

THE INTERNATIONAL JOURNAL OF SCIENCE & TECHNOLEDGE

Electronic and Structural Study of Hexagonal Wurtzite Zinc Oxide Using Ab-Initio Technique

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Abstract:

The first principle pseudo potential plane wave method is used to study the electronic structure of wurtzite zinc oxide (ZnO). In this study the relaxed atomic positions for the ZnO structure were obtained by using total energy and force minimization method following the Hellmann-Feynmann approach. The total energy of ZnO per atom is calculated as a function of cutoff energy and Monk-Horst pack mesh grid. The convergence of total force for displaced atom is tested with respect to cutoff energy and k-points. Moreover, the equilibrium lattice constant is calculated and compared with experimental and previous computational values of lattice constant.

Keywords: Zinc oxide, density functional theory, electronic structure, total energy, total force

1. Introduction

Zinc oxide is a transparent piezoelectric semiconductor which occurs naturally in the mineral called zincite. Including the various categories of semiconducting materials, metal oxide semiconductors have been attracted immense interest due to their potential applications in the technological industries [i]. Among an enormous number of oxides which play a dominant role in very recent applications; zinc oxide (ZnO) is such an example. Zinc oxide (ZnO) is a very promising material for semi-conductor device applications [ii]. It has a direct wide band gap of 3.37 eV and relatively high Curie temperature [iii] and a large exciton binding energy of 60 meV [iv]. It is also available as a high-quality bulk single crystal [v]. Owing to these properties, it is of a great technological importance for using in various fields such as photo voltaic, optical coatings, catalysis, and ceramics [vi]. ZnO is also well known for its large piezoelectric constants. In piezoelectric materials, an applied voltage generates a deformation in a crystal and vice versa. It has high conductance, chemical and thermal stability, a good radiation resistance and is harmless to the environment [-vii, viii]. Low dimension of ZnO has great potentiality for being used in preparing solar cell, acoustic, electrical and optical devices, chemical sensors, catalysts, pigments, cosmetics, varistor and gas sensors. The conductivity of ZnO thin films is very sensitive to the exposure of the surface to various gases. It can be used as a cheap small sensor capable of detecting the freshness of foods and drinks due to high sensitivity to trimethylamine present in the odor. ZnO crystal and, in particular, thin films exhibit large second and third order nonlinear optical behavior, suitable for nonlinear optical devices. It has been also observed that ZnO exhibits exceptionally high radiation hardness, which is important for application at high altitude or in space.

In this study, we are more interested to study the hexagonal wurtzite structure of ZnO as it is a stable structure. Based on the density functional theory methodology the electronic and structural properties of ZnO structure are calculated. The convergence issues of total energy per atom, total force per atom and lattice constant is investigated with respect to the cutoff energy and k-point sampling.

2. Conceptual Framework and Work Package

It is known that many body problems are very difficult to solve. That is, the state of motion cannot be solved analytically for systems in which three or more distinct electrons interact. In recent years, there has been remarkable surge activity in the application of density functional techniques to many body systems such as molecular and solid state systems and to problems of chemical interest [ix]. The fundamental tenet of density functional theory is that any property of the system of many interacting particles can be viewed as a functional of the ground state density $n_0(r)$; that is one scalar function of position $n_0(r)$, in principle determines all the information in the many body wave functions for the ground state [x, xi]. To study the electronic structure of ZnO the density functional theory with the help of QUANTUM ESPRESSO package is used [xii]. The plane wave self-consistent field (PWSCF) code is employed as our first principle energy code. PWSCF is a first principle energy code that uses norm conserved pseudo potential (PP) and ultrasoft pseudo potentials (US-PP) with in density functional theory (DFT). The pseudo potential theory is based on the ansatz which separate the total wave function in to an oscillatory and smooth part (Pseudo wave function). The strong true potential of the ion is replaced by a weaker potential valid for the valence electrons, the pseudo potentials which approaches the unscreened Coulomb potential. The main feature of "Pseudising" process is to eliminate the strong Coulomb potential within the core region. Thus, the norm conserved

pseudo potentials with Perdew Zunger (PZ) version of the local density approximation (LDA) exchange correlation functional and the ultra-soft pseudo potentials with Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange correlation functional are employed respectively. ZnO has a hexagonal crystalline wurtzite-type structure. $4s^2 3d^{10}$ and $2s^2 2p^6$ states will be treated as valence electrons for Zn and O respectively. For choice of plane wave basis set, the cut of kinetic energy at 25 Ry, and the cut of charge density at 250 Ry is used as trial cut of energy and charge density respectively. For k point sampling of bulk ZnO we start with Monk horst pack mesh grid (4x4x4). The convergence issue will be checked in two ways. The minimum total energy will be found by varying cut off energy (ecutwfc) for fixed Monk horst pack mesh. Moreover, the minimum total energy will be obtained by varying the Monk horst pack mesh grid or the k point sampling for fixed cut off energy.

3. Results and Discussions

It has been reported in different literatures that ZnO crystal has two different phases: face centered cubic (zinc blende) and hexagonal (wurtzite) structures. From these structures, hexagonal (wurtzite) structures are more stable ones energetically. In this research, we have considered hexagonal (wurtzite) structure for total energy calculation. Here the density functional theory (DFT) within the frame work of both local density approximation (LDA) and generalized gradient approximation (GGA) has been involved to carry out the wurtzite structure of ZnO. In this study the relaxed atomic positions for the ZnO structure were obtained by using total energy and force minimization method following the Hellmann-Feynman approach.

3.1. Total energy of ZnO with respect to cutoff energy

In this part the total energy of ZnO per atom is calculated as a function of cutoff energy. An increment of cutoff energy is made until the convergence is achieved. While changing the cut of energy, the lattice constant and the Monk Horst Pack Mesh (\vec{k} -points) are fixed respectively. In this calculation, the lattice constants $a=b=6.1413$ bohr and $c/a=1.602$ bohr. The \vec{k} -points are 4x4x4. The total energy per atom versus cutoff energy is shown in Figure.

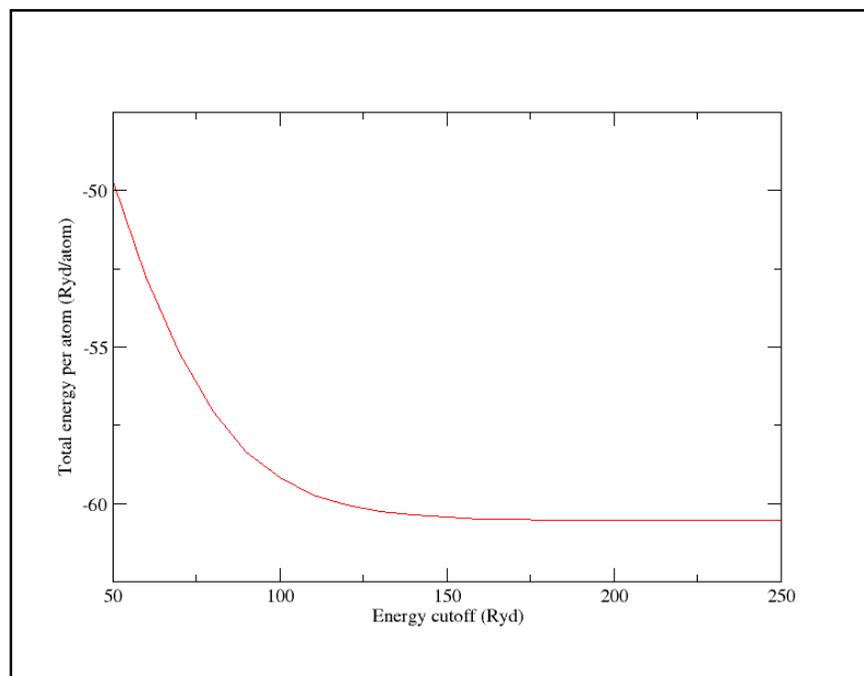


Figure 1: Total energy of ZnO per atom versus cutoff energy

In this calculation, the converged cutoff energy appears to be approximately 200 Ryd for the given lattice constant and \vec{k} -point grid. The trend of the graph in Figure 1 shows that the total energy per atom is monotonically decreasing with increasing cutoff energy. This behavior is the direct result of variational principle. The accuracy of the ground state energy depends on the number of basic functions or plane waves. As the number of basic functions approach to infinity we can get the energy that close to the ground state energy.

3.2. Total energy of ZnO with respect to Monk-Horst pack mesh grid

The total energy of ZnO per atom is calculated as a function of \vec{k} -points using PWSCF. For this calculation, the other parameters such as lattice constant, cutoff energy etc. are made fixed. That is the lattice constants $a = b = 6.1413$ bohr and $c/a = 1.602$ bohr and cutoff energy is 200 Ryd. Moreover, the total energy of ZnO per atom versus \vec{k} -point's grid size is shown in Figure 2.

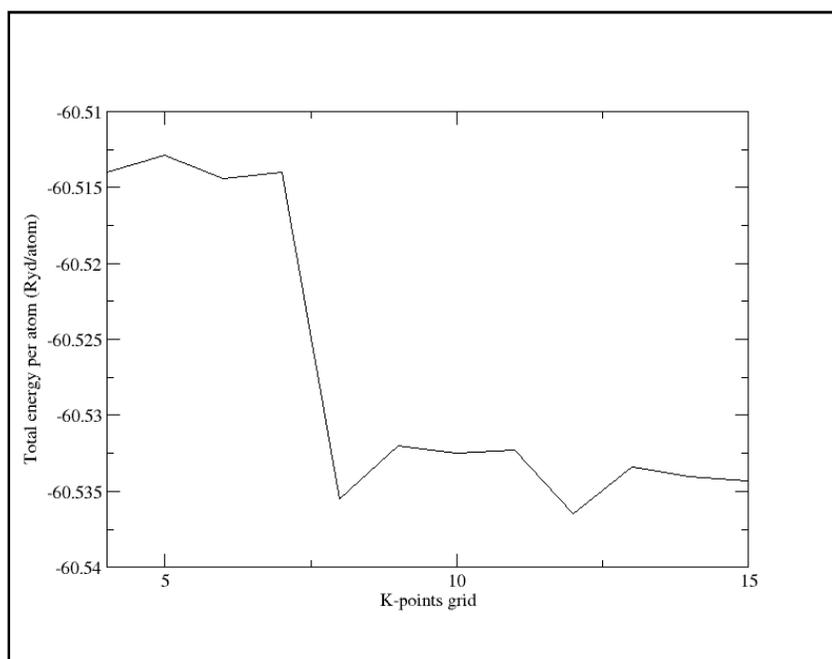


Figure 2: Total energy of ZnO per atom versus \vec{k} -points grid

As it can be observed that the total energy of ZnO per atom converges at $8 \times 8 \times 2$ \vec{k} -points' grid, for the fixed lattice constant and cutoff energy. There is no systematic trend can be predicted from just increasing the k- points grid for the approximation to the integral.

3.3. Convergence of Forces with Respect to Cutoff Energies

In the previous calculations, the forces on ZnO are zero in x, y and z directions. However, it is possible to create forces by displacing a Zn atom by 0.05 bohr in the z directions. We calculated force on ZnO as a function of cutoff energy by keeping other parameters fixed. For this calculation, we used the lattice constants $a = b = 6.1413$ bohr and $c = 1.602$ bohr and $8 \times 8 \times 2$ \vec{k} -point grids respectively. In this simulation convergence is achieved when the cutoff energy is equal to 250 Ryd. The force at this cutoff energy is 0.11782 Ryd/bohr. This simulation is demonstrated in Figure 3.

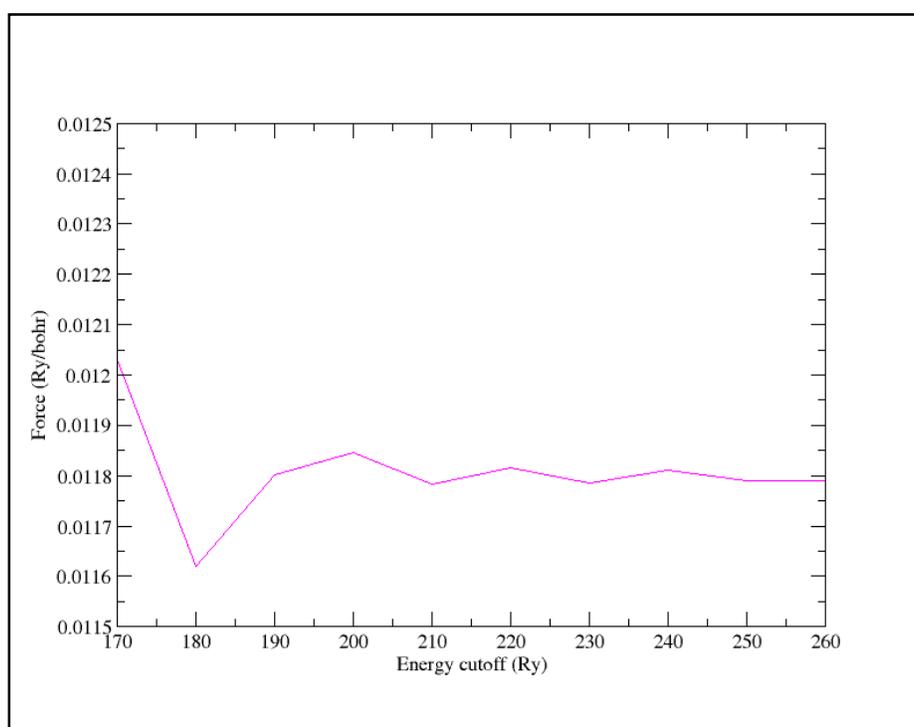


Figure 3: Total force of ZnO versus cutoff energy

3.4. Convergence of FORCES with RESPECT to \vec{k} -point GRID SIZE

In this part, we have calculated the force on 0.05 bohr displaced ZnO as a function of \vec{k} - point size, by fixing the other parameters such as a lattice constant = $b = 6.1413$ bohr and $c/a = 1.602$ bohr and cutoff energy is 200 Ryd. The calculated force with respect to \vec{k} - point grid size is tabulated in Table 1.

\vec{k} - points	Total force(Ryd/bohr)	\vec{k} - points	Total force(Ryd/bohr)
$4 \times 4 \times 1$	0.013352	$11 \times 11 \times 1$	0.025511
$6 \times 6 \times 1$	0.029701	$12 \times 12 \times 1$	0.025813
$8 \times 8 \times 1$	0.029701	$13 \times 13 \times 1$	0.025946
$10 \times 10 \times 1$	0.026657	$14 \times 14 \times 1$	0.025463

Table 1: The total forces per atom corresponding to different \vec{k} - point grid size

The total force convergence at cutoff 200 Ryd achieved at grid size of $11 \times 11 \times 1$ \vec{k} - points. It is observed that the \vec{k} - point requirement for the broken symmetry used for the displaced Zn atom is higher than the \vec{k} - point requirement for completely symmetric case. Generally, it is clear that different structural geometries will require different \vec{k} - point meshes so as to reach convergence. If we completely change the crystal symmetry from hexagonal (wurtzite) to face centered (zinc blende), it requires large \vec{k} - point density. The trend of the total force convergence with respect to \vec{k} - point mesh fixing the other parameters constant is demonstrated in Figure 4.

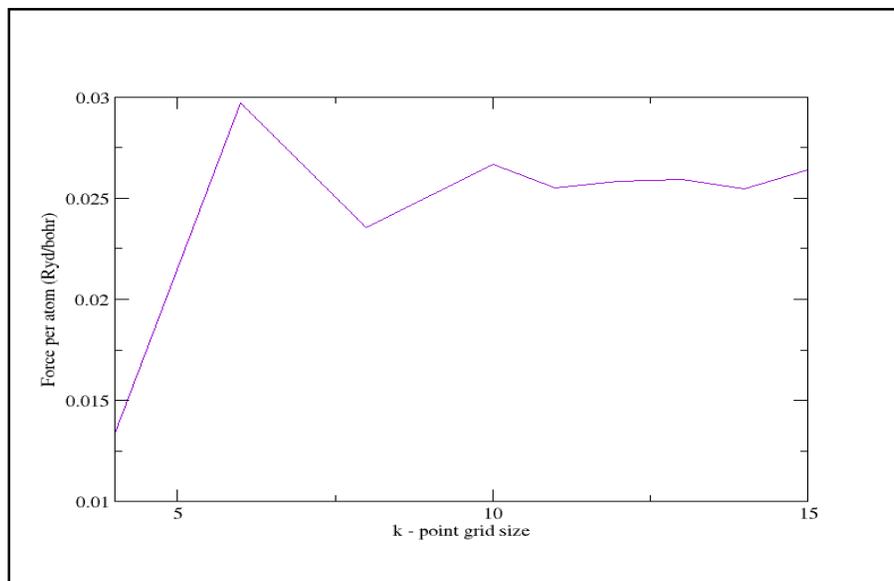


Figure 4: Total force of ZnO versus k-point grid size

3.5. Equilibrium Lattice Constant of ZnO

The equilibrium lattice constant of ZnO, hexagonal wurtzite structure is calculated using plane wave self-consistent field (PWSCF). The experimental value of lattice constant is $a = b = 6.202$ bohr and $c = 9.9355$ bohr, and the ratio $c/a = 1.602$ bohr. Using the cutoff and \vec{k} - point grid criteria for energy convergence in the previous calculations we determined the lattice constant numerically. Our numerical calculation shows that the equilibrium lattice constants are $a = b = 6.1$ bohr and $c/a = 1.62$ bohr which implies $c = 9.882$ bohr. This numerical simulation is shown in Figure 5. The results are in good agreement with experimental results [xiii, xiv], and theoretical results [xv, xvi].

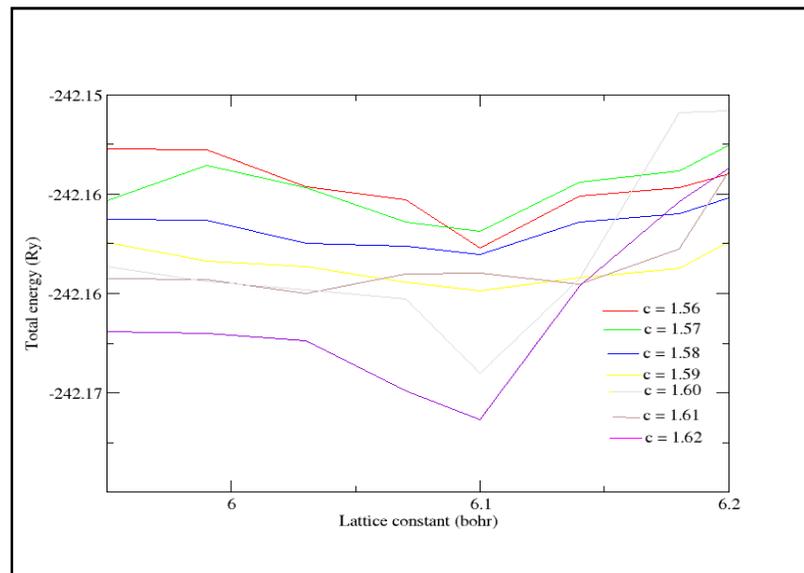


Figure 5: Total energy of ZnO versus lattice constant

3.6. Band structure of ZnO

To know the electronic properties of ZnO wurtzite structure, we have performed band structure calculation along the high symmetry direction of the Brillouin zone as described in Figure 6. It is observed that the structure is semiconducting with a direct generalized-gradient approximation (GGA) band gap of 0.76 eV. The experimental value is four times greater than these values. The band gap of ZnO is severely underestimated by the commonly used generalized-gradient approximation (GGA). However, it is successful in predicting the trends of electronic structure of semiconductor systems.

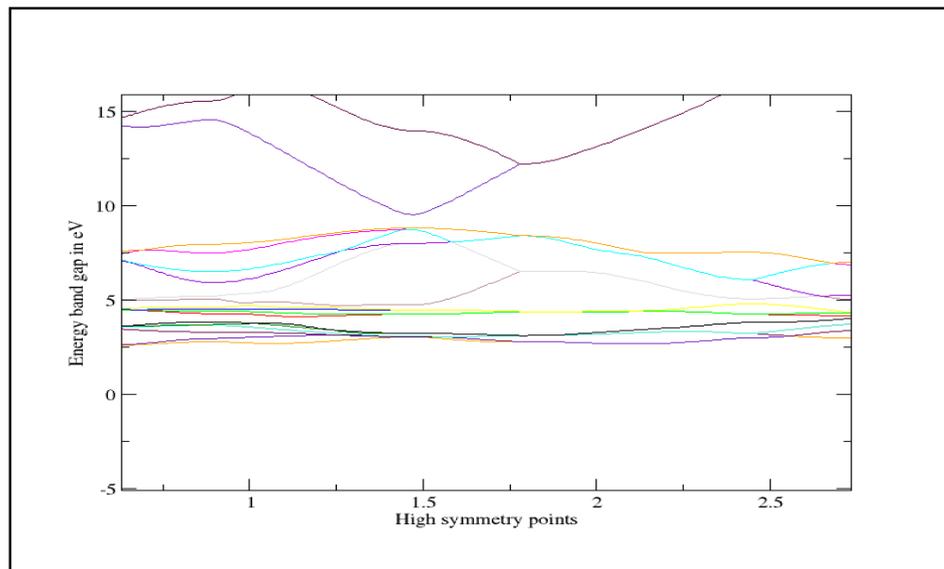


Figure 5: Band structure of ZnO for high symmetry points

4. Conclusions

The structural and electronic properties of wurtzite structure have been theoretically studied; within the frame work of the density functional theory, plane wave basis set and pseudo potentials. The norm conserved pseudo potentials with Perdew Zunger (PZ) version of local density approximation (LDA) and the ultra-soft pseudo potentials with Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation exchange-correlation functional are employed respectively. The total energy calculation using a unit cell containing 4 atoms is performed as a function of cutoff energy and Monk-Horst pack-mesh grid respectively fixing the other parameters constant. Energy convergence is achieved, at the energy cutoff 200 Ryd for the first case and at $8 \times 8 \times 2 \vec{k}$ -point grid for the second case. The minimum total energy per atom is -60.536 Ryd for both cases. The total force on ZnO as a function of cutoff energy and Monk-Horst-Pack mesh is calculated by displacing Zn atom by 0.05 bohr. Total force convergence is achieved for the cutoff energy 250 Ryd and for Monk-Horst-Pack mesh at $11 \times 11 \times 1 \vec{k}$ -point grid. Our numerical calculation shows that the

equilibrium lattice constant $a = b = 6.1 \text{ bohr}$ and $c/a = 1.62 \text{ bohr}$. These results are in good agreement with experimental results. Finally, to understand the electronic properties of ZnO wurtzite structure we have performed band structure calculation along the high symmetry of the Brillouin zone. The band gap with respect to our calculation is 0.76 eV which is approximately one-fourth of the experimental value. This may be resulted from defects which often induce occupied states in the band gap. These states have a certain ratio of conduction versus valence band character, and therefore their positions with respect to valence band maximum (VBM) can be underestimated by large amount. This uncertainty has an influence on the prediction of transition levels and formation energies, leading to potentially amplified errors, particularly in the case of wide band gap semiconductors such as zinc oxide.

5. Acknowledgments

Authors are thankful to the Research and Post Graduate studies of College of Natural Sciences, Jimma University for a financial support.

6. References

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