# Many-Body Effects in CdSe/CdTe Coloidal Quantum Dots

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***Abstract*—We present a theoretical method for calculations of 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.**

## I. 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 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. For this process to occur the the energy of the exciton (which usually consists of a high energy electron-hole pair in the ground state) has to be at least twice as big as the energy of the effective optical gap $E_{e_n} - E_{h_0} \geq 2\left|E_{e_0} - E_{h_0}\right|$, 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. Theoretical predictions indicate that MEG has the potential to enhance the efficiency of a single gap cell from 33% to 42% [2]. Full realization of this potential requires that the energy threshold for MEG be minimized. An attractive interaction between excitons reduces the threshold by the biexciton binding energy, $B_{\mathrm{XX}}$, but this has been found to be small (-10 meV) for type I QDs [3]. Previous calculations of $B_{\mathrm{XX}} = E_{\mathrm{XX}} - 2E_{\mathrm{X}}$ in type II CdSe/CdTe QDs have found a large repulsion between excitons [4], while the experiment suggest the opposite, i.e., possibilities of larger attraction between excitons in the bi-exiton. To resolve this ambiguity and gain deep insight in the excitonic structure of CdSe/CdTe QD we investigate the many-electron effects, like correlation and exchange, on the excitonic structure in such class of QDs.

## II. Theoretical method

When compare to the single material QD, the core/shell structures can offer extra degree of freedom in designing a type-II structure in which the conduction and valence band states can be spatially separated. This separation is schematically shown in Fig. 1. In the case of QDs with a CdSe core and CdTe shell, the valence band states are, after certain shell thickness, strongly confined into the shell region, while conduction band states are either confined in the core or spread over the whole structure. Our approach can be divided into two parts: first we calculate the single-particle electron and states, and then we use those informations 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 used the 8-band $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian that includes effects of strain and piezoelectric at the core/shell interface. [4], [5] The Hamiltonian is parameterised by material parameters taken either from experiment or from *ab initio* hybrid density functional calculations using B3LYP and PBE0 functionals [6]. The large difference in dielectric permittivities of QD and colloid materials induces significant surface charges which strongly interact with the charges inside QD. [7], [8]. This effect is fully taken into consideration in our model by spatial variation of the dielectric constant $\epsilon = \epsilon(r)$ that enters the expression for the Coulomb integrals $V_{iljk}$. [9] The self-polarization term is calculated using the method developed by Bolcatto et al. [10] The many-body Hamiltonian contains only particle-conserving terms, and is given by

$$\begin{aligned} H &= \sum_i E_i \hat{e_i}^\dagger \hat{e_i} - \sum_i E_i \hat{h_i}^\dagger \hat{h_i} + \frac{1}{2}\sum_{ijkl} V_{iljk} \hat{e_i}^\dagger \hat{e_j}^\dagger \hat{e_k} \hat{e_l} \quad (1) \\ &+ \frac{1}{2}\sum_{ijkl} V_{iljk} \hat{h_i}^\dagger \hat{h_j}^\dagger \hat{h_k} \hat{h_l} - \sum_{ijkl} \left(V_{iljk} - V_{ikjl}\right) \hat{e_i}^\dagger \hat{h_j}^\dagger \hat{h_k} \hat{e_l}, \end{aligned}$$

To get excitonic states we write the Hamiltonian, Eq. (1), 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 $|i,j,k,l\rangle = |e_i\rangle\,|h_j\rangle\,|e_k\rangle\,|h_l\rangle$. [5].

## III. Results and Discussion

We apply our method to study CdSe/CdTe QDs with core radius of 15 Å and varying shell thickness. We assume the dielectric constant of QD, $\epsilon_{\mathrm{dot}} = 5.8$, and the colloid, $\epsilon_{\mathrm{col}} =$

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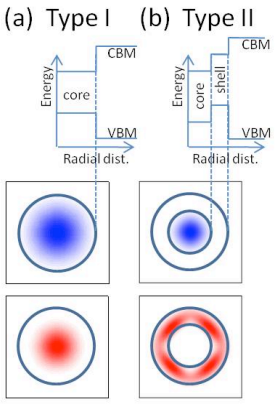


**Fig. 1:** Schematic of CV and VB band edges and electron and hole ground state quantum confining in: (a) QD with core only that is also type I, and (b) QD with core and shell that are type II alingn.

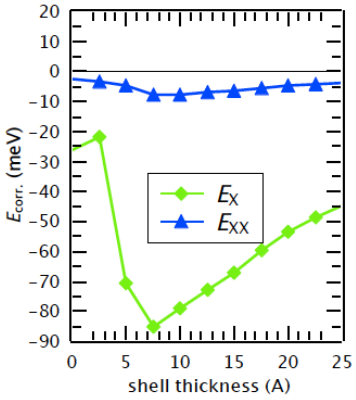


**Fig. 2:** Correlation energy of $E_{\mathrm{X}}$ (solid circles) and $E_{\mathrm{XX}}$ (solid squares) as a function of shell thickness on 15 Å core CdSe/CdTe core/shell QD.

1.1. For CI calculations we use the first 12 electron and 12 hole states (always including all shell 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, $E_b = E_X - E_{e0,h0}$. We have estimated very large exciton binding energy, $E_b = 450$ for CdSe QD. With the addition of CdTe shell, $E_b$ decreases to $\sim$ 200 meV, for the structure with shell thickness of 15 Å. This suggest crucial importance of the that the Coulomb potential in accurate determination of energy levels. To investigate the influence of exchange and correlation on the excitonic structure, in Fig. 2 we compare the full CI calculations obtained by diagonalization of the many-electron Hamiltonian in Eq. 1, with calculation that do not take into account the configuration interaction (but include exchange effects). To calculate many-body states that do not include the correlation effect we use only single particle ground states ($1s_{1/2}$ electron and $1s_{3/2}$ hole) in construction of the many-body Hamiltonian. We found that the correlation interaction amounts for between 2 meV to $\sim$10 meV on the exciton energies of various core/shell structures, with characteristic minimum at the shell thickens of 7.5 Å. However, the correlation effect is much more pronounced on the energy of bi-excitons, especially in case of type-II structures. Figure 2 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 $\sim$80 meV for type-II structures with 5–7.5 Å shell. The effect of correlations on $E_{\mathrm{XX}}$ is not just simply the double of the effect it has on $E_{\mathrm{X}}$, highlighting the importance of proper treatment of this many-body effect when predict the bi-exciton binding energy $B_{\mathrm{XX}}$ for MEG applications.

## IV. Summary and Conclusions

We showed that the many-body effects captured by configuration interaction are significant in the calculations of bi-exciton energies, and thus perturbative methods are not enough to accurately predict the energies of bi-exciton states. Our work provides a very important conceptual message – with appropriate treatment of relevant dialectic and many – electron effects like correlation and exchange the multi–band envelope function Hamiltonians in combination with CI are fully capable of capturing the all relevant effects determining excitonic structure of core/shell QD based MEG solar cells.

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