Abstract

In the present thesis, we calculate the electronic structure of technologically important II-VI semiconductor quantum dots (QDs), employing *ab initio* methods based on density functional theory within pseudopotential approximation. We focus on calculating the optical absorption spectra of small clusters of zinc selenide (ZnSe) and then understand the effects of magnetic doping in ZnSe and zinc oxide (ZnO) clusters.

To begin with, a systematic study of size evolution of bare and surface passivated (ZnSe)$_n$ ($n = 1$–13, 33, and 34) clusters were initiated. Clusters with $n$ up to 5 have two dimensional (2D) structures and for larger sizes, cage-like three dimensional (3D) structures become favorable. At $n = 13$, the clusters start getting an atom inside the cage to attain a bulk-like local structure. However, for $n = 33$ and 34, hollow cages were energetically favourable as compared to cage/core isomers, where a Zn$_{28}$Se$_{28}$ hollow cage encapsulates a Zn$_{5}$Se$_{5}$ and Zn$_{6}$Se$_{6}$ core, respectively.

For the bare clusters, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) gap increases from a small value for ZnSe dimer, and beyond $n = 3$, the variation is small. On the other hand, the HOMO-LUMO gap of the clusters passivated with partially charged hydrogen atom decreases monotonically with increasing size. But the values remained higher compared to that of the bare clusters, indicating the opening up of gaps due to passivation. The optical absorption spectra and the corresponding optical gap of these clusters have been calculated within the framework of time-dependent local density approximation (TD-LDA). A decreasing trend in the optical gap as a function of the increasing cluster size has been observed. This trend compares well with the experimental results available on larger clusters in the literature, though the calculated values underestimate the optical absorption gap, as expected, within the LDA framework.

Stoichiometric Zn$_n$Se$_n$ clusters with $n = 13$ and 34, are stable and hence magic. However, when a single Mn impurity is substitutionally doped at a surface Zn site in (ZnSe)$_n$ ($n = 12$, 13, and 34) clusters, there is a change in magic behaviour. Calculations predict the existence of a new non-stoichiometric, magnetic, magic Zn$_{11}$MnSe$_{13}$ structure derived from doping of Mn in $n = 12$, with an additional Se atom attached to the impurity from inside the hollow cage. The stoichiometric Zn$_{n-1}$MnSe$_n$ QDs have a large magnetic moment of 5 $\mu_B$ that is predominantly localised on the Mn site. Whereas, the non-Stoichiometric cluster has a reduced magnetic moment of 3 $\mu_B$, due to strong covalent bonding of Mn atom with the excess Se atom and a small HOMO-LUMO gap. These results might provide insights in the possible growth mechanism of larger doped QDs and a new ground for understanding such QDs of compound semiconductors.
In the case of undoped (ZnO)$_n$, clusters with $n = 12$ and 34 are abundant and hence magic. But with Mn doping in QDs with $n = 12, 13, 34$ and 35, our calculations confirm a similar change in the magic nature, as observed in the case of Mn doped ZnSe clusters. Thus, O rich, non-stoichiometric Zn$_{12}$MnO$_{15}$ and Zn$_{34}$MnO$_{37}$ QDs are obtained when Mn is substituted in $n = 13$ and 35 that become magic. The magnetic moment in these stable clusters can be reduced to 1 $\mu_B$, as a maximum of five O atoms can bond directly with the doped impurity. Further, the Mn doped clusters can be viewed as nanocomposites, where an MnO$_x$ molecule ($x = 1$ to 4) is attached to (ZnO)$_n$ ($n = 12$ and 34) cage from outside. Similar results hold when Mn is replaced by a Cr impurity which leads to a neutral, fully oxidized, non-magnetic Zn$_{12}$CrO$_{15}$ nanocluster with a large HOMO-LUMO gap of 2.24 eV. These results provide new ground to understand doped nanostructures of ZnO and also shed light on magnetism in Mn doped ZnO thin films.