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In a conventional solar cell the energy of an absorbed photon in excess of the bandgap is wasted as heat. Multiple exciton generation (MEG) in colloidal quantum dots (QDs) uses this energy to instead produce additional free charges, increasing the photocurrent and cell efficiency [1]. 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, Bxx, but this has been found to be small (-10meV) for type I QDs [3]. Previous calculations of Bxx in type II CdSe/CdTe QDs have found a large repulsion between excitons [4]. Here, we show that, by taking into account CI, combinations of core diameter and shell thickness can be found for a CdSe/CdTe core/shell QD that result in large values of Bxx<0.
Our theoretical methodology is based on a 14-band **k.p** Hamiltonian, with the correct atomistic symmetry, C2v, of the zinc-blend structure, which incorporates the effects of band mixing between the p-bonding, s-anti-bonding and p-anti-bonding states, spin-orbit interaction, crystal-field splitting, strain between core/shells and piezoelectric potentials [5]. Exciton states were found using CI method that explicitly includes the effects of Coulomb interaction, as well as exchange and correlations between many-electron configurations. We paid particular attention to accurate modelling of electrostatic interaction between quasiparticles. The model includes surface polarization and self-polarization effects due to the large difference of dielectric constants at the surface of the QD. Relevant dipole matrix elements that couple different bands at the Gamma point as well as the dielectric constants of CdSe and CdTe at the transition energies are predicted using *ab initio* time-dependent density functional theory [6].
We conclude that: (i) it is not possible to predict biexciton binding using the Hartree approximation alone; it can only be predicted with a full CI Hamiltonian; (ii) CI predicts Bxx = -55 meV for structures with 0.5 nm thick shell; (iii) by ignoring the dielectric confinement, it is not possible to predict biexciton binding for structures with shell thickness > 0.75 nm; (iv) a proper calculation of Bxx requires the inclusion of correlations and surface polarization effects but the effect of self-polarization is negligible. The strong biexciton binding found is explained by a stronger reduction in the Coulmbic repulsion between holes than reduction in the attraction between electrons and holes on the addition of the CdTe shell layer, which is a consequence of 4 fold degeneracy of the h-ground state imposed by symmetry of the structure.

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