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DMol^3 Calculation of Electronic Properties of ZnO with different LDA approximation

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Abstract : ZnO is a II-IV semiconducting material having band gap 3.37 eV at room temperature. It has been good interest in recent years due to the wide application of ZnO in laser, Green-Blue LED, solar cell, robotic etc. Applying the first principle DFT we can calculate various properties of ZnO like lattice constant, band plot, magnetic properties and optical properties etc. In this work DFT *first-principle* calculation using DMol^3 code with LDA-PWC and LDA-VWN approximation for electronic structure calculation of ZnO performed and compared both the result with experimental data. DOS and PDOS plotted and analyzed for both functional.

Keywords: ZnO, DFT, DMol^3, LDA-PWC, LDA-VWN, DOS, PDOS

1. Introduction

Semiconductor show some unique behaviour such as high conductivity at room temp, required less input power, no requirement of filament heating etc. Due to these unique properties ZnO is a versatile material used in different electronic such as diodes, LEDs, spintronic, transistors, MOSFET etc. According to band gap theory ZnO is a wide band gap (WBG) semiconductor having band gap 3.37 eV [1] and high excitation binding energy (60 meV) [2] can be used for short wavelength optoelectronic devices. Due to its large electrochemical coupling shows strong pyroelectric, piezoelectric properties and show applications in solar cell [3-4], chemical sensor [5-6] and piezoelectric sensor [7-9]. Structural, electronic, optical, magnetic properties of semiconductor materials can be studied using Density functional theory (DFT) using different approximations such as Local density approximation (LDA) [10], Generalized gradient approximation (GGA) [11], Predew Bruke-Ernzerhof (PBE) [12], PW91 [13] and many more local hybrid function.

In this work we studied electronic properties of hexagonal wurzite ZnO using LDA- Perdew-Wang (LDA-PWC) and LDA- Vosko-Wilk-Nusair (LDA-VWN) functional using DMol^3 code using Biovia material studio, for better result Harris approximation used. DFT calculation is done to calculate energies. Then band plot calculation done and plotted to calculate band gap. The total and partial density of states were calculated and plotted.

2. Computational Methods

First- principle calculation of DFT is one of the most dependable computational method to verify the structural, electronic, optical properties of materials. In this work we use computational code of Biovia with DMol^3 module and local density approximation (LDA). LDA consists of two different functional one is Perdew-Wang (PWC) functional and another is Vosko-Wilk-Nusair (VWN) functional. In the work we use both the functional for our calculation and compared the results in both cases.

In this work, we use different LDA functional with SCF tolerance used as 1.0e-6 with 50 maximum SCF cycles. In all calculations, The K-point grid taken as 5 ×5 ×3. Single particle Kohn sham equations to be solved and the band structure, density of state plotted for ZnO. The band energies, density of state and band gap calculations done for hexagonal wurzite ZnO. ZnO has wide band gap of 3.37 eV as per the experimental data. ZnO lattice constant a=b=3.2492 Å, c=5.2054 Å. Used for this calculation. The primitive cell of ZnO is shown in Fig.1 and ZnO crystal structure is shown in Fig.2.

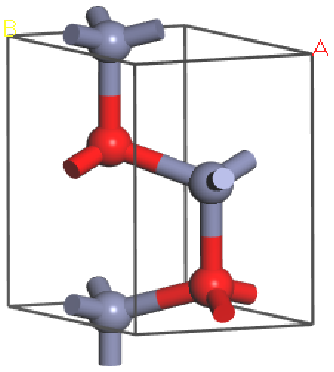

Fig.1 Primitive cell of ZnO. Zn in grey and O in red

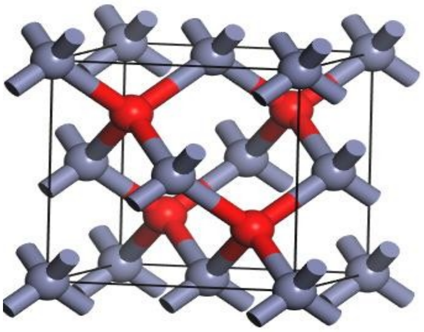

Fig.2 Crystal structure of ZnO. Zn in grey and O in red

3. Result and Discussion

Density functional theory DFT calculation performed using LDA-PWC and LDA-VWN functional for ZnO using DMol^3 code. All calculation done with DNP basic set of 3.5 basic files. Core treatment for all electrons of ZnO are performed. In calculation for better results we considered Harris approximation. SCF tolerance used as 1.0e-6 with 50 maximum SCF cycles. Maximum size of subspace for DIIS procedure taken six.

Electronic properties

The calculation performed using hexagonal wurzite ZnO crystal with lattice constant a=b= 3.2492Å and c=5.2054 Å. The electronic configuration of Zn is $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ and electronic configuration of O is $1s^2$ $2s^2$ $2p^4$.For this calculation $3p^6$ $3d^{10}$ electrons of Zn and $2s^2$ $2p^4$ electrons of O taken as valence electron. DFT Calculation were performed to find band gap, density of states and partial density of states using DMol^3 module.

We started the calculation to find out lattice constants of hexagonal wurzite ZnO primitive cell. These calculations require the determination of wave function and all position of valence electrons and nuclei. The lattice constant of a crystal corresponding to the size of the conventional unit cell and to obtain by plotting the total energy as a function of cell volume. The calculated lattice constants for ZnO after geometry optimization a=b= 3.2135 Å and c= 5.1694 Å. For LDA-PWC and a=b= 3.2192 Å and c=5.1782 Å for LDA-VWN *approximation* Which is good agreement with the experimental lattice constant values (a=3.24, c=5.20).

Table.1 Lattice parameters and Band gap of ZnO using Different LDA formalism with DMOL^3

DMol^3 Functional	Lattice parameters (in Å)		Lattice parameter after Geometry optimization (in Å)		c/a	Band gap (in eV)
	a=b c		a=b	c		
LDA-PWC	3.2492	5.2054	3.2135	5.1694	1.6086	2.081
LDA-VWN	3.2492	5.2054	3.2192	5.1782	1.6085	2.089

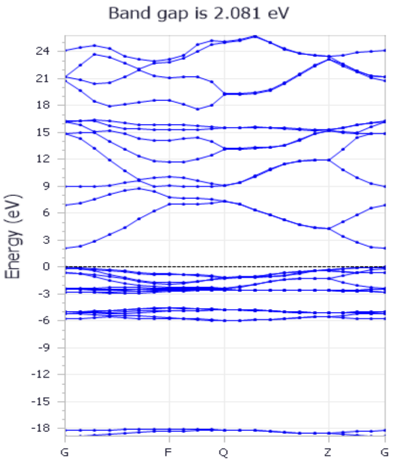

Fig.3. Band structure of ZnO using LDA-PWC

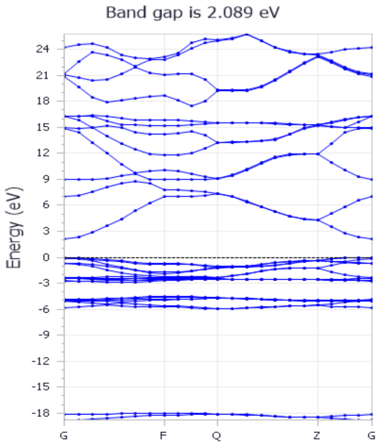

Fig.4 Band structure of ZnO using LDA-VWN

Figure.3 represents the calculated energy band structure of wurzite ZnO using LDA-PWC formalism whereas Fig.4 represents the calculated energy band structure of wurzite ZnO using LDA-VWN formalism. Here in both formalism top of the valence band is taken zero on the energy axis. In both LDA-PWC and LDA-VWN formalism top of the valence band and bottom of the conduction band occurs at a same symmetry line i.e gamma line which indicate the direct band gap characteristics of ZnO. Calculated band gap using LDA-PWC and LDA-VWN approximation is 2.081eV and 2.089 eV respectively whereas experimental band gap of ZnO 3.37 eV so our calculated band gap underestimated the experimental band gap value. The calculated error is 38.24% and 38.01% for LDA-PWC and LDA-VWN respectively. The smaller band gap compared to experimental value is due to the inherent drawbacks of theoretical calculations. So this can be said that LDA-VWN gives better results for energy value calculation.

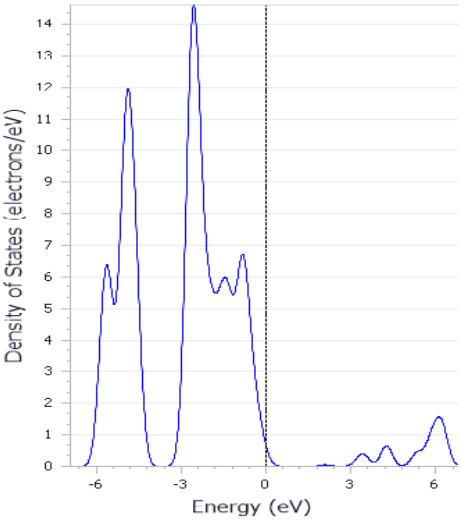

Fig.5. Density of states of ZnO using LDA-PWC

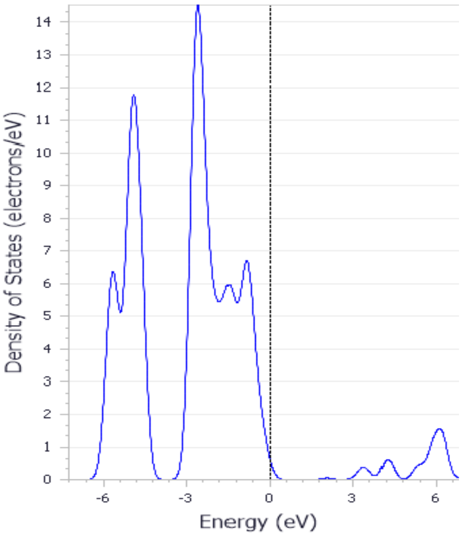

Fig.6. Density of states of ZnO using LDA-VWN

The total density of states (DOS) of ZnO using first principle DFT calculation with DMol^3 code using LDA-PWC shown in Fig .5 and using LDA-VWN shown in Fig .6. Here calculated density of states are plotted against energy. Dotted line represents the Fermi energy. The left side of fermi energy represented valence band and right side conduction band. From DOS plot it clearly shown the number of electrons more in valence band compared to conduction band that indicate the semiconductor behavior of ZnO.

The Partial density of states (PDOS) of ZnO using first principle DFT calculation with DMol^3 code using LDA-PWC shown in Fig .7 and using LDA-VWN shown in Fig.8. Dotted line represents the Fermi energy. The contribution of electrons towards the density of states can be seen by partial density of states. The PDOS plot indicate ‘d’ state and ‘p’ state contributes more in valence band whereas ‘s’ and ‘p’ states contribute more in conduction band in both LDA-PWC and LDA-VWN formalism.

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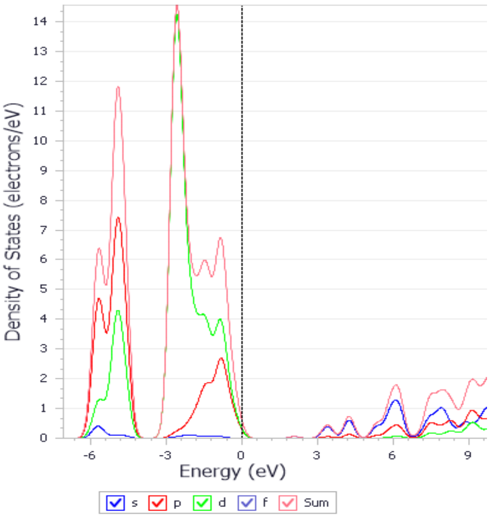

Fig.7. PDOS of ZnO using LDA-PWC formalism

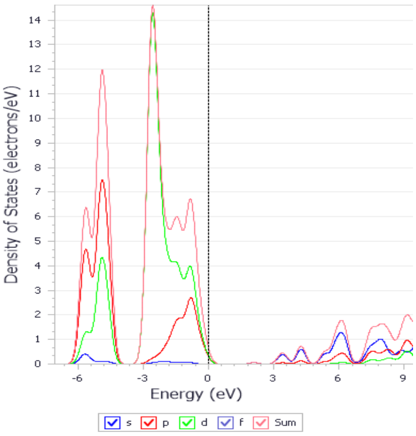

Fig.8. PDOS of ZnO using LDA-VWN formalism

4. Conclusion

The first principle DFT calculation performed to study the electronic properties of ZnO with DFT using DMOL^3 module with LDA-PWC and LDA-VWN approximation. The band plot using both LDA-PWC and LDA-VWN indicate ZnO is a direct band gap semiconductor. Calculated Band gap for LDA-PWC and LDA-VWN formalism **2.081eV and 2.089 eV respectively. The energy band plot, DOS and PDOS plots and calculated for both LDA formalisms. Semiconductor behaviour of ZnO clearly indicated by DOS plot. The contribution of electrons to the density of levels clarified using PDOS plot.**

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