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Influence of dielectric environment on exciton and bi-exciton properties in colloidal, type II quantum dots

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Abstract. We present theoretical calculations of type II CdSe/CdTe quantum dots systems. We use an 8-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian that includes spin-orbit interaction, strain, and first order piezoelectric effects. Exciton and bi-exciton states are found using the configuration interaction (CI) method that explicitly includes the effects of the Coulomb interaction, as well as exchange and correlation effects between many-electron configurations. We study convergence of the CI Hamiltonian with respect to the number of single particle states used in creation of the Hamiltonian. We show that there is a very strong correlation between the dielectric constant of the environment and exciton and bi-exciton energies.

1. Introduction

When a photon with energy greater than the energy of the bandgap is absorbed in a conventional solar cell, part of the energy (energy of the photon minus the energy of the bandgap) is always lost due to rapid thermalization and Auger processes. However in a quantum dot solar cell part of this energy can be utilized due to the multiple exciton generation (MEG) process. In this process the high energy photon creates a high energy exciton that can decay into a bi-exciton (shown in Fig.1a). To observe MEG, the energy of the exciton (which usually consists of a high energy electron and a hole in the ground state) has to be at least twice as big as the energy of the effective optical gap ($E_{e_n} - E_{h_0} \geq 2(E_{e_0} - E_{h_0})$), where e_0 and h_0 are the conduction band minimum and valence band maximum. This allows for a full utilization of high energy photons and dramatically increases solar cell efficiency. The MEG process competes with other radiative and non-radiative recombination processes (such as phonon and Auger cooling [1]).

To design the most optimal quantum dots it thus necessary to know what affects exciton and bi-exciton energies and how. In this work we focus on convergence issues of the CI Hamiltonian and the influence of the environmental dielectric constant on the exciton and bi-exciton energies.

2. Theory

Our approach to the calculation of exciton and bi-exciton energies consists of two major steps: solution to a single particle Hamiltonian, and application of the single particle states to create and solve the configuration interaction (CI) Hamiltonian.

In the first step we apply an 8-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian that includes continuum mechanical strain and piezoelectric effects [2, 3]. The Hamiltonian is parameterized using material



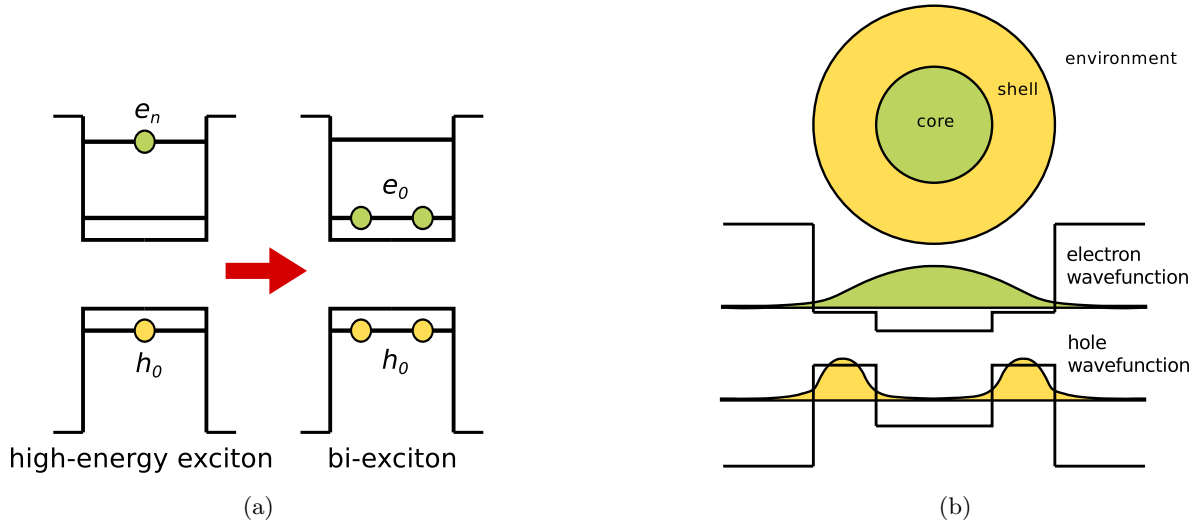


Figure 1: (a) Representation of the multiple exciton generation process. An exciton that consists of a high energy electron e_n and valence band maximum hole h_0 decays into a bi-exciton state that consists of 2 conduction band minimum states e_0 and 2 valence band maximum states h_0 . (b) Structure of a CdSe/CdTe core/shell type II quantum dot. In CdSe/CdTe core/shell QDs hole wavefunctions are confined in the shell region.

parameters taken either from experiment or from ab initio hybrid density functional calculations using B3LYP and PBE0 functionals.

Because of the large difference in dielectric permittivities, each charge inside the dot induces significant surface charges which strongly interact with the charges inside the dot. This is known as the surface polarization effect [4, 5]. The exact form of the Coulomb potential can be obtained by directly solving the Poisson equation, resulting in two terms: $V_P(\mathbf{r}_1, \mathbf{r}_2)$, the two-particle interaction term, and $V_{SP}(\mathbf{r})$, the self-polarization potential originating from the interaction of a charge with its own induced surface charge. The full potential is

$$V(\mathbf{r}_1, \mathbf{r}_2) = V_P(\mathbf{r}_1, \mathbf{r}_2) + V_{SP}(\mathbf{r}_1) + V_{SP}(\mathbf{r}_2). \quad (1)$$

To speed up calculations, in this work we use the following approximation for the two-particle interaction

$$V_P(\mathbf{r}_1, \mathbf{r}_2) \approx V_P(|\mathbf{r}_1 - \mathbf{r}_2|) = \frac{e}{4\pi\epsilon_0\epsilon(|\mathbf{r}_1 - \mathbf{r}_2|)|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (2)$$

where $\epsilon(r) = \epsilon_{\text{dot}}$ for $r < R_b$ and $\epsilon(r) = \epsilon_{\text{env}}$ for $r > R_b$. The self-polarization term $V_{SP}(\mathbf{r})$ is calculated using the method developed by Bolcatto et al. [6]. The many-body Hamiltonian contains only particle-conserving terms, and is given by

$$\begin{aligned} H = & \sum_i E_i \hat{e}_i^\dagger \hat{e}_i - \sum_i E_i \hat{h}_i^\dagger \hat{h}_i + \frac{1}{2} \sum_{ijkl} V_{iljk} \hat{e}_i^\dagger \hat{e}_j^\dagger \hat{e}_k \hat{e}_l \\ & + \frac{1}{2} \sum_{ijkl} V_{iljk} \hat{h}_i^\dagger \hat{h}_j^\dagger \hat{h}_k \hat{h}_l - \sum_{ijkl} (V_{iljk} - V_{ikjl}) \hat{e}_i^\dagger \hat{h}_j^\dagger \hat{h}_k \hat{e}_l, \end{aligned} \quad (3)$$

where Coulomb integrals V_{iljk} are defined as

$$V_{iljk} = \sum_{b=1}^8 \sum_{b'=1}^8 \int d^3\mathbf{r} \int d^3\mathbf{r}' \psi_b^{(i)}(\mathbf{r})^* \psi_b^{(l)}(\mathbf{r}) V(\mathbf{r}, \mathbf{r}') \psi_{b'}^{(j)}(\mathbf{r}')^* \psi_{b'}^{(k)}(\mathbf{r}'). \quad (4)$$

3. Results

First we focus on convergence issues of the CI Hamiltonian. Figs. 2a and 2b show convergence of bi-exciton energy (Exx) as a function of the number of single particle states for two different types of quantum dot: a CdSe core only QD and a CdSe/CdTe QD. Fig. 2a shows convergence of the CdSe type I QD with a fixed number of valence band states and a varying number of conduction band states and vice-versa. One can see that to reach a reasonable convergence it is enough to use 12 conduction band states and 20 valence band states. The analogous test for the case of the CdSe/CdTe type II quantum dot (Fig. 2b) indicates that convergence can be reached faster using only 10 conduction band states and 12 valence band states.

Next we focus on the influence of the environmental dielectric constant on the exciton and bi-exciton energies. In Fig. 3a we show the difference in energies (of excitons and bi-excitons) between two identical systems immersed in environments with $\epsilon_{\text{env}} = 2.0$ and $\epsilon_{\text{env}} = 1.9$, i.e. $\Delta Exx = |Exx_{1.9} - Exx_{2.0}|$ and $\Delta Ex = |Ex_{1.9} - Ex_{2.0}|$. One can immediately see that even a very small difference in the dielectric constant of the environment has a profound impact on the exciton and bi-exciton energies by approximately 15 and 30 meV respectively. In addition, this impact becomes even more pronounced for bi-excitons when the structure becomes type II, which happens for shell thicknesses larger than 4 Å.

Finally we calculate exciton and bi-exciton energies for the same CdSe/CdTe core/shell QD for ten different values of environmental dielectric constant. In Fig. 3b one can see rapid increase of both exciton and bi-exciton energies with increasing value of the dielectric constant of the environment. The electron-hole binding energy is much larger for small values of ϵ_{env} (when the ratio of ϵ_{QD} to ϵ_{env} is the biggest). For small values of ϵ_{env} the polarization part of the Coulomb potential (1) dominates [7], hence the polarization effect increases the binding energy of electron-hole pairs.

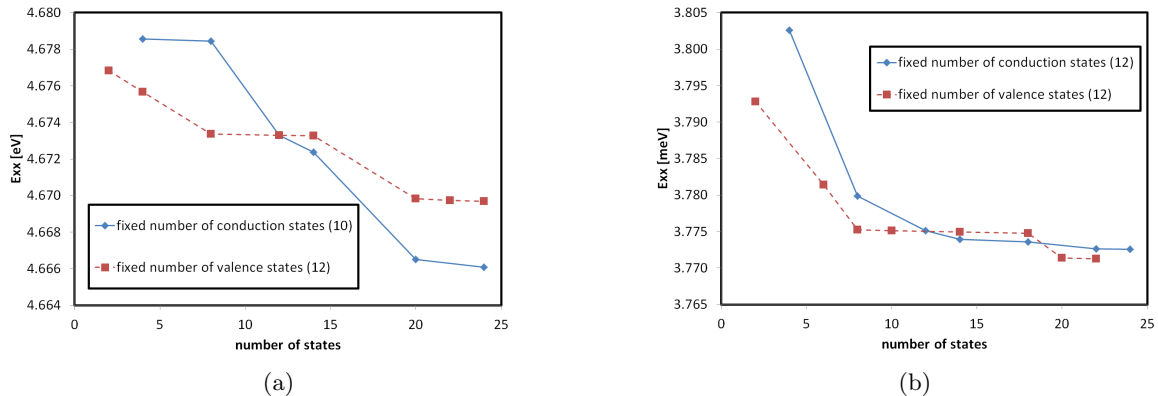


Figure 2: Convergence of bi-exciton energy with increasing number of states in CI Hamiltonian. (a) CdSe core only (type I) quantum dot with 15 Å radius. (b) CdSe/CdTe core/shell structure (type II) with CdSe core (15 Å radius) and 5 Å thick CdTe shell.

4. Summary and conclusions

In conclusion, we calculated exciton and bi-exciton energies in type I CdSe and type II CdSe/CdTe colloidal quantum dots for various values of the environmental dielectric constant

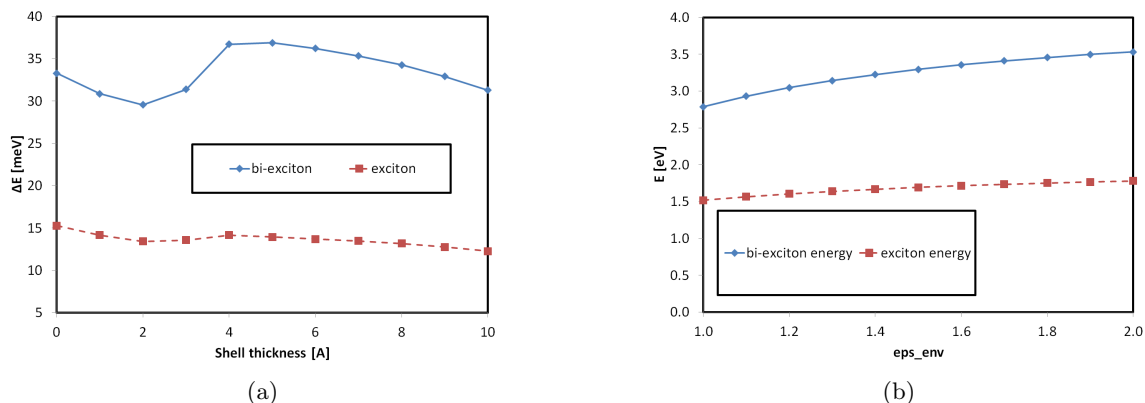


Figure 3: (a) Difference in excitation and bi-exciton energies for identical type II QDs with $\epsilon_{\text{env}} = 2.0$ and $\epsilon_{\text{env}} = 1.9$. (b) Exciton and bi-exciton energies of QDs (CdSe core with 20 Å radius and 5 Å thick shell) as a function of environmental dielectric constant..

and varying shell thickness. We showed that to get convergence of 1 meV it is necessary to take at least 20 valence band and 12 conduction band states (20/12) for type I QDs and 12/10 for type II QDs. We showed that the environmental dielectric constant has a significant impact on both exciton and bi-exciton energies, becoming even greater for type II QDs. Finally we proved that polarization effect increases the binding energy of excitons and bi-excitons and that this effect is even more pronounced for type II QDs.

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