Multi-Exciton Generation in CdSe Nanocrystals

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One of the potential routes toward improving the efficiency of semiconductor solar cells involves the use of semiconductor nanocrystals (NCs) where generation of many electrons and holes following the absorption of a single photon becomes possible [1-3]. In this MEG process, the excess energy of a highly excited exciton is converted into excitation of additional electron-hole pairs instead of being dissipated through lattice vibrations. Here we discuss the fundamental elements necessary to realize MEG - the exciton and bi-exciton - in a CdSe nanocrystal [4]. We compute the electron and hole states using the atomistic tight-binding approach with model surface passivation technique and the one-pair (exciton) and two-pair (bi-exciton) spectrum using configuration interaction (CI) approach including direct and exchange Coulomb interactions. The Auger processes mixing the low-energy bi-exciton and highly excited exciton states are treated exactly. Our results indicate that the simple picture of exciton and bi-exciton as excitations of s-shells does not apply to CdSe NCs. We find that the top of the valence band is composed of four quasi-degenerate states well separated from the rest by a gap. This degeneracy leads to the characteristic band of low lying exciton states, exciton fine structure, controlled by the electron-hole exchange interaction. For a bi-exciton, the degeneracy leads to a manifold of closely lying strongly correlated states, resulting in a fine structure of bi-exciton spectra. The bi-exciton fine structure leads to a Stokes shift in the bi-exciton absorption and emission spectra. The effect of Auger broadening is found to be very weak , resulting in only minor shifts of intensity and line broadening of emission spectra.

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