

Bonding Formation and Orbitals Nature of ZnO Structure

Ghadah S. Alghamdi and Ali. Z. Alzahrani

Department of Physics, Faculty of Science, King Abdulaziz University,
P.O. Box 80203 Jeddah 21589 Saudi Arabia

Abstract: The structural and electronic properties of wurtzite ZnO structure have been theoretically investigated within the framework of the density functional theory and plane wave pseudopotential method. In contrast to recent studies, our calculations reveal that the Zn-O bonds have a pure ionic nature and no appreciable degree of covalency has been observed. The highest occupied and lowest unoccupied states have been found to originate from the p orbitals of the Zn atoms, suggesting different approach of charge transfer between the O and Zn atoms. Detailed calculations on the fundamental structural and electronic properties of the ZnO structure have been determined and compared with the available studies.

Key words: Density functional theory (DFT) • LDA • GGA • Ionic bonds • Molecular orbitals • Band structure

INTRODUCTION

Nature provides the physicists with a vast range of exotic materials with fascinating properties which could be considered as potential candidates for brilliant applications. Including the various categories of semiconducting materials, metal oxide semiconductors have been attracted immense interest due to their potential applications in technological industries. There are an enormous number of oxides which play a dominant role in very recent applications; zinc oxide (ZnO) is such an example. The ZnO materials have gained much more interest in both technological and industrial applications due to their wide band gap of 3.37 eV and relatively high Curie temperature [1-3]. It is classified into the II-VI semiconducting-materials category which crystallizes into two different crystal structures: hexagonal wurtzite and face-centered cubic. Without being perturbed, the stable phase of ZnO is predicted to be wurtzite while the zincblende phase can be achieved by applying appropriate growth conditions.

Despite the unique properties and flexible applications of ZnO, a few experimental and theoretical works have been performed to understand and appreciate its atomic, electronic, optical and electrical properties for their use in potential fields such as transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics [4-10].

Using X-ray diffraction spectroscopy and linear augmented plane waves (LAPW) method, Karzel *et al.* [11] have presented investigations for the lattice dynamics and hyperfine interactions in ZnO at high pressure. Their results reveal that the covalence between Zn and O atom is a characteristic property of ZnO. However, the covalency feature in ZnO has gained much contradiction in the available literature [12, 13]. Recently, Decremps *et al.* [12] have determined the structural properties of ZnO at high external pressure using energy-dispersive X-ray spectroscopy. Very recently, Mohammadi and coworkers [13] have presented a first-principles investigation for ZnO crystal using density functional theory (DFT) within its generalized-gradient approximation (GGA) method. They have shown that the inclusion of Hubbard potential (U) in the calculations leads to a modification of the energetic position of the molecular orbitals and hence the energy gap of ZnO structure. However, this point is a subject of a long-term debate and is still not clear enough.

In the present work, based on the DFT methodology, a detailed theoretical study on the structural and electronic properties of ZnO structure is provided. The purpose of such an investigation is to reveal the inconsistency of the bond formation and orbital nature of the states. Furthermore, we will examine whether the use of the Coulomb's interaction correction in the calculation would modify the electronic properties or not.

Theoretical Framework: The density functional theory (DFT) [14] within the framework of both the local density approximation (LDA) and generalized gradient approximation (GGA) has been involved to carry out the calculations of ZnO structure. The plane wave basis set as implemented in the QUANTUM ESPRESSO simulation package [15] is considered. The electron–electron interactions were expressed using the Perdew–Burke–Ernzerhof exchange–correlation scheme (GGA) [16] and the LDA scheme as parameterized by Perdew and Zunger [17]. The electron–ion interaction was treated by using the ultrasoft pseudopotentials [18]. The single-particle Kohn–Sham [19] wave functions were expanded using a linear combination of plane-wave basis sets with a kinetic energy cutoff of 25 Ry. The Kohn–Sham equations were Self consistently solved by employing a $4 \times 4 \times 2$ **k**-points Monkhorst–Pack set [20] within the corresponding Brillouin zone. The wurtzite ZnO unit cell was modeled by employing 16 atoms along with our theoretically calculated lattice parameters. These potentials and parameters have been carefully chosen after several convergence tests as seen later.

Relaxed atomic positions for the ZnO structure were obtained by using the total-energy and force minimization methods following the Hellmann–Feynman approach. The equilibrium atomic positions were determined by relaxing all atoms in the cell except the second lowest layer which was kept in its original position.

RESULTS AND DISCUSSION

Before performing the calculations of bulk ZnO structure, one initially needs to determine the adequate stable structure (zincblende or wurtzite), exchange–correlation scheme (LDA or GGA), equilibrium lattice parameters, energy cutoff and **k**-point set. In the next subsections, several calculations, using a unit cell containing 4 atoms, were carried out to examine the above requirements.

Convergence Tests: It has been reported in literature that the ZnO crystal has two different phases: face-centered cubic (zincblende) and hexagonal (wurtzite) structures. To determine the most stable structure we have considered both structures for total-energy calculations. Considering wurtzite with four atoms and zincblende structures with extended cell (containing four atoms), our results indicate that the wurtzite is energetically more stable than the zincblende structure, suggesting agreement with the previously reported results.

Electron-Electron Interaction Scheme: Due to the inconsistency in using either LDA or GGA for the electronic calculations of II-V structures, there is a need for an overall examination to determine the suitable exchange–correlation scheme for the present study. For such a purpose, we have tested the total energies of the system using both the LDA and GGA approaches. Our results suggest that the LDA method is much more suitable than GGA for such an investigation. This is in agreement with several works [21, 22] that suggest that LDA is much more powerful for some IV and II-V groups than GGA.

Lattice Constants: Having determined that the hexagonal phase is the ground–state structure of ZnO, important parameters for such a structure have been reexamined, such as lattice constants, energy cut off and special **k**-points. We have calculated the change of the total energy of the wurtzite ZnO structure as a function of lattice constants. Clearly shown in the Fig. 1 is that at $a = 6.2$ a.u and $c/a = 1.61$, the energy curve has a local minimum, resulting in lattice parameters as following.

$$a=b=3.28092 \text{ \AA}$$

$$c=5.282275 \text{ \AA}$$

These values are in excellent agreement with the experimental results [11,12]. The little difference between them can be regarded as the underestimation of the LDA method.

Energy Cutoff: As an important input for well-converged results, the kinetic energy cutoff for the plane wave basis set has been examined, as shown in Fig. 2.

Figure 2 shows that including several energy cutoffs, a very well converged total energy calculations have been obtained when $E_{\text{cut}}=25$ Ry.

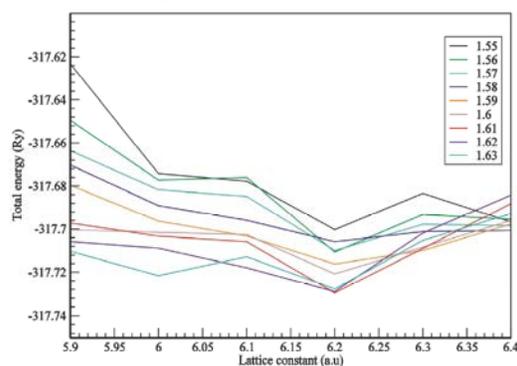


Fig. 1: The variation of the total energy as function of lattice parameters of ZnO structure.

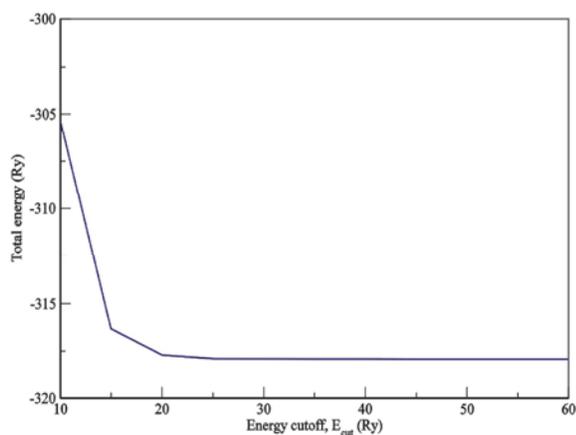


Fig. 2: The examination of the proper energy cutoff used in the present calculations

Choice of K-Points Set: Table 1 suggests that sampling the unit cell using a of $4 \times 4 \times 2$ k points set is good enough to obtain well-converged results. It is clearly shown that also a $4 \times 4 \times 3$ k -point mesh gives well-converged results. However, to save our time and the shortage of large calculation facilities, we decided to consider $4 \times 4 \times 2$ k -point set since both are almost similar in their total energies. Therefore, a set of $4 \times 4 \times 2$ k -points will be considered for the further calculations in the present manuscript.

Structural Properties: Within the DFT-LDA pseudopotential method, the lattice constants a and c of the wurtzite ZnO structure are found to be 3.280 and 5.282 Å, respectively, with a c/a ratio of 1.61. These values are in the acceptable range measured by several experiments [11, 12]. Karzel *et al.* [11] have studied the ZnO structure using X-ray measurements at high external pressure. Their experimental results indicate that the lattice parameters are $a = 3.2496$ and $c = 5.2042$ Å which are in good agreement with the present study. Using high-pressure combined energy-dispersive X-ray diffraction and X-ray absorption spectroscopy experiments, Decremps and coworker [12] found that the lattice constants of ZnO are $a = 3.25$ and $c = 5.201$ Å. They also have presented LDA calculation and found that the lattice parameters a and c are 3.238 and 5.232 Å, respectively. Recently, Mohammadi *et al.* [13] have investigated the electronic structure ZnO using the DFT within GGA scheme. The equilibrium lattice parameters are determined to be $a = 3.28$ and $c = 5.26$ Å which are in excellent agreement with the present calculations. Using these parameters we have relaxed the ZnO crystal, as shown in Fig. 3, to obtain the ground-state structure of ZnO.

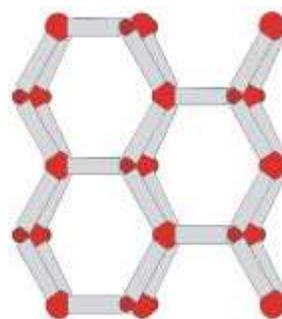


Fig. 3: The structural configuration of the ZnO structure. Small and large circles indicate Zn and O atoms, respectively.

Table 1: A summary of the total energies corresponding to different k -points is tabulated

k -points	Total energy (Ry)	k -points	Total energy (Ry)
$2 \times 2 \times 1$	-317.89735026	$6 \times 6 \times 2$	-317.90202190
$4 \times 4 \times 1$	-317.88193467	$8 \times 8 \times 2$	-317.90201561
$6 \times 6 \times 1$	-317.88185393	$4 \times 4 \times 3$	-317.90231717
$8 \times 8 \times 1$	-317.88171107	$6 \times 6 \times 3$	-317.90226735
$4 \times 4 \times 2$	-317.90199982	$8 \times 8 \times 3$	-317.90217150

Table 2: A comparison between the present lattice parameters and other experimental and theoretical results is summarized

a (Å)	c (Å)	c/a	Reference
3.280	5.282	1.61	This work
3.281	5.256	1.60	Exp. [13]
3.258	5.220	1.60	Exp. [12]
3.250	5.204	1.60	Exp. [11]
3.238	5.232	1.62	Theor. [12]
3.292	5.292	1.61	Theor. [22-24]
3.198	5.167	1.62	Theor. [25]
3.183	5.124	1.61	Theor. [26]
3.219	5.197	1.61	Theor. [27]

Relaxing all atoms except one layer, we get a structure with an average Zn-O bond length of 2.0 Å which is in agreement with the reported value of 1.98-2.0 Å. Yu *et al.* [23] have presented the total energy of ZnO as a function of Zn-O distance using GGA-DFT method. They concluded that the structure has local minimum when Zn-O distance is 1.99 Å. This value is consistent with the summation of their covalent radii of 1.9 Å. This indicates that the LDA is sufficient for ZnO calculations. Furthermore the tetrahedral Zn-O-Zn bond angle has been averaged to be 110° indicating that the charge is strongly localized around the components. This value is actually fallen within the well-known tetrahedral angle of 109.5° . We have presented a comparison of our theoretically calculated lattice parameters with other theoretical and experimental values in Table 2.

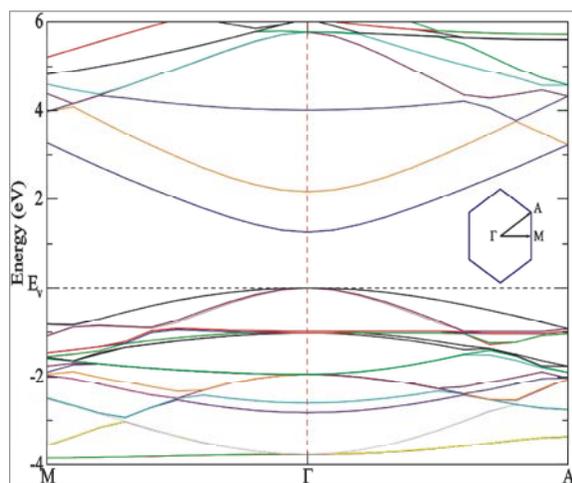


Fig. 4: Band structure plot of ZnO along the high symmetry direction. The zero energy is set at the top of the valence band. A sketch of the Brillouin zone is inserted in the inset.

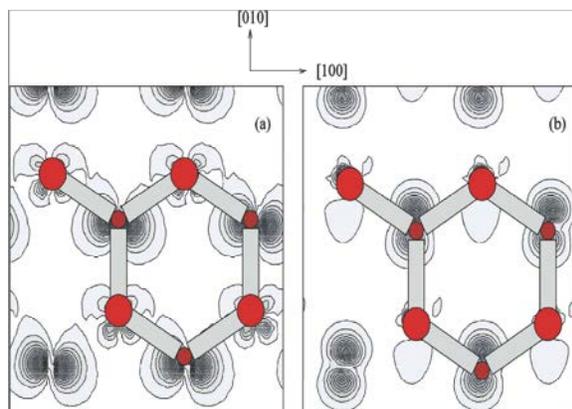


Fig. 5: Partial charge density of the (a) HOMO and (b) LUMO states at the Γ point.

Electronic Properties: To understand the electronic properties of ZnO structure, we have performed band structure calculation along the high symmetry direction of the Brillouin zone, as shown in Fig. 4. It is clearly shown that the structure is semiconducting with a direct LDA band gap of 1.26 eV. This value is smaller than the experimental value due to the well-known underestimation of LDA. However, our calculated LDA band gap is much better than the recently-reported value of 0.75 eV that has been calculated within the GGA scheme [13]. In their work, Mohammadi *et al.* [13] claimed that the inclusion of the potential correlation (U) in the GGA method leads that the band gap to be improved to 1.6 eV. In our calculations, using the same computational procedure in Ref [13],

we have considered a similar Hubbard potential for both the GGA and LDA schemes. We found that the gap is significantly overestimated to about 5.3 eV which is not physically acceptable. The mismatch between our results and theirs is not understood yet. Since the calculated gap is much better than the previously reported values, we believe that the inclusion of U in the calculations is not essential.

At 3.2 eV above the valence band maximum (VBM), we clearly find a degeneracy which is also observed at 4.3 eV. These degeneracies are also defined in other theoretical works which are characteristic properties of ZnO. Below the top of the valence state, there are a number of dispersive curves along the whole direction, indicating very good conducting behavior. At the Γ point, a few number of bands are degenerate with zero effective masses just around the point (i.e. the bands conduct a linear E-k behavior or nondispersive bands). Similar energetic degeneracy is also observed at the edges of the Brillouin zone.

To elucidate the orbital nature of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) states, we have plotted the partial charge density of the HOMO and LUMO states in a [100]/ [010] plane at the Γ point, as shown in Fig. 5.

Panel (a) shows that the HOMO state originates from the P orbital of the Zn atoms with a heavy p_x nature. It is also shown that a little amount of charge appears around the O atoms which are almost ignorable. The LUMO state, as shown in panel (b), is derived from the p_y orbitals of the Zn atoms with ZnO structure.

To support the results obtained for the band structure calculations, we have performed total density of states (DOS) of the studied system, as shown in Fig 6. Consistent with the band structure results, it is clearly shown that the band gap is approximately 1.26 eV. Below the VBM, we can divide the spectrum into two main intervals: E_v-6 eV to $E_v-4.8$ eV and $E_v-3.8$ eV to $E_v-1.0$ eV. In the former interval, two sharp and well-defined peaks appear at -6.0 and -4.8 eV. Between these sharp peaks at approximately -5.5 eV, a peak which is not very well-developed is observed, which is very close to the sharp peak at $E_v-4.8$ eV. In the latter region, three developed peaks, much smaller than the previous, exist at -3.8, -2.0 and -1.0 eV, respectively, with a smallest peak at -2.5 eV. At energies above the VBM, several peaks are observed in the interval $E_v+4.2$ eV to $E_v+10.2$ eV, with no observable peaks just around the VBM.

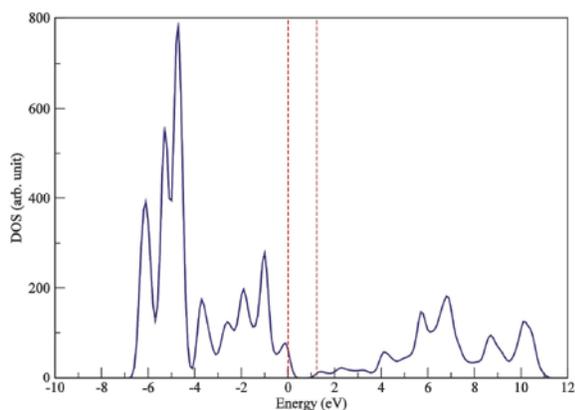


Fig. 6: Total DOS for wurtzite ZnO. The zero energy is set at the top of the valence band. The region between dotted lines represents the energy gap.

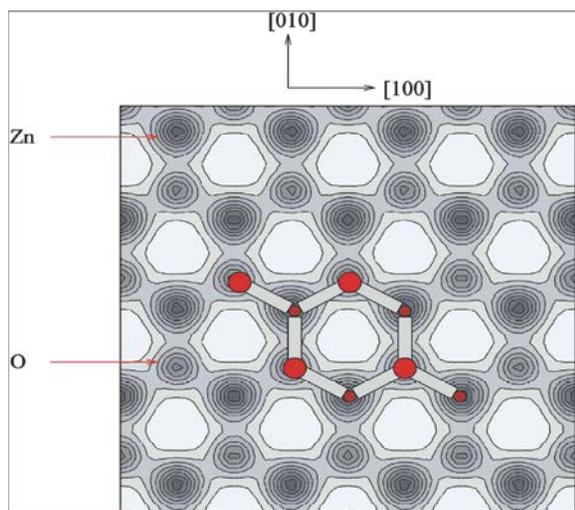


Fig. 7: Total charge density plot in the [110] plane for wurtzite ZnO.

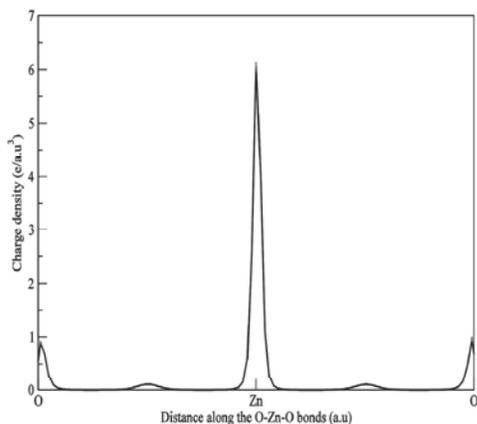


Fig. 8: The total charge density along the line joining the Zn atom with its next neighbors.

To evaluate the charge distribution (accommodation) around the main components of the wurtzite ZnO crystal, total charge density has been plotted, as shown in Fig 7. We have chosen the [100]/[010] plane which passing through both the Zn and O atoms. It is clearly shown that a large amount of charge is localized around the Zn atoms with a small amount being localized around the O atoms, indicating that the Zn-O bond has a large ionicity nature. This conclusion contradicts with the results obtained by Karzel *et al.* [11] and Mohammadi *et al.* [13] where they suggest a degree of covalent nature in the ZnO bond formation.

To support our conclusion, we have performed a plot for the total charge density along the lines joining the Zn atom with its nearest neighbors O atoms, as shown in Fig 8.

It is clearly shown that the charge is extremely localized around the Zn atom with very little amount of charge being accommodated around the O atoms.

CONCLUSION

Within the framework of the plane wave pseudopotential method and density functional theory, we have performed *ab initio* calculations to investigate the structural and electronic properties of ZnO structure. Our results indicate that the system is a direct band-gap semiconductor with an LDA energy gap of 1.26 eV. The total charge density plots suggest that the Zn-O bonds have a large amount of ionicity with no appreciable degree of covalency. The highest occupied and lowest unoccupied states have been found to originate from the *p* orbitals of the Zn atoms. Unlike the recently reported results, the inclusion of Hubbard potential is not physically meaningful in such calculation which leads to a significant overestimation in the energy band gap value.

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