Chapter 5

Mn doped ZnO clusters and their composite structures

Undoped cages of (ZnO)$_n$ nanoclusters are magic with $n = 12$ and 34. However with Mn doping, our \textit{ab initio} calculations show that O rich, non-stoichiometric Zn$_{12}$MnO$_{15}$ and Zn$_{34}$MnO$_{37}$ nanoclusters become magic with 1 $\mu_B$ magnetic moment. The Mn doped nanoclusters can be viewed as nanocomposites, where a MnO$_x$ molecule ($x = 1$ to 4) is attached to (ZnO)$_n$ ($n = 12$ and 34) cage. Mn atom can be fully oxidized in these nanoclusters with the highest binding energy for $x = 3$. Further replacement of Mn by Cr 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. *

5.1 Introduction

Zinc oxide has attracted great attention as a wide band gap semiconductor, with reports of fabrication of blue LED [89]. Room temperature ferromagnetism was observed, when doped with impurities such as Mn [90]. With growing interest in nanomaterials, colloidal Mn doped ZnO (ZnO:Mn) nanoparticles [91] have been produced with potential applications in miniature optoelectronic devices, sensors and biomedical applications [92]. Most of these studies consider substitution of Mn impurity at a Zn site that results in Zn$_{n-1}$MnO$_n$ stoichiometric nanoclusters. Bulk ZnO films often have oxygen vacancies arising spontaneously [93]. However, here we show using \textit{ab initio} calculations that, Mn doping in small ZnO nanoclusters leads to strongly

*Much of the work presented in Chapter 5 will appear in print: S. P. Nanavati \textit{et al}., Phys. Rev. B (submitted and under review)
non-stoichiometric magic clusters with excess oxygen. These nanoclusters can be considered as composites made of a ZnO cage and a MnO$_x$ ($x = 1$-$4$) molecular unit.

*Ab initio* calculations on undoped, small ZnO nanoclusters have shown cage-like structures and (ZnO)$_{12}$ to be magic [67,68,94,95]. It is the smallest hollow cubic cage with six 4-membered (rhombus) and eight 6-membered rings (hexagons), similar to the well-known structure of (BN)$_{12}$ [96]. This molecular unit can be assembled to form more stable and larger nanoclusters of ZnO [97,98]. The clusters obtained from ZnO bulk powder by laser ablation method [18], have shown high abundance of (ZnO)$_n$ nanoclusters, with $n = 34$, 60, and 78 (magic clusters) shown in Fig. 1.2c. Substitution of a magnetic impurity, such as a Mn atom at a Zn site in Zn$_{12}$O$_{12}$ nanocluster, leads to a stable structures with 5 $\mu_B$ magnetic moment [99–101]. Here the $4s^2$ electrons of Mn participate in bonding, similar to Zn, leaving 5 unpaired $3d$ electrons on the Mn site. However, it is known that Mn can exist in multiple oxidation states, most commonly from +2 to +7. This was also found in our recent study on Mn doped ZnSe nanoclusters, where non-stoichiometric nanoclusters were found to be magic. This is due to the unpaired $3d$ electrons on Mn which facilitate further binding of Se atoms with favorable gain in energy (chapter 4). Among the Mn:(ZnSe)$_n$ ($n = 12$, 13 & 34), Zn$_{11}$MnSe$_{13}$ was shown to be strongly magic with the possibility of high abundance [69]. Therefore, we expected similar behavior in ZnO:Mn. However, we found that doping of one Mn in small ZnO nanoclusters leads to O-rich non-stoichiometric structures based on $n = 13$ & 35, and thereby changing the magic nature of ZnO nanoclusters. The atomic structures of these doped systems are composites of MnO$_x$ and ZnO nanocluster. These results are likely to have wider implications, not only for doped nanoparticles but also for the understanding of magnetism in transition metal doped ZnO, both in, thin films and bulk.

### 5.2 Computational Methodology

We use projector augmented wave pseudopotential [42] plane wave method [87], with spin-polarized, generalized gradient approximation (GGA) [35] for the exchange-correlation energy. The energy cut-off for the plane wave expansion has been set to 400 eV. The nanoclusters are placed in a large cubic supercell such that the distance between the outermost atom in the nanocluster and the simulation box boundary is at least 6 Å, that is large enough to keep interaction between the nanocluster and its periodic images negligibly small. The convergence criteria for energy and forces are taken to be $\sim 0.0001$ eV and $\sim 0.004$ eV/Å, respectively. The valence configurations of Zn, O, Mn, and Cr were taken, respectively, as $3d^{10} 4s^2$, $2s^2 2p^4$, $3d^5 4s^2$ and $3d^5 4s^1$. 
5.3 Results

We studied the effect of Mn doping in (ZnO)_n nanoclusters with n = 12, 13, 34, and 35. Our results show that n = 13 and 35 doped nanoclusters become magic with similar behaviour [102].

Figure 5.1:
Figure 5.1: Optimized atomic structures of (ZnO)$_{12}$ nanoparticles substitutionally doped with one Mn atom. White balls represent Zn, small red balls O, while blue balls show the Mn impurity. The values in the bracket are the relative energies in eV.

5.3.1 Mn:(ZnO)$_{12}$ clusters

Undoped (ZnO)$_{12}$ is a hollow, cubic, closed structure [94] composed of 8 six-membered and 6 four-membered rings (Fig. 5.1a). To find out the most favorable position for doping Mn in this cage, we place the Mn impurity at two different locations in the (ZnO)$_{12}$ cage, viz., inside the cage (endochemical doping) and on the surface, above two O atoms of the 4-membered ring. The optimized structures of Zn$_{12}$MnO$_{12}$, are shown in Figs. 5.1d and 5.1b, respectively. However, the energy of the endohedrally doped cluster was 1.48 eV higher than that of the surface doped cluster, though the lower energy cluster had an unfavourable feature of formation of Zn-Mn bond. Another structure was derived from O centered Zn$_{13}$O$_{13}$ (Fig. 5.2e), where the central O was removed and Mn was substituted at the surface Zn site. This structure lies ∼0.55 eV higher than Zn$_{12}$MnO$_{12}$-I. Finally, we substituted an Mn atom in (ZnO)$_{12}$ nanocluster at the surface Zn site. The resulting Zn$_{11}$MnO$_{12}$ nanocluster (Fig. 5.1e), had the highest binding energy (BE) among all the four clusters studied. Thus, the triply bonded surface cationic site is the most favourable position for doping Mn impurity in these clusters. This result is consistent with those reported earlier in the literature [99]. Experimentally, Mn was also shown to be substitutionally doped, replacing Zn, in the ZnO:Mn QDs of larger size [103].

These clusters have 5 $\mu_B$ magnetic moment (MM) because of the 5 unpaired 3d electrons in Mn. Further addition of O atoms, quench the magnetic moments. We added one O on Mn in two ways (i) from inside and (ii) from outside the cage. The resulting non-stoichiometric structure of Zn$_{11}$MnO$_{13}$ has a reduced MM of 3 $\mu_B$ in both the cases. The structure with O attached inside the cage (Fig. 5.1f) has a larger HOMO-LUMO gap as compared to the one with O attached
outside the cage (Fig. 5.1g). For more details refer to Table 5.1. Further addition of O to this cluster results in Zn$_{11}$MnO$_{14}$ (Fig. 5.1h) nanocluster with a MM of 1 $\mu_B$. The substituted Mn impurity is bonded to five O atoms: three triply bonded surface atoms and two single bonded O atoms, one from outside the cage and the other from inside. The binding energy (BE) of this cluster increased to 3.45 eV/atom and the gap is maintained at 0.9 eV. This structure is lower in energy by $\sim$ 2.13 eV as compared to the structure where two O atoms are embedded inside the cage (Fig. 5.1i). If one more O is attached to Zn$_{11}$MnO$_{14}$-I, either from inside or outside the cage, two nearly degenerate structures of Zn$_{11}$MnO$_{15}$-I (Fig. 5.1j) and Zn$_{11}$MnO$_{15}$-II (Fig. 5.1k), are formed. In the first case, the two O atoms inside the cage form a dimer and detach from the Mn impurity to get suspended inside the cage. However, the $E_g$ of the second structure is 0.73 eV as compared to 0.3 eV of the first one.

From this simple exercise of doping a Mn impurity in (ZnO)$_{12}$ cluster, following inferences can be drawn:

- Mn doping is energetically a favourable process.
- The BE of the doped cluster can be further enhanced by increasing the O concentration and making it non-stoichiometric.
- Mn can form a maximum of five bonds with O atoms. Out of these five O atoms, two form only single bond with Mn. This is evident from the case of stable Zn$_{11}$MnO$_{14}$-I.
- The magnetic moment (MM) of the cluster can be reduced from 5 to 1 $\mu_B$, but not 0, with the increase in oxygen concentration. Thus the maximum oxidation state of Mn observed in this case is +6.
- The HOMO-LUMO gap ($E_b$) of Zn$_{12}$O$_{12}$ is 2.35 eV. Upon Mn doping, it reduces to 0.8 eV for the Zn$_{11}$MnO$_{12}$ case, but increases slightly to $\sim$ 0.9 eV with the increase in O concentration.

Keeping the above inferences in mind, the behaviour of Mn doping in bigger sizes, viz., n=13, 34 & 35, are studied.

### 5.3.2 Mn:(ZnO)$_{13}$ clusters

We have explored five isomers of undoped (ZnO)$_{13}$, mostly based on the stable structures reported in the literature. The structures of undoped and Mn doped clusters of (ZnO)$_{13}$ are shown in Fig 5.2. We have studied five undoped isomers, viz.,
Figure 5.2:
Figure 5.2:
Figure 5.2: Optimized atomic structures of (ZnO)$_{13}$ nanoparticles substitutionally doped with one Mn atom. White balls represent Zn, small red balls O, while blue balls show the Mn impurity. The values in the bracket are the relative energies in eV. The numeric labels on 5.2a and 5.2b denote the substitutional doping sites for Mn.

(i) Zn$_{13}$O$_{13}$-I: Structure obtained by attaching a ZnO dimer between two 4-membered rings (rhombus) of Zn$_{12}$O$_{12}$ cage [68] as shown in Fig. 5.2a.

(ii) Zn$_{13}$O$_{13}$-II: Structure obtained by attaching a ZnO dimer been two 6-membered rings (hexagons) of Zn$_{12}$O$_{12}$ cage [68] as shown in Fig. 5.2b.

(iii) Zn$_{13}$O$_{13}$-III: As shown in Fig. 5.2c, a hollow distorted cage [104] with a 8-membered ring,

(iv) Zn$_{13}$O$_{13}$-IV: As shown in Fig. 5.2d, a hollow cage [67] and

(v) Zn$_{13}$r$_{13}$O$_{13}$-V: an O centered cluster similar to CdSe [16] and ZnSe [88] as shown in Fig. 5.2e.

We find that energetically, Zn$_{13}$O$_{13}$-I structure is the lowest, corroborating the results obtained by Wang et al., [68], while the O centered, filled cage and the hollow structures are, respectively, 0.95 eV and 0.437 eV higher in energy.

Mn can be substituted at different Zn sites in all the five undoped nanoclusters to yield the structure of Zn$_{12}$MnO$_{13}$ as shown in Figs. 5.2f to 5.2n. Even after Mn doping, the isomers derived from the lowest energy structure of Zn$_{13}$O$_{13}$-I & II, have a lower energy in comparison to the other two structures. In this case, Mn has been substituted at five different cation sites as indicated in Fig. 5.2a and 5.2b, viz.,

- structure 1 (Fig. 5.2f) in which Mn is at a doubly bonded Zn site which is the part of the attached ZnO dimer between two rhombus,

- structure 2 (Fig. 5.2g) in which Mn is at a doubly bonded Zn site which is the part of the attached ZnO dimer between two hexagons,

- structure 3 (Fig. 5.2h) where is a triply bonded neighbouring Zn site out of which one O is the part of the externally attached ZnO dimer,

- structure 4 (Fig. 5.2i): a triply bonded Zn site such that none of the bonded O atoms are the part of the externally attached ZnO dimer, and

- structure 5 (Fig. 5.2j), a triply bonded Zn site which is a part of the Zn$_{12}$O$_{12}$ cage.
The results show that energetically, structure 3 is slightly favourable, as its energy is lower by \( \sim 0.02 \text{ eV} \) from structure 1 and \( \sim 0.08 \text{ eV} \) as compared to other three structures. However, as shown later, more stable O rich, non-stoichiometric structures could be obtained from structure 1 & 2, as the doped Mn can be saturated by more and more O atoms, since it is only doubly coordinated. Mn doped at surface Zn site of the hollow cage-like structure (Fig. 5.2k) and O centered 3-D structure (Fig. 5.2n), are higher in energy by 0.53 & 0.93 eV, respectively, than the structure with lowest energy. The isomer in Fig. 5.2l is obtained from Zn\(_{13}\)O\(_{13}\)-V. In this case the surface Zn is substituted by a Mn atom and the central O is removed and attached from outside. Zn\(_{12}\)MnO\(_{13}\)-VIII (Fig. 5.2m), on the other hand, is obtained by attaching a Mn impurity from outside to the Zn\(_{12}\)O\(_{12}\) cage and then adding one more O to it. The magnetic moment of all these clusters is 5 \( \mu_B \), except for Zn\(_{12}\)MnO\(_{13}\)-VII, which is 3 \( \mu_B \).

To prepare O rich clusters, we further added one more O to the Mn impurity to obtain a 3 \( \mu_B \) MM, non-stoichiometric Zn\(_{12}\)MnO\(_{14}\) structures shown in Fig. 5.2o to 5.2v. In these cases, the additional O atom can be attached to the Mn impurity of the Zn\(_{12}\)MnO\(_{13}\) structures, either from inside or outside the cage. Thus the pair of figures 5.2o and 5.2p, 5.2q and 5.2s, 5.2r and 5.2t, 5.2u and 5.2v, represent the optimized Zn\(_{12}\)MnO\(_{14}\) structures when the additional O atom is attached from inside or outside the cages of Zn\(_{12}\)MnO\(_{13}\)-I, II, III, & V clusters, respectively.

After structural optimisation, Zn\(_{12}\)MnO\(_{14}\)-I is found to be the lowest energy structure. Here the three O atoms bonded to Mn form an elevated MnO\(_3\) crown such that, each of these O has two bonds: one with Mn and the other with a cage Zn atom. The additional O atom quenches the MM of the nanocluster from 5 to 3 \( \mu_B \) and the oxidation state of Mn becomes Mn\(^{4+}\). However, the BE and \( E_g \) increase to 3.43 eV/atom and 1.37 eV, respectively, which is highest among all the Zn\(_{12}\)MnO\(_{14}\) isomers.

Since, Mn can be in higher oxidation state, an O atom was further attached to Mn from outside the cage of Zn\(_{12}\)MnO\(_{14}\)-I to form a Zn\(_{12}\)MnO\(_{15}\) nanocluster (Fig. 5.2w). Interestingly this structure has the highest BE of 3.48 eV/atom among all the nanoclusters we have studied, but \( E_g \) is reduced to 0.31 and the MM to 1 \( \mu_B \). This is in contrast to ZnSe nanoclusters where Mn doping leads to non-stoichiometric nanoclusters with 3 \( \mu_B \) MM and the formation of Se-Se bonds in the cases where Se is in excess. Since oxygen has higher electronegativity than Se, Mn is in higher oxidation state (+6) in ZnO nanoclusters. Another isomer of Zn\(_{12}\)MnO\(_{15}\) (Fig. 5.2x) lies \( \sim 0.43 \text{ eV} \) higher in energy. In this isomer, an O atom was added from inside the cage.

We further explored a Zn\(_{12}\)MnO\(_{16}\) structure, as there was room for further addition of a O atom inside the cage. The added O atom, slips inside the cage to form a composite nanoparticle where MnO\(_4\) molecule is attached over the Zn\(_{12}\)O\(_{12}\) cage. The MM is retained at 1 \( \mu_B \), while the
values of the BE and \( E_g \) are, respectively, 3.47 eV/atom and 0.2 eV. This result shows that O addition is energetically less favorable. The MM lies on the added O due to a hole and it could be completely quenched to 0 \( \mu_B \) if the nanocluster is charged with an electron. On the other hand one can form cation of Zn\(_{12}\)MnO\(_{15}\) or substitute Cr in place of Mn to obtain Zn\(_{12}\)CrO\(_{15}\), both of which have zero MM. The Zn\(_{12}\)CrO\(_{15}\) nanocluster, which has similar structure as that of Zn\(_{12}\)MnO\(_{15}\), has \textit{exceptionally large \( E_g \) of 2.24 eV and can be expected to be highly stable} while for the cation of Zn\(_{12}\)MnO\(_{15}\), it is only 0.34 eV.

Zn\(_{12}\)MnO\(_{15}\) structure can also be independently obtained from Zn\(_{13}\)O\(_{13}\)-I, by replacing Mn with Zn (at site 1), attaching two O atoms to the impurity, one above and one below and then optimizing this structure. Similar procedure can be repeated for Zn\(_{12}\)MnO\(_{14}\), where only one O atom is attached to the impurity from inside the cage.

Another possible way to generate the Zn\(_{12}\)MnO\(_{15}\) structure is to attach an O atom to the Zn\(_{12}\)MnO\(_{15}\) cage from outside, while there is already an O inside the cage. Even in this case, the MnO\(_4\) crown was retained and O-O bonding appeared as shown in Fig. 5.2z. However, the energy of this optimized structure is \( \sim \) 0.36 eV higher than the one discussed earlier.

### 5.3.3 Mn:(ZnO)\(_{34}\) clusters

Recently Dmytruk \textit{et al.}, [18] observed (ZnO)\(_n\) nanoparticles with \( n = 34, 60, \) and 78 to be magic clusters by mass spectrum experiment. Further, Wang \textit{et al.}, [95] have shown that the optimized geometry of (ZnO)\(_{34}\), nanoparticle is a hollow, cage-like, 3-fold symmetric structure and not the previously nominated onion-like nested cage of (ZnO)\(_6\)@(ZnO)\(_{28}\) [18]. We have considered two structures: \textit{viz.}, a hollow one given by Wang \textit{et al.}, (Fig. 5.3a) and one more hollow structure composed of a Zn\(_{28}\)O\(_{28}\) base cage with six additional ZnO dimers attached from outside to its six, 4-membered rings (rhombus) (Fig. 5.3b). However, this structure has higher energy in comparison to the hollow structure by \( \sim \) 6.72 eV. Hence, we have substituted Mn in a hollow cage of Zn\(_{34}\)O\(_{34}\)-I at two different surface Zn sites, either on the 6-membered ring (Fig. 5.3c) or 4-membered ring (Fig. 5.3d). These nearly degenerate nanoclusters have 5 \( \mu_B \) MM and a BE of 2.40 eV/atom. However there is a variation in the \( E_g \) of these clusters, with the values of 0.69 and 0.40 eV for the I and II isomers of Zn\(_{33}\)MnO\(_{34}\). Increasing the O concentration in these nanoparticles results in a 3 \( \mu_B \) MM isomers of Zn\(_{33}\)MnO\(_{35}\), where the additional O is attached either inside (Fig. 5.3e) or outside the cage (Figs. 5.3f and 5.3g). Figure 5.3h depicts the structure of Zn\(_{33}\)MnO\(_{36}\) (1 \( \mu_B \) MM) where the Mn impurity is bonded to five O atoms, out of which three are nearest neighbours on the ZnO cage, while the other two are attached from either inside or outside the cage.
Figure 5.3: Optimized atomic structures of (ZnO)$_{34}$ nanoparticle substitutionally doped with one Mn atom. White balls represent Zn, small red balls O, while blue balls show the Mn impurity. The values in the bracket are the relative energies in eV.

5.3.4 Mn:(ZnO)$_{35}$ clusters

Similar to the case of Zn$_{13}$O$_{13}$, we find that when a ZnO dimer is attached to Zn$_{34}$O$_{34}$ cage from outside, a structure of Zn$_{35}$O$_{35}$ is obtained (Fig. 5.4a). When Mn is substituted on the surface Zn of this nanoparticle, a magnetic nanoparticle of Zn$_{34}$MnO$_{35}$ is obtained as shown in...
Fig. 5.4b. Further populating the doped Mn with O gives structures of Zn$_{34}$MnO$_{36}$, Zn$_{34}$MnO$_{37}$, and Zn$_{34}$MnO$_{38}$, as shown in Figs. 5.4c, 5.4d, and 5.4e, respectively. The O-O bond formation starts in the Zn$_{34}$MnO$_{38}$ structure.

5.3.5 Composite structures

We find that the lowest energy structures, magnetic moments, HOMO-LUMO gaps and energetics obtained by attaching the MnO$_{x}$ ($x = 1, 2, 3$ and 4) molecule to the hollow Zn$_{12}$O$_{12}$ and Zn$_{34}$O$_{34}$ cages, are similar to those obtained when Mn is doped in (ZnO)$_{n}$ ($n = 13 & 35$) clusters and then its stoichiometry is varied by increasing the oxygen concentration as discussed above. The formation energies of few different combinations of these composite clusters are given below.

\[ E(\text{MnO}_{4}) + E(\text{Zn}_{12}\text{O}_{12}) - E(\text{Zn}_{12}\text{MnO}_{16}) = 2.04 \text{ eV} \]

\[ E(\text{MnO}_{3}) + E(\text{Zn}_{12}\text{O}_{12}) - E(\text{Zn}_{12}\text{MnO}_{15}) = 2.70 \text{ eV} \]

\[ E(\text{MnO}_{3}) + E(\text{Zn}_{34}\text{O}_{34}) - E(\text{Zn}_{34}\text{MnO}_{37}) = 2.37 \text{ eV} \]

This indicates that Zn$_{12}$MnO$_{15}$ is a stable cluster as the formation energy is high. The second derivative of energy $\Delta^{2}E$ for Mn:(ZnO)$_{n}$ $n = 12, 13, 34, \text{ and } 35$ has been tabulated in Table 5.2 and calculated as given in Eq. 5.1 and 5.2 below,

\[ \Delta^{2}E = E(\text{Zn}_{n-1}\text{MnO}_{n}) + E(\text{Zn}_{n-1}\text{MnO}_{n+2}) - 2E(\text{Zn}_{n-1}\text{MnO}_{n+1}), \quad (5.1) \]

\[ \Delta^{2}E = E(\text{Zn}_{n-1}\text{MnO}_{n+1}) + E(\text{Zn}_{n-1}\text{MnO}_{n+3}) - 2E(\text{Zn}_{n-1}\text{MnO}_{n+2}). \quad (5.2) \]

The energy E used in these calculations is the lowest among the energies of various isomers studied for a given $n$. The results indicate that in the cases of $n = 12, 13, \text{ and } 35$, the structures with 1 $\mu_B$ MM, viz., Zn$_{11}$MnO$_{14}$ Zn$_{12}$MnO$_{15}$ & Zn$_{34}$MnO$_{37}$, respectively, calculated by Eq. 5.2, are the most abundant one. This is in contrast to the case of (ZnSe):Mn where the structure of Zn$_{11}$MnSe$_{13}$ with 3 $\mu_B$ MM is the most stable one [69]. Since, oxygen is highly electronegative, it can further oxidize Mn to reduce its magnetic moment up to 1 $\mu_B$. For the case of $n = 34$, the structure of Zn$_{33}$MnO$_{35}$ with 3 $\mu_B$ MM is stable.
Figure 5.4: Optimized atomic structures of (ZnO)$_{35}$ nanoparticle substitutionally doped with one Mn atom. White balls represent Zn, small red balls O, while blue balls show the Mn impurity. The values in the bracket are the relative energies in eV.

5.4 Electronic structure

Figure 5.5a shows the total density of states (DOS) for undoped and Mn doped (ZnO)$_{13}$ nanoclusters with different configurations. Also we have shown in Fig. 5.5b, the partial DOS (PDOS) of Mn 3$d$ states and the 2$p$ states of its nearest O atoms. For the undoped (ZnO)$_{13}$, the states arising from the 3$d$ orbitals of Zn ion at the site where Mn is substituted, are shown. In general the O 2$s$ state lie deep in energy at $\sim -17$ eV (not shown in the figure), followed by Zn 3$d$ states. For the undoped case, the O 2$p$ states lie near the HOMO and the $E_g$ is 2.00 eV. The 4$s$ states of Zn atoms become mostly unoccupied. Substitution of one Mn impurity on the surface Zn site reduces the HOMO-LUMO gap to 1.04 eV in Zn$_{12}$MnO$_{13}$. 
Table 5.1: Binding energy $E_b$ (eV/atom), HOMO-LUMO gap $E_g$ (eV), and magnetic moment MM (in $\mu_B$) of one Mn doped ZnO nanoparticles. The values in the bracket represent the corresponding results from GGA+U method.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$E_b$</th>
<th>$E_g$</th>
<th>MM</th>
<th>Structure</th>
<th>$E_b$</th>
<th>$E_g$</th>
<th>MM</th>
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<tr>
<td>Zn$<em>{12}$O$</em>{12}$</td>
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<td>0.0</td>
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<tr>
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<td>0.97</td>
<td>5.0</td>
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<td>2.00</td>
<td>0.0</td>
<td>Zn$<em>{12}$MnO$</em>{13}$-VII</td>
<td>3.29</td>
<td>0.39</td>
<td>3.0</td>
</tr>
<tr>
<td>Zn$<em>{13}$O$</em>{13}$-III</td>
<td>3.21</td>
<td>1.92</td>
<td>0.0</td>
<td>Zn$<em>{33}$O$</em>{34}$-I</td>
<td>3.37</td>
<td>1.88</td>
<td>0.0</td>
</tr>
<tr>
<td>Zn$<em>{13}$O$</em>{13}$-IV</td>
<td>3.20</td>
<td>1.88</td>
<td>0.0</td>
<td>Zn$<em>{34}$O$</em>{34}$-II</td>
<td>3.27</td>
<td>1.55</td>
<td>0.0</td>
</tr>
<tr>
<td>Zn$<em>{13}$O$</em>{13}$-V</td>
<td>3.18</td>
<td>1.98</td>
<td>0.0</td>
<td>Zn$<em>{33}$MnO$</em>{34}$-I</td>
<td>3.40</td>
<td>0.69</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-I</td>
<td>3.32</td>
<td>1.19</td>
<td>5.0</td>
<td>Zn$<em>{33}$MnO$</em>{34}$-II</td>
<td>3.40</td>
<td>0.40</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-II</td>
<td>3.31(3.29)</td>
<td>1.04(1.63)</td>
<td>5.0</td>
<td>Zn$<em>{33}$MnO$</em>{35}$-I</td>
<td>3.43</td>
<td>0.52</td>
<td>3.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-III</td>
<td>3.32(3.30)</td>
<td>0.64(1.27)</td>
<td>5.0</td>
<td>Zn$<em>{33}$MnO$</em>{35}$-II</td>
<td>3.42</td>
<td>0.36</td>
<td>3.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-IV</td>
<td>3.31(3.30)</td>
<td>1.15(1.86)</td>
<td>5.0</td>
<td>Zn$<em>{33}$MnO$</em>{36}$</td>
<td>3.42</td>
<td>0.67</td>
<td>1.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-V</td>
<td>3.31(3.30)</td>
<td>0.79(1.64)</td>
<td>5.0</td>
<td>Zn$<em>{35}$O$</em>{35}$</td>
<td>3.35</td>
<td>1.70</td>
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</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-VI</td>
<td>3.30</td>
<td>0.65</td>
<td>5.0</td>
<td>Zn$<em>{34}$MnO$</em>{35}$</td>
<td>3.39</td>
<td>0.69</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-VII</td>
<td>3.28</td>
<td>1.63</td>
<td>5.0</td>
<td>Zn$<em>{34}$MnO$</em>{35}$</td>
<td>3.39</td>
<td>0.69</td>
<td>5.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{13}$-IX</td>
<td>3.28</td>
<td>0.72</td>
<td>5.0</td>
<td>Zn$<em>{34}$MnO$</em>{36}$</td>
<td>3.43</td>
<td>1.38</td>
<td>3.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{14}$-I</td>
<td>3.43</td>
<td>1.37</td>
<td>3.0</td>
<td>Zn$<em>{34}$MnO$</em>{37}$</td>
<td>3.45</td>
<td>0.29</td>
<td>1.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{14}$-II</td>
<td>3.40</td>
<td>0.64</td>
<td>3.0</td>
<td>Zn$<em>{34}$MnO$</em>{38}$</td>
<td>3.44</td>
<td>0.27</td>
<td>1.0</td>
</tr>
<tr>
<td>Zn$<em>{12}$MnO$</em>{14}$-III</td>
<td>3.40</td>
<td>0.53</td>
<td>3.0</td>
<td>Zn$<em>{12}$CrO$</em>{15}$</td>
<td>3.56</td>
<td>2.24</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 5.5: DOS of ZnO:Mn and DOS of Zn12CrO15.
Figure 5.5: (a) Density of states (DOS) and (b) partial DOS (PDOS) of (ZnO)$_{13}$, for selected ZnO:Mn, and (c) Zn$_{12}$CrO$_{15}$ nanoclusters. In (d) the DOS and PDOS of Zn$_{12}$MnO$_{13}$-II are plotted with and without GGA+U correction. In all the above cases, DOS is smeared by a Gaussian of standard deviation 0.1 eV. Except for (d), the HOMO is shifted to 0 eV. The solid red line in the upper half and the dashed green line in the lower half of each plot in (a), (b) and (d) represent, respectively, the spin-up (↑) and spin-down (↓) components of the DOS. The Zn[3$d^{10}$] states lying between -8.0 to -4.0 eV have been trimmed horizontally to save space. For PDOS in (b), the red solid line represents Mn 3$d$ orbitals whereas, the dashed green curve shows the PDOS arising from $p$ orbitals of the nearest neighbour O. For Zn$_{12}$O$_{13}$, top panel of (b), the PDOS of 3$d$ orbitals of Zn which is later substituted by Mn in Zn$_{12}$MnO$_{13}$-II, is shown. For Zn$_{12}$MnO$_{16}$, dotted pink line represents the $p$ orbital of the O which when added to Mn atom, forms the part of the Zn$_{12}$O$_{12}$ cage. In (c), the DOS (lower panel) and PDOS (upper panel) of Zn$_{12}$CrO$_{15}$ are plotted. For PDOS, the Cr[3$d$] states are plotted in solid red curve, while the 4$p$ states of the nearest neighbour O are plotted in dashed green lines. In (d), DOS of Zn$_{12}$MnO$_{13}$-II are plotted with and without GGA+U correction to the Mn[3$d$] orbitals, similar to that of (a), but without shifting the HOMO to 0 eV for comparison. The PDOS is also plotted in the same graph where the dotted pink line represent the Mn 3$d$ orbitals whereas, the dotted-dashed blue curve shows the PDOS arising from $p$ orbitals of the nearest neighbour O, similar to (b).

Table 5.2: Second derivative of energy $\Delta^2E$ calculated as in eq. 5.1 for (ZnO)$_n$Mn, $n = 12$-I, 13-I, 34-I, and 35-I. For $n = 12$-II, 13-II, and 35-II, $\Delta^2E$ is calculated by eq. 5.2

<table>
<thead>
<tr>
<th>Structure</th>
<th>12-I</th>
<th>12-II</th>
<th>13-I</th>
<th>13-II</th>
<th>34-I</th>
<th>35-I</th>
<th>35-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta^2E$ (eV)</td>
<td>0.72</td>
<td>1.82</td>
<td>1.47</td>
<td>1.75</td>
<td>1.73</td>
<td>1.40</td>
<td>1.75</td>
</tr>
</tbody>
</table>

In this case the spin-up states of Mn 3$d$ orbitals hybridize with the $2p$ states of O atoms and form the HOMO, while the LUMO is composed of Mn 3$d$ spin-down states. There is a net MM of 5 $\mu_B$ in this cluster. However, with the addition of one more O, MM reduces to 3 $\mu_B$ in Zn$_{12}$MnO$_{14}$ but the $E_g$ increases slightly to 1.37 eV, because of higher symmetry of the structure. The depleted Mn 3$d$ levels shift to higher BE due to more positive charge on Mn ion, a trend which is persistent even for higher O-rich species. In Zn$_{12}$MnO$_{15}$, where one more O is attached from outside the cage, MM gets saturated to 1 $\mu_B$, but because of the strong hybridization of Mn 3$d$ and O 2$p$ orbitals, their levels become tightly bonded, thus making this cluster most stable with a BE of 3.48 eV/atom. However, $E_g$ decreases to 0.31 eV as the LUMO is composed of spin-up Mn 3$d$ orbital which gets shifted just above the HOMO. Finally in Zn$_{12}$MnO$_{16}$, the added O detaches from Mn and becomes a part of the Zn$_{12}$O$_{12}$ cage. While the MM is retained at 1 $\mu_B$, the PDOS reveals that the MM is due to the unpaired $p$ electron on the added O (dotted pink curve in the PDOS). Its spin-down unoccupied state becomes LUMO thereby making $E_g$ very small (0.2 eV). Since Zn$_{12}$MnO$_{15}$ is the most stable and Zn$_{12}$MnO$_{16}$ is slightly higher in energy, Zn$_{12}$MnO$_{15} \Rightarrow$ Zn$_{12}$MnO$_{16}$ conversion is realizable by controlling oxygen pressure, like a monostable oscillator. This will lead to switching of spin between surface Mn and caged oxygen.
Charging this cluster with an electron quenches the MM to zero as the \( p \) orbital of the added O gets fully saturated, thereby weakening the bond between \( \text{Zn}_{12}\text{O}_{12} \) and the \( \text{MnO}_4 \) molecule, as revealed from the increase in the average bridging Zn-O bond lengths.

In Fig. 5.5c, the DOS and PDOS of \( \text{Zn}_{12}\text{CrO}_{15} \) nanocluster are plotted, which show zero MM. The DOS depicts a large gap of \( \sim 2.24 \) eV. The corresponding PDOS, where the Cr \( 3d \) and \( 4s \) states are plotted along with the \( 2p \) orbitals of the four nearest neighbour O atoms, show that Cr \( d \) orbitals are shifted to higher BE and have a strong hybridization with O \( p \) orbitals. The HOMO is composed of O \( p \) states while the LUMO is made up of hybridized Cr \( 3d \) states and O \( 2p \) states. The Cr atom gets completely oxidized with an oxidation state of \( \text{Cr}^{+6} \), thereby pushing the unoccupied \( 3d \) states much above the HOMO. Thus, we find that with the increase in the non-stoichiometry in the nanoclusters by adding more and more O atoms, the exchange-splitting in Mn and Cr \( 3d \) orbitals reduces and becomes zero for the fully oxidized cases of \( \text{Zn}_{12}\text{MnO}_{15} \) cation, \( \text{Zn}_{12}\text{MnO}_{16} \), and \( \text{Zn}_{12}\text{CrO}_{15} \).

In Fig. 5.5d, the DOS and P-DOS of \( \text{Zn}_{12}\text{MnO}_{13}-\text{II} \) are replotted, for GGA and GGA+U case, separately. The two peaks near the HOMO in GGA, which are primarily made up of hybridization of Mn \( d \) states with O \( p \) states, merge to form a single peak in GGA+U. Because of this change, the DOS of GGA+U gets shifted to lower energies as compared to that of GGA, explaining the increase in HOMO-LUMO gap (Table 5.1). The Mn \( d \) orbitals in GGA+U, become more localized, shift to lower energy and hybridize less with the nearest O \( p \) states, as compared to that plain GGA. MM, in both the cases, remains unchanged to 5 \( \mu_B \). The electronic charge density of the valence electrons in the magic \( \text{Zn}_{12}\text{MnO}_{15} \) cluster is shown in Fig. 5.6. Its atomic structure consists of a \( \text{MnO}_4 \) molecule that is attached to \( \text{Zn}_{12}\text{O}_{11} \) cage. The total valence charge density (Fig. 5.6a) shows that the Zn-O bonds in the cage are ionic with some covalent character. However in Mn-O bonds, there is a charge transfer from Mn to O atoms, the most significant being in the case of the terminal O. The spin-polarization \( (\rho_\uparrow - \rho_\downarrow) \) shows that it is localized on Mn with some polarization on the surrounding O, resulting in 1 \( \mu_B \) MM. However, there is some spin-down polarization on the two surrounding O. This is also evident from the strong occupied spin-down peaks in the PDOS (Fig. 5.5b). These two O atoms are strongly bonded to Mn atom as their bond lengths are smaller (1.59 & 1.7 Å). The excess and depletion of charge have been calculated by subtracting from the total charge, the charge densities of the \( \text{MnO}_4 \) molecule and the \( \text{Zn}_{12}\text{O}_{11} \) cage, keeping the atomic positions the same as in the composite nanocluster. It is clear that there is a significant charge transfer from the cage to O ions of the molecule. There is also some re-organization of the charge on the \( \text{MnO}_4 \) molecule.

The effects of Mn doping in \( n = 35 \) case are similar to those discussed above for \( n = 13 \).
Figure 5.6: Isosurfaces of (a) total valence charge density ($\rho_↑ + \rho_↓$) in similar orientation as in Fig. 5.2, (b) spin-polarization ($\rho_↑ - \rho_↓$) of Zn$_{12}$MnO$_{15}$ nanocluster. The large dark magenta lobes represent the net spin-up states mostly localized on Mn atom, while the blue region shows the net spin-down states, localized on the two neighbouring O ions. (c) and (d) show, respectively, depletion and excess of charge when the sum of the charge densities of Zn$_{12}$O$_{11}$ cage and the MnO$_4$ molecule keeping their atomic positions the same as in Zn$_{12}$MnO$_{15}$, is subtracted from the total charge density. The Zn atoms of the Zn$_{12}$O$_{11}$ cage donate charge to the O atoms of the MnO$_4$ molecule.
The results show that the behavior of ZnO:Mn nanoclusters can be classified into two categories according to their stability. For \( n = 34 \), nanocluster with \( 3 \mu_B \) MM and atomic configuration of \( \text{Zn}_{33}\text{MnO}_{35} \) is the most stable structure. Whereas, \( \text{Zn}_{11}\text{MnO}_{14}, \text{Zn}_{12}\text{MnO}_{15} \) and \( \text{Zn}_{34}\text{MnO}_{37} \) (Fig. 5.4d) structures with \( 1 \mu_B \) MM are the most stable for \( n = 12, 13 \) & 35, respectively. Note that for \( \text{(ZnO)}_{35} \), the atomic structure is obtained by attaching a Zn-O dimer on the surface of \( \text{(ZnO)}_{34} \) (Fig. 5.4a), just like the \( \text{(ZnO)}_{13} \) case. The BE, MM, and \( E_g \) in all the cases are given in Table 5.1. Thus with Mn doping, the magic clusters become non-stoichiometric with reduced magnetic moments.

5.5 Conclusion

The \textit{ab initio} calculations of Mn doped \( \text{(ZnO)}_n \) \( (n = 12, 13, 34, \) and 35) nanoclusters show the formation of non-stoichiometric, magic nanoclusters of \( \text{Zn}_{12}\text{MnO}_{15} \) and \( \text{Zn}_{34}\text{MnO}_{37} \) with a reduced magnetic moment of \( 1 \mu_B \). This is in contrast to \( n = 12 \) and 34 magic undoped nanoclusters. Thus Mn doping changes the magic nature and the nanoclusters formed by doping \( \text{(ZnO)}_{13} \) are the most stable with highest binding energy. Since O is highly electronegative, it fully quenches the magnetic moment of Mn thereby forming a composite structure, where a MnO \(_4\) molecule is attached to stable cages of \( n = 12 \) and 34. GGA+U corrections make the Mn \( d \) orbitals more localised. These orbitals shift to lower energy, thereby opening the HOMO-LUMO gap. However, there is no change in the magnetic moment and the binding energy reduces slightly, as compared to GGA calculations. We also find a neutral \( \text{Zn}_{12}\text{CrO}_{15} \) cluster with a large HOMO-LUMO gap. We believe that these results would have important implications for the understanding of magnetism in \( \text{ZnO} \) nanostructures as well as thin films of Mn doped ZnO, for which recent experiments suggest mixed and higher oxidation states of Mn, \textit{viz.}, Mn\(^{+3}\) and Mn\(^{+4}\).