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2014 J. Phys.: Conf. Ser. 526 012005

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Theoretical studies of excitons in type II CdSe/CdTe quantum dots

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Abstract. We present a method for calculating exciton and bi-exciton energies in type-II colloidal quantum dots. Our methodology is based on an 8-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian of the zinc-blend structure, which incorporates the effects of spin-orbit interaction, strain between the core and the shell and piezoelectric potentials. Exciton states are found using the configuration interaction (CI) method that explicitly includes the effects of Coulomb interaction, as well as exchange and correlation between many-electron configurations. We pay particular attention to accurate modelling of the electrostatic interaction between quasiparticles. The model includes surface polarization and self-polarization effects due to the large difference in dielectric constants at the boundary of the QD.

1. Introduction

In a standard solar cell, all of the energy of an absorbed photon in excess of the effective bandgap of the material is dissipated as heat and essentially wasted. In colloidal QDs (for example made of CdSe, CdTe), this excess photon energy can be utilized due to a process known as multiple exciton generation (MEG) or direct carrier multiplication. In this process the high energy photon creates a high energy exciton that can decay into a bi-exciton (shown in Fig. 1a). For this process to occur 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 electron and hole ground states, and e_n is a state higher in the conduction band. This allows for full utilization of high energy photons and dramatically increases solar cell efficiency. The MEG process competes with other radiative and non-radiative recombination processes, most of all with Auger cooling [1, 2, 3]. To further increase the solar cell efficiency it is necessary to optimize the shape and composition of the QD in order to maximize the ratio of MEG to cooling processes.

It is hypothesized that one way to increase the MEG/cooling ratio is to introduce a shell layer. Contrary to a simple single material colloidal QD, a core/shell structure can offer extra degrees of freedom in designing devices with desirable properties. In this paper we focus on the development of a theoretical method that allows for quick and reliable determination of exciton and bi-exciton energies in core/shell structures.



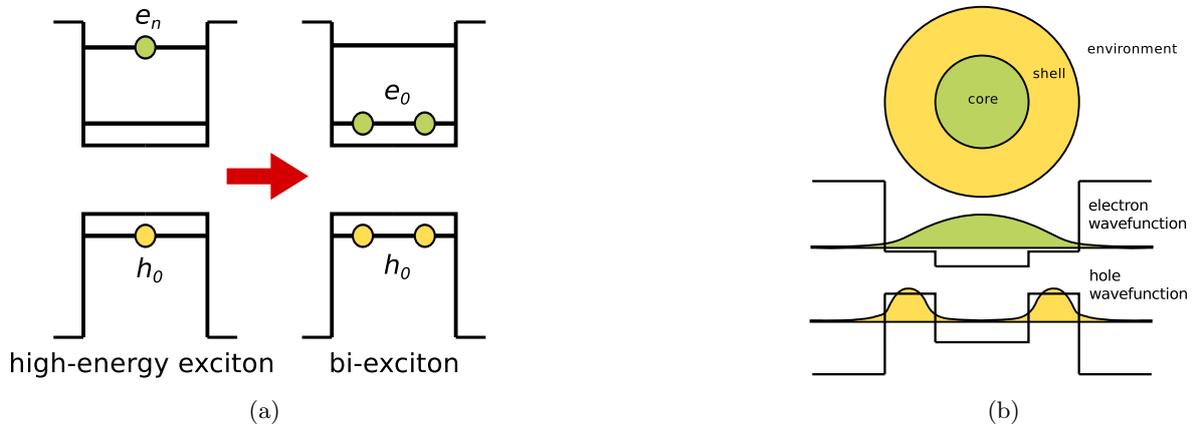


Figure 1: (a) Representation of the multiple exciton generation process. An exciton that consists of high energy electron e_n and ground state hole h_0 decays into a bi-exciton state that consists of 2 ground state electrons e_0 and 2 ground state holes h_0 . (b) Structure of a CdSe/CdTe core/shell type-II quantum dot. In CdSe/CdTe core/shell QD hole wavefunctions are contained in the shell region.

2. Theory

Contrary to single material QDs, a core/shell QD can form a type-II structure in which the conduction and valence band states are spatially separated. This separation is schematically shown in Fig. 1b. In the case of QDs with a CdSe core and CdTe shell, the valence band states are usually strongly confined to the shell region while conduction band states are spread equally over the whole structure.

Our approach can be divided into two parts: in the first part we calculate single-particle eigenfunctions and eigenenergies of the confined electrons and holes, while in the second part we use functions from step one to build the many-body Hamiltonian that is used to calculate many-body states such as excitons and bi-excitons.

To find single-particle states we apply an 8-band $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian that includes continuum mechanical strain and piezoelectric effects [4, 5, 6]. The Hamiltonian is parameterized using material parameters taken either from experiment or from ab initio hybrid density functional calculations using B3LYP and PBE0 functionals [7].

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 [8, 9]. The exact formula for the Coulomb potential can be obtained by directly solving the Poisson equation, resulting in two terms: $V_P(\mathbf{r}_1, \mathbf{r}_2)$, 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

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

where $\epsilon(r) = \epsilon_{\text{dot}}$ for $r < R_b$ and $\epsilon(r) = \epsilon_{\text{env}}$ for $r > R_b$. We assumed that the dielectric permittivity is the same in both core and shell and R_b is the radius of the whole QD. The

self-polarization term $V_{\text{SP}}(\mathbf{r})$ is calculated using the method developed by Bolcatto et al. [10]. The many-body Hamiltonian contains only particle-conserving terms, and is given by

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

where Coulomb integrals V_{iljk} are defined as

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

In Eq. (3) we ignore terms that do not conserve the number of particles so that we can solve it for excitons and bi-excitons separately. To get excitonic states we write the Hamiltonian in a two particle basis (one electron and one hole) $|i, j\rangle = |e_i\rangle |h_j\rangle$, and for bi-excitons we use a four particle basis $|i, j, k, l\rangle = |e_i\rangle |h_j\rangle |e_k\rangle |h_l\rangle$.

3. Results

We apply our method to study CdSe/CdTe quantum dots with varying shell thickness. The CdSe core has radius of 15Å. Because the difference between the dielectric constants of CdSe and CdTe is very small, they are assumed to be equal, with $\epsilon_{\text{dot}} = 5.8$. The dielectric constant of the environment is assumed to be $\epsilon_{\text{env}} = 1.1$. In the results presented here the effect of self-polarization is ignored, i.e., the formula for Coulomb potential is limited to Eq. (2). For CI calculations we use the first 12 electron and 12 hole states (always including all degenerate states).

To evaluate the the effect of the many-electron interaction in CdSe/CdTe QDs we compare the difference between the ground state exciton energy and the energy difference between e_0 and h_0 single particle states. From Fig. 2a one can see that the exciton binding energy is very large, up to 450 meV ($\sim 24\%$ of the bulk bandgap) for a pure CdSe QD (corresponds to the zero thickness point on the graph). It decreases with the addition of CdTe shell, but even for 15Å thickness, it is still around 200 meV, which is significant. This suggest that the Coulomb potential is crucial in accurate determination of energy levels.

To estimate the importance of polarization, we compare exciton and bi-exciton energies calculated with and without the polarization effect. The lack of polarization is implemented by setting $\epsilon_{\text{env}} = \epsilon_{\text{dot}} = 5.8$. Fig. 2b indicates that polarization also plays a very important role in exciton and bi-exciton energy. After taking into consideration the polarization effect, the exciton energy is reduced by roughly 100 meV (200 meV in case of bi-excitons).

Finally, we investigate the influence of exchange and correlation. In Fig. 2c we compare full CI calculations obtained by diagonalization of the many-electron Hamiltonian in Eq. (3) with calculation that do not take into account the correlation effect. To build the many-body Hamiltonian we use the first 24 single particle states (12 hole and 12 electron states) which is enough to get a reasonable convergence of the first exciton and bi-exciton states.

To calculate many-body states that do not include the correlation effect we use only single particle ground states (2 electron and 4 hole) in the construction of the many-body Hamiltonian. We found that the correlation interaction has negligible influence on exciton energies for both core and core/shell structures. It does however have a strong impact on bi-exciton energies, especially in case of type-II structures. Figure 2c shows a comparison of full CI calculations with the corresponding Hartree approximation equivalent (no correlation). The difference ranges from 20 meV for type-I QDs to 60 meV for type-II structures with 15Å shell.

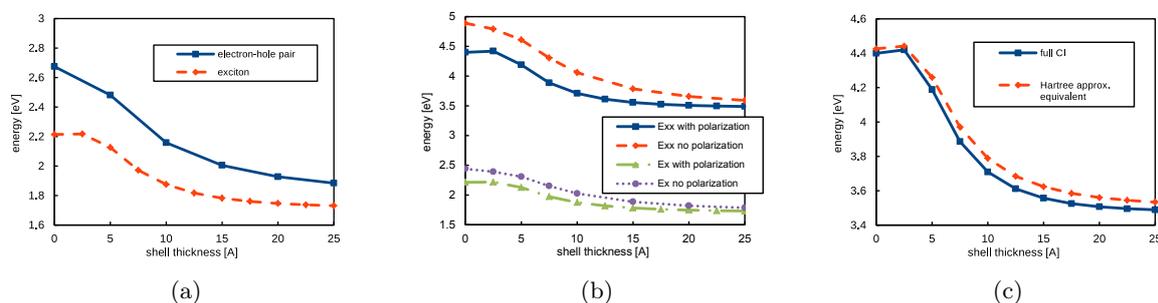


Figure 2: (a) Comparison between energies of single particle electron-hole pair (no Coulomb interaction) and exciton. (b) Comparison between exciton (Ex) and bi-exciton (Exx) energies calculated with and without the polarization effect. (c) Comparison between energies of bi-excitons using full CI calculations and the Hartree approximation equivalent.

4. Summary and conclusions

In conclusion we calculated exciton and bi-exciton energies in type-I CdSe and type-II CeSe/CdTe colloidal quantum dots. We showed that the electron-hole pairs indeed interact strongly and it is necessary to take into account the Coulomb interaction in energy level calculations. We proved that inclusion of the polarization effect is important because of the large dielectric constant mismatch at the dot/environment boundary. Finally, we showed that the configuration interaction is significant in the calculations of bi-exciton energies. Our theoretical results of ground state exciton energy agree very well with experimental measured results for CdSe QDs of radius 1.5 nm [11].

5. Acknowledgements

This research is funded by: EPSRC grant “Enhanced multiple exciton generation in colloidal quantum dots” and the Royal Society grant “High Performance Computing in Modeling of Innovative Photo-Voltaic Devices”. We acknowledge help from the N8 Research Partnership and Science and Technology Facilities Council for providing the computational resources used to conduct this research. We would also like to express our gratitude to Prof Wendy Flavell, Prof Paul O’Brien and Thomas Walsh for useful discussions.

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