Resembling the molecules and atoms, the electronic structure in solid is of fundamental importance. The electron distributions, van der Waals and electrostatic interactions are responsible for the formation of solids. The valence electrons play crucial role in the bonding of solids. Also, the electronic distribution can be considerably modified from the isolated atom. Consequently, for a description of solid electronic structure must be taken into account carefully. Thus, in this chapter we will begin MO treatment of band theory. Later we will discuss the different tools available for studying electronic structure of solids. Our results of the charge density, band structure, and density of states (DOS) analyses on pure and Mn-doped and pure ZNO will be presented. We will illustrate from the band structure and DOS calculations that Mn doping reduces the band gaps of the three phases of Zno. By examination of the partial DOS, it will be further shown that this reduction in band gaps is due to generation of additional bands arising from the Mn impurities. Finally, the decreased band gaps will be used to suggest that doping with Mn in ZnO makes this material suitable to be used for photoelectrochemical splitting of water to produce hydrogen.
**Introduction**

**3.1 Band theory and molecular orbitals**

Molecular orbitals are formed by splitting the atomic orbitals to give discrete energy levels. However, when a large number of atomic orbitals are mixed, the resulting energy levels no longer remain distinct. In solids, a large number of atomic orbitals interact with each other to form crystal orbitals; these are often called as bands.

![Diagram of molecular orbitals](source_ref1)

*Figure 3.1. Schematic representation of bands from molecular orbitals. (Source ref 1)*

The formation of these bands can be understood by taking a simplistic example of linear chains of Hydrogen atoms.

---

Linear Hydrogen chain
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The symmetry adopted linear combination give the bonding and anti bonding orbitals as follows:

\[
\psi_{bonding} = \chi_1 + \chi_2 + \chi_3 + \chi_4 \ldots
\]  

(3.1.1)

\[
\psi_{anti-bonding} = \chi_1 - \chi_2 + \chi_3 - \chi_4 \ldots
\]  

(3.1.2)

In solids, the formation of these symmetry-adopted linear combination is done by formation of Bloch’s equations.

\[
\psi_k = \sum_n e^{ikna} \chi_n
\]  

(3.1.3)

For \( k = 0 \)

\[
\psi_0 = \chi_1 + \chi_2 + \chi_3 + \chi_4 \ldots
\]

For \( k = \frac{\pi}{a} \)

\[
\psi_{\frac{\pi}{a}} = \chi_1 - \chi_2 + \chi_3 - \chi_4 \ldots
\]  

(3.1.4)

Clearly, the Bloch’s function at 0 and \( \frac{\pi}{a} \) represents the bonding(valance band) and anti-bonding orbitals(conduction band) respectively.

The band structure is calculated as follows:

\[
E_k = \frac{\langle \psi_k | H | \psi_k \rangle}{\langle \psi_k | \psi_k \rangle}
\]  

(3.1.5)

The calculations of band structure (BS) and Density of states (DOS) are central to computational material science. BS and DOS are very useful to predict various properties of solids. These are qualitatively explored using the basic molecular orbital picture to obtain useful information about that structure, reactivity and molecular interactions. BS
represents the molecular orbitals in a solid. It is a plot of energy verses \( k \), where \( k \) is the wave vector that represents the phase of atomic orbital and the wave length of electronic wavefunction. The number of lines in a bandstructure plot is equal to the number of orbitals in the unit cell. Molecular orbitals can be used as a guide to predict and interpret the BS and DOS. The center of gravity of each band is determined qualitatively using the MO diagram. Molecular overlap determines that whether a band will run uphill or downhill or flat. The band picture can also predict that the electrons are localized or delocalized within the solid. Wide band represents delocalization of electrons with the large intermolecular overlap. Whereas narrow bands represents the localization of electrons with weak intermolecular overlap.

Using the above discussed tools, we have performed charge density, band structure and DOS calculations for pure and Mn-doped ZnO in order to develop an understanding photoelectrochemical behavior for possible use in photosplitting of water to produce hydrogen.

### 3.2 Mn doped ZnO: Hydrogen production

The problem of hydrogen production is clearly another big hurdle to practically utilize the hydrogen economy. A possible solution to overcome this difficulty is to use the solar light driven photoelectrochemical (PEC) splitting of water. Many research efforts have been made to produce the hydrogen by using such PEC approaches [1-6]. The most important issue in such process is to optimize the semiconductor properties of the working electrode. The electrode should be modified in a way that will facilitate not only the efficient absorption of solar light but also quick separation and migration of photogenerated charge carriers across electrode – electrolyte junction in the desired direction. After the first report by Fujishima and Honda, who used single crystal TiO₂ as photoanode to demonstrate the feasibility of PEC splitting of water, considerable progress has occurred [7]. Gerischer presented a thorough overview of the theory of the process [8], while Nozik provided a good account of the various PEC devices [9]. Heller made an
excellent analysis of efficiencies of various PEC systems involving the use of different semiconductors [10]. Yet, the development of an efficient and commercially viable PEC device for this purpose remains an unfinished task, and the quest for a semiconductor having ideal optical properties and well aligned band edge energetic still continues [6].

Zinc oxide (ZnO) finds a wide range of scientific and technological applications [11-13]. Most applications depend on its defect chemistry. The interest in doping ZnO arises from the possibility of tailoring its electrical, magnetic and optical properties for such applications [14-17]. The doping of transition metal elements into ZnO offers a feasible mean for fine tuning its optical behavior, particularly the band gap. Mn doped ZnO has currently attracted much attention for its potential use in the novel memory and optical devices, varistor in multicomponent systems, ferromagnetism and magneto-optical applications at room temperature [18-20]. However, severe suppression of the luminescence of Zn$_{1-x}$Mn$_x$O even at very low doping levels is also reported [21]. Mn doping in ZnO is known to reduce its band gap for low concentration doping (< 3 mol% of Mn). For higher concentrations (> 3 mol%) the band gap increases as expected on the basis of virtual crystal approximation (VCA), as the band gap of MnO is ~ 4.2 eV [22]. There are only few reports on Mn incorporated ZnO nanostructures and nanostructured thin films and their optical and structural properties still need to be explored [23]. Besides, the behavior of Mn incorporated nanocrystalline ZnO in PEC splitting of water possibly remains unstudied so far. In our previous reports we presented the PEC splitting of water using Cr, Ni, Cu and Ru incorporated ZnO [15-17]. As thorough experimental analysis of zinc oxide with each type of dopant is quite demanding, it can be quite effective to use first principle based density functional theory calculations in short listing of dopants that have promise for enhanced photoelectrochemical property of ZnO. Such calculations[25-28] are quite useful in for determination of the trends in band gap upon doping of given material. The recent investigation with Mn incorporated ZnO has also shown that it is an even better choice for above application.
3.3 Methodology

All calculations were performed using VASP (Vienna ab-Initio simulation packages) implementation of DFT within the generalized gradient approximations (GGA). We have used projector augmented wave (PAW) approach to evaluate all the properties.

We simulated the effects of Mn doping using a 2x2x2 (32 atoms) ZnO supercell and replacing one Zn atom by Mn atom, amounting 12.5% doping amount. Calculated crystal parameters of the unit bulk wurtzite ZnO are \( a = 3.28 \) Å and \( c = 5.28 \) Å, in good agreement with experimental data. A Monkhorst-Pack mesh of 2x2x2 K points was used in sampling. The integrals over the Brillouin zone, and a much finer mesh was used in accurate determination of the density of electronic states. Kohn Sham wave functions were represented in plane-wave basis with an energy cutoff of 520 eV, and the charge density was represented with a plane-wave basis with the cutoff energy of 460 eV. Structural optimization was carried out by using Hellman-Feynman Forces to minimize total energy. To check the convergence of our results, we carried out our test calculation with higher energy cutoff on the plane-wave basis and finer mesh of K-points, making sure that there are negligible changes in energy and in the electronic structure. We have employed DFT with plane wave pseudopotential based approach using projector augmented wave (PAW) as implemented in VASP code. A kinetic energy cutoff of 520 eV was employed for primitive cell calculation, while a 460 eV cutoff was taken for full unit cell.

Calculations all geometry optimization were carried out without geometry constraint. All forces were calculated using Hellman-Feynman theorem. Geometries were considered and optimized with maximum force found smaller than 0.01 eV/Å. Real space projection were used to evaluate PAW character of wave functions. The primitive cell of ZnO was built from the crystal structure of ZnO that was taken from experimental data and a 2x2x2 K-Points grid generated by Monkhorst-Pack scheme was applied to it.
3.4 Results and Discussions

In order to identify the way Mn doping influences the electronic states of ZnO, the first-principle DFT computations were made to explore the band structures of doped and undoped ZnO (Fig. 8, Table 5). Since, DFT considers the electronic ground state, the band gap predictions from it are approximate. One needs to use hybrid functional or self interaction corrections in DFT to accurately estimate the absolute bandgap energies. While, valence band properties and offsets are described accurately well with DFT, the conduction band properties cannot be portrayed properly. The present set of computations was focused more towards the qualitative understanding on the way band gap energy of Mn doped ZnO.

<table>
<thead>
<tr>
<th>a (Å)</th>
<th>c/a</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2495</td>
<td>1.6024</td>
<td>Experimental [24]</td>
</tr>
<tr>
<td>3.28</td>
<td>1.61</td>
<td>GGA-PBE [this work]</td>
</tr>
</tbody>
</table>

Table 3.1 Lattice parameters of wurtzite ZnO.

As is clear from the Fig3.2 that top of the valence band and bottom of the conduction band is at G point of Brillouin zone, suggesting that doped and Undoped ZnO is a direct band gap material.
Figure 3.2. Bandstructure of ZnO unit cell at GGA PBE method.

Figure 3.2 illustrates the bandstructure of ZnO unit cell, the peaks the conduction band are primarily formed by p orbital of Oxygen atoms. However the band near -18 eV is due the s orbital of oxygen. The conduction band is formed by the overlap of d orbitals of Zn and p orbitals of p orbitals of Oxygen. The calculated band gap at GGA PBE method was found to be 0.78 eV. The calculated band is in agreement to the previously reported values. However, the calculated band gap is significantly underestimated. It is well established that GGA method underestimates the band gap.

ZnO Density of States shows clear agreement with band structure. The fermi level is set to zero in all density of states and bandstructure calculations. Figure 3.3 showcase the projected density of states (PDOS) of ZnO unit cell. PDOS clearly supports the bandstructure with clearly identifying the contribution of different orbitals. PDOS confirms that the conduction band of ZnO is mainly formed by Zn(d) and O(p) orbitals.
Figure 3.3 Total density of states of ZnO unit cell at GGA PBE level.

Figure 3.4 PDOS of ZnO unit cell at GGA PBE level.
The exchange and correlation functionals within DFT are based on various approximations. LDA is based on homogeneous electron gas approximation. Furthermore, the interactions are calculated based on mean field approximation. This approximation cannot calculate highly sensitive properties like band gaps.

Various attempts are made to deal with the problem in DFT. One effective approach is use many body formalism. Another widely used method is LDA (or GGA) + U method. The LDA+U method is used to take care strong electronic correlation by adding Hubbard-like Hamiltonian. Resulting energy depends on the site specific electronic occupancy. The band gaps calculated by LDA+U methods are improved when compared to experimental values.

Figure 3.5 illustrates the bandstructure of ZnO unitcell at GGA+U level, the band gap by GGA+U found to be 1.27 eV. This band gap is clearly improved when compared to without the introduction of U.

![Figure 3.5 Band structure of ZnO unit cell at GGA+U PBE level.](image)
**Figure 3.6** Total density of states of ZnO unit cell at GGA+U PBE level.

**Figure 3.7** PDOS of ZnO unit cell at GGA+U PBE level.
The effect of U electronic structure can be explored by comparing the PDOS of ZnO unit cell with and without inclusion of U. It is clear from figure 3.7 and figure 3.4 that inclusion of U shifts the Zn(d) peaks near fermi level.

The band structure of ZnO 2x2x2 is presented in figure 3.8. When comparing the band structure of unit cell and super cell, the band of super cell are overlapped. Due to this overlaps it becomes difficult to interpret the band structure of super cells. This overlapping of bands arises due to the band folding.

However, the band gap does not change with the size of cell. Figure 3.9 shows the total DOS of ZnO 2x2x2 super cell. The projected DOS of ZnO super cell are similar to that of PDOS of unit cell.

Figure 3.10 shows the charge density slice of ZnO 2x2x2 super cell and Mn doped ZnO. From the charge density slice of Mn doped ZnO it is clear that charge density on Mn atom is lower when compared to the charge density on Zn atom. Also, the charge density on oxygen atoms surrounding Mn atoms is higher when compared to oxygen atoms surrounding Zn atoms. Clearly, Mn doping significantly enhance the charge transfer.
Figure 3.8 Bandstructure of ZnO \(2 \times 2 \times 2\) supercell GGA+U PBE level.

Figure 3.9 Charge density slice of (a) \(2 \times 2 \times 2\) supercell (b) \(2 \times 2 \times 2\) Mn doped ZnO 6.25% Mn.
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**Figure 3.10** Total DOS of ZnO 2x2x2 supercell GGA+U PBE level.

**Figure 3.11** PDOS of ZnO 2x2x2 supercell GGA+U PBE level.
From the above discussion it is clear that Mn doping influences the charge transfer in ZnO. Motivated by the charge transfer we study the band structure and DOS of Mn doped ZnO, to reduce the ZnO band gap and make this material suitable for photoelectrochemical splitting of water for H$_2$ production. Produced H$_2$ can be stored by suitable storage material.

**Figure 3.12** Total DOS of Mn doped ZnO by GGA PBE method.

**Figure 3.13** PDOS of Mn doped ZnO by GGA PBE
Conclusions:

We have discussed various tools to investigate the electronic structure of solid. We have investigated the lattice parameters, charge density, bandstructure and density states of ZnO unitcell, superecell and Mn-doped ZnO supercell. Our results suggest that Mn doping at low concentrations can reduce the band gap of ZnO. Due to the reduced band gap and high charge transfer Mn-Doped ZnO can be used for electro photochemical splitting of water for hydrogen production. Interestingly, our experimental collaborators could synthesize this material at low Mn concentrations. They have found good photo electrochemical activity of this material for splitting of water.

References:


