Comparison of calculated by DFTB electronic excitation energies of CdS nanosized clusters with DFT results

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Nano-dimensional crystalline cadmium sulfide is a semiconductor that exhibits size-dependent opto-electronic properties, determined by the effects of quantum confinement. Due to these effects, it is possible to adjust the optical properties of the final cadmium sulfide clusters by varying their size. In this work we report the results of a theoretical study of CdS nanoparticles with the methods of the density functional tight-binding (DFTB) and the time-dependent density functional theory TD DFT. The calculations of the electronic absorption spectra of CdS crystals were performed on cadmium sulfide nanoparticles with an amount of from 5 to 137 atoms. The DFTB method was used for the structural optimization of the studied nanoparticles. The optimization results showed that the clusters will be a wurtzite structure and the geometrical parameters of the structure are close to the known experimental data for a CdS crystal. For the obtained optimized structures, the electronic absorption spectra were calculated by the linear response methods in the DFTB approximation and the time-dependent density functional theory of the TD-DFT approximation. It is shown that the data obtained by the DFTB method are close to those that can be obtained using DFT calculations for cadmium sulfide clusters. Especially good agreement is obtained when using large clusters with small values of the dipole moment.

Keywords: CdS clusters, tight-binding density functional theory, TD DFT method, electronic absorption spectra, dipole moment.

Introduction

Recent advances in the field of obtaining nanomaterials require a deep understanding of nanostructures, their properties and factors affecting them. Among

all nanostructures, semiconductor clusters and nanoparticles have always played a key role. They were the first systems for which the quantum confinement effect was described. Since then, they have remained in a focus of research and development.

Cadmium sulfide is an II-VI semiconductor. For several hundred years, cadmium sulfide has been used as a pigment. The unique electronic nature of similar materials gives them an advantage for a wide range of practical applications. For example, the creation of biological markers [1], displays [2], solar cells [3], quantum dot lasers [4] and photocatalysts [5].

Despite the huge number of works published on this topic, disagreements remain in the interpretation of the observed experimental data. Quantum chemistry techniques can clarify some of these questions.

Calculations method

We used the method of the density functional tight-binding (DFTB), which is especially well suited for calculating the electronic structures of large systems (several thousand atoms) or for simulating dynamics over a long time interval [6]. Therefore, the DFTB method is well suited for large threads of started tasks. The electronic structure of several tens of thousands of atoms can be obtained by single point calculation. The implementation of the DFTB method (for example, in the deMon or DFTB + software packages) is well parallelized. This makes it possible to reduce the computation time on computer clusters. A full DFT calculation cannot provide the required amount of big data in a reasonable amount of time. Therefore, DFT calculations were used only to validate/test the DFTB method.

The cluster charge in all calculations was determined by the following formula $2 \times (g\text{-}j) - k$ for a cluster with the general formula $Cd_g S_j (SH)_k$. This formula was proposed by Frenzel et al., [7] to correctly describe the optical properties of cadmium sulfide nanocrystals.

The dipole moment value for the considered CdS clusters was calculated using the following formulas. For a neutral system the formula (1) will be applied:

$$\mu = \sum_{i=1}^{N} q_i r_i, \tag{1}$$

where q_i and r_i are the charge and coordinate of atoms in a cluster. To a charged systems we was used the next equation (2):

$$\mu = \sum_{i=1}^{N} q_i (r_i - r_c), \tag{2}$$

where r_c is the coordinate of the center of mass of the molecule/group of particles. The charge distribution was estimated by the Mulliken method.

The method for calculating the electronic spectrum in the DFTB approximation – the linear response theory [8]. All DFTB calculations were carried out using the deMon software package on a high-performance computing resource at the

Technical University of Dresden (ZIH, Zentrum fur Informationsdienste und Hochleistungsrechnen).

The Gaussian09W software package was used for DFT calculations. Calculations using the Gaussian09W software package were carried out at the High-performance cluster of the National scientific laboratory of shared utilization of informational and space technologies at KazNTU named after K.I. Satpayev. The electronic absorption spectra of model clusters were calculated by the TD DFT method [9].

In the TD DFT method for the considered CdS clusters, the effective core potential LanL2DZ basis set for cadmium atoms, 3-21G basis set for hydrogen atoms, and the standard 6-31G(d) basis set for sulfur atoms were used as atomic basis sets. In the calculations, we used the LC-wPBE functional [10] with a long-range correction of the transition energy during charge transfer, since we previously showed that its use allows one to more or less accurately determine the energies of electronic transitions [11].

The absorption spectra were visualized using the GaussView 5.0 software package at a given FWHM 0.15 eV using a Gaussian curve.

Calculations results

In order to carry out calculations for the optimization and calculations of electronic transitions by the DFTB method, the SKF (Slater-Koster files) data were obtained for Cd, S and H atoms. For 7 clusters of the wurtzite structure $[Cd_1(SH)_2]$, $[Cd_4S_1(SH)_6]$, $[Cd_{10}S_1(SH)_{18}]$, $[Cd_{16}S_4(SH)_{24}]$, $[Cd_{19}S_4(SH)_{30}]$, $Cd_{28}S_{10}(SH)_{36}]$, $[Cd_{37}S_{16}(SH)_{42}]$ with the number of atoms from 5 to 137, the calculation of the optimized structure was carried out by the DFTB method (Figure 1). All these clusters had a neutral charge.
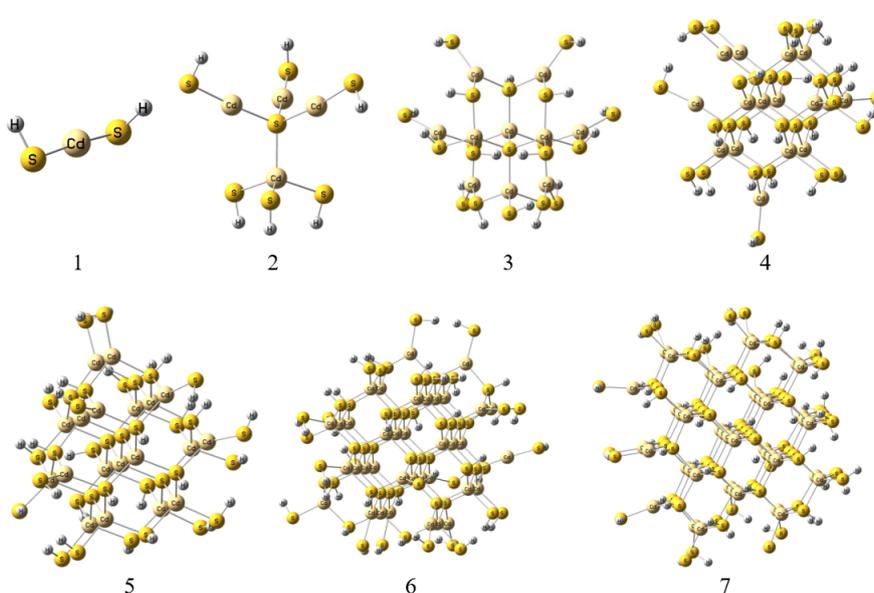

Figure 1. Clusters structures 1 - $[Cd_1(SH)_2]$, 2 - $[Cd_4S_1(SH)_6]$, 3 - $[Cd_{10}S_1(SH)_{18}]$, 4 - $[Cd_{16}S_4(SH)_{24}]$, 5 - $[Cd_{19}S_4(SH)_{30}]$, 6 - $[Cd_{28}S_{10}(SH)_{36}]$, 7 - $[Cd_{37}S_{16}(SH)_{42}]$.

According to the optimization results, the structure of the clusters remained wurtzite and the geometric parameters of the structure are close to the known experimental data for the CdS crystal. To the obtained optimized structures, the electronic absorption spectra were calculated using the linear response methods in the DFTB approximation and the time-dependent DFT approximation method. The data obtained are presented in Table 1 and Figure 2.
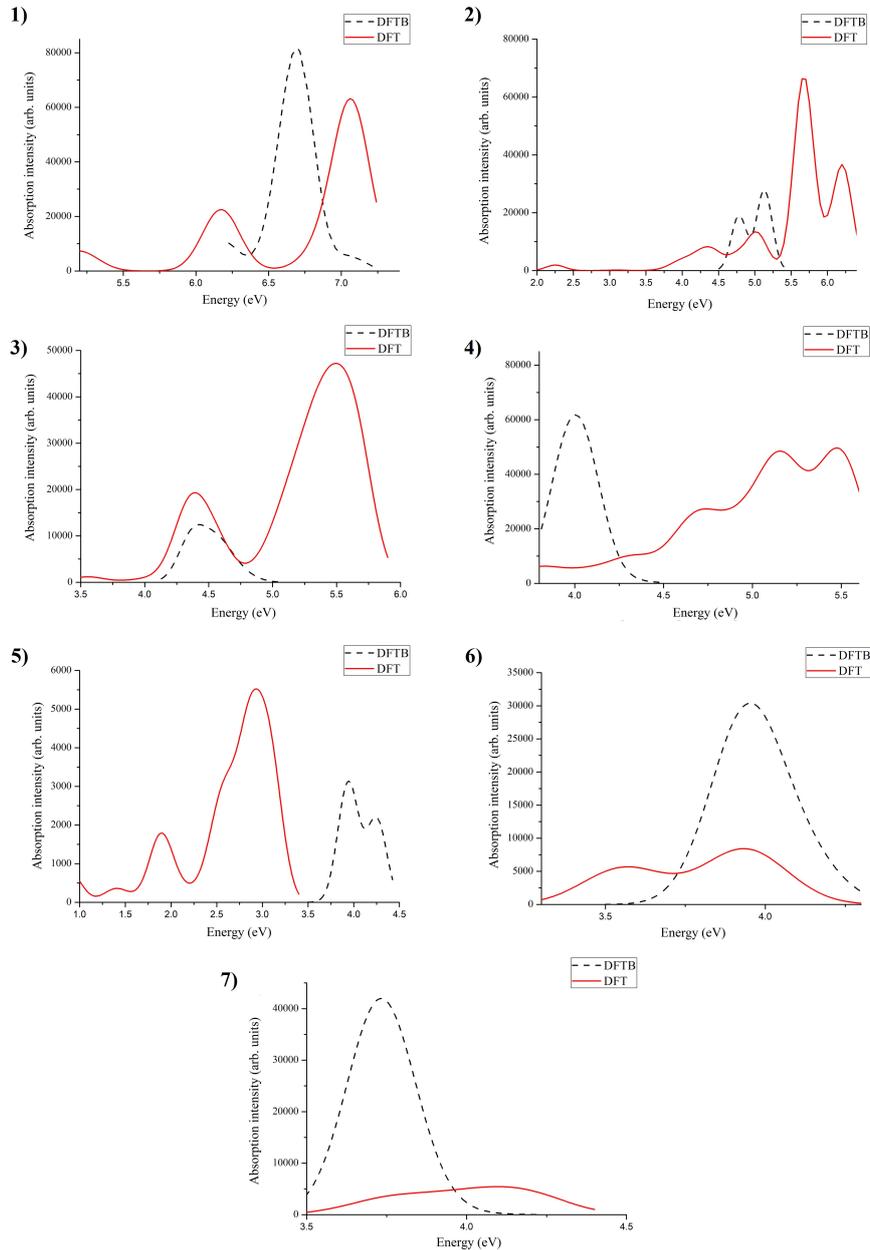

Figure 2. Visualization of the absorption spectra of the CdS clusters calculated by the DFTB and DFT methods: 1 - $[Cd_1 (SH)_2]$, 2 - $[Cd_4 S_1 (SH)_6]$, 3 - $[Cd_{10} S_1 (SH)_{18}]$, 4 - $[Cd_{16} S_4 (SH)_{24}]$, 5 - $[Cd_{19} S_4 (SH)_{30}]$, 6 - $[Cd_{28} S_{10} (SH)_{36}]$, 7 - $[Cd_{37} S_{16} (SH)_{42}]$.

Table 1.
Low energy transitions and dipole moment for CdS clusters calculated by DFTB and DFT methods.

Clusters structures	DFTB		DFT		Dipole moment, 10^{-29} Coulomb×m
	E_1 (eV)	Oscillator strength	E_1 (eV)	Oscillator strength	
$[Cd_1(SH)_2]$	5.665	0.0005851	5.0785	0.0277	1.02
$[Cd_4S_1(SH)_6]$	4.777	0.0210681	2.1761	0.0012	6.65
$[Cd_{10}S_1(SH)_{18}]$	4.355	0.0056562	3.5530	0.0130	11.54
$[Cd_{16}S_4(SH)_{24}]$	3.928	0.0232130	3.6946	0.0041	21.82
$[Cd_{19}S_4(SH)_{30}]$	3.880	0.0008064	0.8032	0.0004	38.05
$[Cd_{28}S_{10}(SH)_{36}]$	3.884	0.1280460	3.5435	0.0194	4.17
$[Cd_{37}S_{16}(SH)_{42}]$	3.721	0.1811313	3.6917	0.0087	0.33

As can be seen from the results obtained for the clusters $[Cd_1(SH)_2]$, $[Cd_{16}S_4(SH)_{24}]$, $[Cd_{28}S_{10}(SH)_{36}]$, $[Cd_{37}S_{16}(SH)_{42}]$ the DFTB method gives values close to those obtained by the DFT method. And for the clusters $[Cd_4S_1(SH)_6]$ and $[Cd_{19}S_4(SH)_{30}]$, there are significant discrepancies between the results of electronic excitations of the DFTB and DFT methods. It can be assumed that such discrepancies correlate with the value of the dipole moment per atom. The two largest clusters considered here, $[Cd_{28}S_{10}(SH)_{36}]$ and $[Cd_{37}S_{16}(SH)_{42}]$, also have the smallest dipole moments per atom. At the same time, the smallest discrepancies are observed for them (less than 0.3 eV).

Conclusion

Thus, we can assume that for large cadmium sulfide clusters (more than a hundred atoms), the results of DFTB calculations of electronic excitations give results close to the results of DFT calculations. It should also be noted that the DFTB method correctly reproduces the quantum size effect for the considered clusters, i.e., a decrease in the energy of the first transition with an increase in the cluster size is observed. These results show that the use of the DFTB method is justified for the correct consideration of electronic transitions in large clusters of cadmium sulfide, especially taking into account the fact that the calculation time by this method is much shorter than in the case of the DFT method.

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