of group II–VI semiconductor quantum dots, we compared the densities of states of ZnSe and CdTe nanocrystals passivated with regular ($Z_H = 1.0\, e$) and fractionally charged ($Z_H^1 = 0.5\, e$, $Z_H^2 = 1.5\, e$) hydrogen atoms. The computed densities of states of Zn$_{28}$Se$_{28}$H$_{66}$ and Cd$_{28}$Te$_{28}$H$_{66}$ dots passivated with regular and partially charged hydrogen are shown in Fig. 3. The continuous distributions of the densities of states in Fig. 3 are obtained from discrete electronic states by applying a Gaussian broadening of 0.1 eV. A comparison of the calculated densities of states demonstrated that the energy gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in ZnSe and CdTe dots were strongly affected by the type of surface passivation: in the Zn$_{28}$Se$_{28}$H$_{66}$ and Cd$_{28}$Te$_{28}$H$_{66}$ nanocrystals passivated with regular hydrogen, the HOMO–LUMO gaps were equal to 2.3 eV and 1.7 eV, respectively, whereas in the Zn$_{28}$Se$_{28}$H$_{66}$ and Cd$_{28}$Te$_{28}$H$_{66}$ nanocrystals passivated with fractionally charged hydrogen, the HOMO–LUMO gaps increased to 4.0 eV and 2.4 eV, respectively. The HOMO–LUMO gaps in the ZnSe and CdTe dots passivated with regular hydrogen were close to or smaller than the band gaps of bulk zinc selenide (2.8 eV) and bulk cadmium telluride (1.6 eV) [62]. In contrast, the HOMO–LUMO gaps in the ZnSe and CdTe dots passivated with partially charged hydrogen were significantly larger than the band gaps of bulk zinc selenide and cadmium telluride. We also analyzed the spatial distribution of the electronic wave functions in the Zn$_{28}$Se$_{28}$H$_{66}$ and Cd$_{28}$Te$_{28}$H$_{66}$ nanocrystals. Our calculations showed that the HOMO and LUMO wave functions were distributed throughout the volume of ZnSe and CdTe nanocrystals passivated with partially charged hydrogen, but were mostly located on the surfaces of ZnSe and CdTe nanocrystals passivated with regular hydrogen. These results demonstrated that the standard hydrogen passivation technique produced localized surface states situated within the energy gaps of ZnSe and CdTe quantum dots, whereas the passivation scheme based on the use of fractionally charged hydrogen atoms removed the surface trap states from the gap edges and increased the HOMO–LUMO gaps in ZnSe and CdTe dots.

Figs. 4 and 5 show the evolution of the computed densities of states in ZnSe and CdTe nanocrystals passivated with fractionally charged hydrogen.
charged hydrogen atoms. The calculated densities of states were broadened by 0.1 eV using a Gaussian function. The zero energy corresponds to the position of the highest occupied electronic state. Our calculations demonstrated that the densities of states of small ZnSe and CdTe quantum dots consisted of a series of isolated peaks corresponding to individual electronic energy levels. The densities of states of large ZnSe and CdTe dots were found to be similar in shape to the continuous densities of states of bulk zinc selenide and cadmium telluride. In agreement with the quantum confinement model, the HOMO–LUMO gaps in ZnSe and CdTe dots decreased with increasing dot diameter. The gaps in ZnSe nanocrystals were approximately 1.1–1.5 eV larger than those in CdTe nanocrystals containing the same number of atoms. The differences between the HOMO–LUMO gaps in ZnSe and CdTe nanocrystals were close to the difference between the band gaps of bulk zinc selenide and cadmium telluride.

The calculated TDDFT absorption spectra of surface-passivated ZnSe and CdTe quantum dots are shown in Figs. 6 and 7, respectively. Because of a high cost of TDDFT calculations, the spectra of the three largest ZnSe and CdTe nanocrystals were computed including only the electronic transitions below a chosen energy threshold. Along with the TDDFT spectra, we also included in Figs. 6 and 7 the spectra of time-independent Kohn–Sham eigenvalues. A Gaussian convolution of 0.1 eV was used to simulate finite broadening of the computed absorption spectra. Unlike the optical spectra of ZnSe and CdTe dots passivated with regular hydrogen atoms, the spectra of ZnSe and CdTe dots passivated with partially charged hydrogen atoms did not display low energy transitions associated with the localized surface states. As the diameters of ZnSe and CdTe nanocrystals increased, the discrete spectra of small quantum dots evolved into quasi-continuous spectra of large quantum dots. We found that the computed oscillator strengths of dipole-allowed transitions near the absorption edge were almost constant throughout the entire range of the studied ZnSe and CdTe quantum dots. This result was different from previous TDDFT calculations for surface-passivated Si and Ge quantum dots, in which the oscillator strengths of dipole-allowed transitions near the gap edge decreased with increasing dot diameter. The difference in the absorption properties of group II–VI and group IV semiconductor quantum dots could be explained by the fact that bulk zinc selenide and cadmium telluride have direct band gaps, whereas bulk silicon and germanium have indirect band gaps. The probabilities of optical transitions near the absorption edge are expected to be higher in nanocrystals made of direct band gap semiconductors than those in nanocrystals made of indirect band gap semiconductors.

Fig. 8 shows the variations of the optical absorption gaps in surface-passivated ZnSe and CdTe quantum dots as a function of the dot diameter. The optical gaps were defined as the energies of the first dipole-allowed transitions in the TDDFT absorption spectra. For...
comparison, we included in Fig. 8 the HOMO–LUMO gaps of ZnSe and CdTe dots evaluated as the differences between the time-independent HOMO and LUMO Kohn–Sham energy levels. The dashed lines showed the positions of the band gaps in bulk zinc selenide and cadmium telluride. We found that the computed values of the TDDFT absorption gaps were approximately 0.1–0.3 eV larger than the HOMO–LUMO gaps obtained from the time-independent DFT calculations. The differences between the TDDFT and time-independent DFT gaps in ZnSe and CdTe nanocrystals were smaller than those predicted for surface-passivated Si quantum dots [12,13]. The larger differences between the TDDFT and time-independent DFT gaps in Si dots could be attributed to the presence of dipole-forbidden transitions at the absorption edge of nanocrystals made of a semiconductor with an indirect band gap [12].

Our calculations showed that the optical absorption gaps in ZnSe and CdTe nanocrystals were significantly larger than the band gaps of bulk zinc selenide and cadmium telluride. The computed TDDFT absorption gaps decreased with increasing the diameters of ZnSe and CdTe quantum dots. The size-dependent variations of the TDDFT absorption gaps in ZnSe and CdTe quantum dots were similar to those observed in surface-passivated group IV and group III–V semiconductor nanocrystals [12–14,20,23]. We did not find any evidence of the presence of localized surface states within the gaps of ZnSe and CdTe quantum dots passivated with fractionally charged hydrogen atoms. The calculated TDDFT optical gaps in surface-passivated ZnSe and CdTe nanocrystals generally agreed with the available experimental data for colloidal ZnSe and CdTe quantum dots. The experiments showed that the photoabsorption and photoluminescence peaks in ZnSe and CdTe dots were blue shifted to higher energies due to the effects of quantum confinement [24,28,36–38]. The positions of the absorption and emission peaks in the experimental spectra of surface-passivated ZnSe and CdTe dots were consistent with the values of the optical gaps predicted by our calculations [28,36,37]. These results suggest that our computational model correctly described the effects of quantum confinement in colloidal group II-VI semiconductor quantum dots.

4. Conclusions

In summary, we calculated the structures, densities of electronic states, absorption spectra, and optical gaps of ZnSe and CdTe
semiconductor quantum dots passivated with fractionally charged hydrogen atoms. Our study demonstrated that the passivation technique based on the use of partially charged hydrogen effectively removed the surface trap states from the gaps of ZnSe and CdTe nanocrystals. At the same time, the energies of electronic states confined within the ZnSe and CdTe nanocrystals were not significantly affected by this passivation method. In agreement with the quantum confinement model, the computed optical absorption gaps in ZnSe and CdTe quantum dots decreased with increasing dot diameter. The variations of the absorption gaps in ZnSe and CdTe quantum dots were similar to those observed in surface-passivated group IV and group III-V semiconductor nanocrystals. The calculated values of the optical gaps in ZnSe and CdTe nanocrystals were consistent with the results of experimental spectroscopic studies for colloidal ZnSe and CdTe quantum dots.

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