TDDFT study of electronic excitations in Mn^{2+} and Co^{2+} doped ZnO quantum dots

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Colloidal quantum dots (QDs) doped with transition metal (TM) atoms (diluted magnetic semiconductor QDs) have drawn considerable attention in recent years due to the high potential for various applications in nanospintronics, biological imaging and magneto-optical electronics. Experimental analysis and design of these materials are often based on spectroscopic probes of dopant-specific electronic structure, such as charge transfer states and the extent of dopant-semiconductor hybridization. We present theoretical characterization of the low-energy (ultraviolet/visible/near-infrared) electronic transitions in Co^{2+} and Mn^{2+} doped ZnO quantum dots with sizes up to 300 atoms using linear response time-dependent hybrid density functional theory (TDDFT). To date, this is the first TDDFT study of the excitations in TM doped ZnO QDs.

This study focuses on i) the interpretation of optical transitions characteristic for doped ZnO nanocrystals and ii) investigation of the QD size effects and also the effects of concentration of TM atoms on the absorption spectra. Experimental spectral assignment is assisted by theoretical identification of two types of charge transfer (CT) states. The TM d-levels to ZnO conduction band (CB) charge transfer transitions ($ML_{CB}CT$) occur within two sub-bands which appear at the sub-band gap energy and span into the ZnO excitonic region. The $L_{VB}MCT$ transitions, which correspond to electron transfer from the ZnO valence band (VB) to the TM *d*-levels, are observed slightly above the ZnO band gap. The intensity of the CT transitions is defined by the symmetry of the participating TM d-levels and the degree of their delocalization. Because the position of the ZnO VB and CB strongly depend on the size of the quantum dot, the charge transfer bands shift to the lower energies with increasing dot size. In addition to charge transfer transitions, the Co^{2+} doped ZnO QDs also exhibit characteristic ligand field *d-d* excitations which do not depend on the QD diameter. Increase in the TM-dopant concentration leads to the broadening of spectral peaks, and to the quenching of the ZnO band gap intensity. New peaks associated with certain distribution and coupling between the dopant ions are identified. For QDs doped with more than one TM atom, the spectra of ferromagnetic and antiferromagnetic electronic configurations are discussed in detail.