

Electronic Calculations of SnO_2 Using Gga+U With Different Pseudopotentials and Relativistic Treatment

Mandakini Baral¹, Padmaja Patnaik^{2*}, Santanu Kumar Nayak³, Dipan Kumar Das⁴

¹Research Scholar, Centurion University of Technology and Management, Odisha, India.

²Professor, Centurion University of Technology and Management, Odisha, India.

³Research Scholar, Centurion University of Technology and Management, Odisha, India.

⁴Research Scholar, Centurion University of Technology and Management, Odisha, India.

Abstract:-

The most complicated calculation in Density Functional Theory (DFT) is for exchange and correlation potential. In this work Generalized Gradient Approximation, Perdew-Burke-Ernzerhof and Local density approximation along with Hubbard parameter U functionals are used for exchange and correlation potential approximation. The suitable pseudopotential and Hubbard U value for SnO_2 calculation are detected computationally so that the results can be used for further calculation of electronic properties like lattice constant, band plot, TDOS and PDOS plots, magnetic properties etc. From these calculations ultra-soft pseudopotential with Schrodinger relativistic treatment having Hubbard U values $U_p = 7\text{eV}$ and $U_d = 9\text{eV}$ improved the electronic properties. Utilizing these parameters, the calculated band gap is 3.628 eV with 0.77% of difference in comparison with the experimental data. Then the results from the TDOS and PDOS plots are discussed and analyzed. Symmetry nature of TDOS shows SnO_2 has no magnetic behavior.

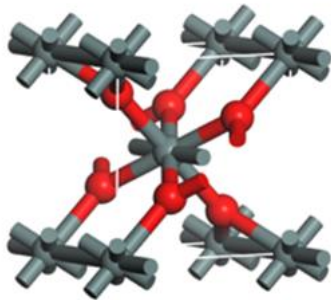
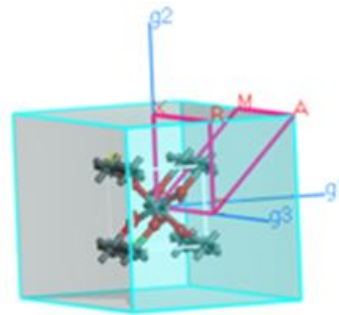
Introduction: -

Semiconductors are used in electronic industry due to high conductivity at room temp, required less input power, no requirement of filament heating etc. Generally, semiconductors have band gap less than 3eV but, some of the semiconductors exhibits band gap more than 3eV, such as GaN (3.4eV), ZnS (3.6eV), SiC (3.26eV) etc. and these are known as wide band gap semiconductors [1]. Tin dioxide SnO_2 looks off-white or white crystalline solid with melting point 1127 °C, 6.95 g/cm³ density and not soluble in water but soluble in concentrated H_2SO_4 , HCl and naturally present in cassiterite mineral. It is tetragonal in structure, belongs to the space group No.136 (P42/MNM) having lattice constants $a = b = 4.74 \text{ \AA}$ and $c = 3.19 \text{ \AA}$. It is a n-type wide band gap semiconductor having band gap of 3.6 eV at room temperature. It has large application as solar cell, Light emitting diodes, sensors, in spintronics, optoelectronics, etc. [2-5]. First principle calculation related to Density functional theory (DFT) utilized to study the electronic properties of SnO_2 . To study some properties like structural, optical and magnetic, DFT requires some approximations such as Local Density Approximation [6], Generalized Gradient Approximation [7], Perdew Bruke- Ernzerhof [8] PW91 [9]. Density functional theory related to exchange- correlation (XC) functional with conventional approximations such as LDA, GGA produce band gap up to nearly 2.0 eV, which underestimate the band gap value of experimental data (~3.6 eV)[10,11]. Research groups [12-15] tried to get 3.6eV band gap of SnO_2 by different methods and utilizing GGA+U approximation and corrected up to 2.75eV, 3.5eV. In this work the GGA approximation with different Hubbard values of U_d and U_p are used to get the band gap nearer to the experimental value.

Computational methods: -

DFT is a reliable method to study properties of material theoretically. This study is carried out by the first principle calculation using DFT [16]. The calculations are performed using BIOVIA material studio [17] using

CASTEP [18] module. The band plots are plotted for DFT calculations without spin polarization. But, for DFT+U calculations the band plots are plotted with spin polarization. To overcome the much less band gap value of SnO_2 using DFT, GGA+U method is used with different Hubbard (U) values of U(p,d) with different pseudopotential, different relativistic treatment and different cutoff energy to verify which pseudopotential with which relativistic treatment and for what value of U, it will be possible to get an appropriate result to match with the experimental data. In this work for OTFG ultra-soft Pseudopotential the cutoff energy is taken as 650eV, for OTFG Norm Conserving pseudopotential the cutoff energy is 950 eV, for Ultra-soft pseudopotential it is 375 eV and for Norm conserving pseudopotential it is 750 eV. A set of $3 \times 3 \times 3$ k-Point scheme used for Brillouine zone. Correlation and exchange correlation energy of electrons are explained with in Ceperley and Alder [19]. Single particle equation formulated by Kohn-Sham [20] is solved and used to study the band gap and valence levels of Bulk SnO_2 .

Fig-1: Unit cell of SnO_2 Fig-2: BZ sampling of SnO_2 primitive cell

Results and Discussions: -

Density functional theory

Density functional theory (DFT) with *first principle* calculation is a computational procedure used to calculate the electronic structure atoms, compound, molecules. DFT based on the principle that total energy of the system can be expressed as a function of electron density. It follows the Kohn-Sham approach for the calculations. The basic idea is the total electron density divided into small regions and calculate the energy associated with that small region, then sum all the energies related to each region for total energy calculation. The traditional electronic calculation methods like Hartree- Fock methods Basis set of atomic orbitals required to described the electronic properties of wave functions but DFT eliminates the need of basis set by introducing electron density as a function of electron co-ordinates. Kohn- Sham equation can be written as

$$H\phi_i - V_{eff}(\mathbf{r})\phi_i = E_i\phi_i$$

Where H is the Hamiltonian of the system and V_{eff} is the effective potential.

The effective potential can be written as

$$V_{eff}(\mathbf{r}) = V_{ext} + V_H + V_{XC}, \text{Where } V_{XC} \text{ is the exchange-correlation potential.}$$

In computational method it is difficult to calculate the exchange correlation term as no exact solution of this correlation and exchange potential is known. Some approximations such as LDA, GGA, PBE, PW91, Hybrid functional etc. and different pseudopotentials such as Ultra soft, OTFG Ultra-soft, OTFG norm conserving and Norm conserving pseudopotentials are required in DFT calculations. Again, in DFT computationally it is difficult to calculate the system consisting of both core and valence electrons. The electrons present in the core are tightly bound with nucleus. It needs high level of information for calculation. To reduce the computational effort in DFT all the above four type of pseudopotentials are used for calculation in Cambridge Series Total Energy Package (CASTEP) computational tool present in BIOVIA material studio.

Pseudopotentials:-

In DFT computationally it is difficult to calculate the system of all electrons such as both for core electrons and valence electrons. In order to reduce the computational effort DFT used pseudopotentials which reduce all the electrons in the form of effective potentials (V_{eff}) which eliminates the core electrons as it required high level

information for calculation as they are tightly bound with nucleus so only valence electrons will consider for calculation. The effective potential consists of coulomb potential and potential due to valence electron. There are different types of pseudopotentials such as Norm conserving, Ultra-soft, OTFG Ultra-soft and OTFG Norm conserving used for calculation in Cambridge Series Total Energy Package (CASTEP) computational tool. Norm conserving pseudopotential consists of a local potential $V_{loc}(\mathbf{r})$ and a non-local potential part $V_{NL} = \sum_i |\chi_i\rangle V_i \langle \chi_i|$

Total pseudopotential $V_{norm-conserving} = V_{loc}(\mathbf{r}) + \sum_i |\chi_i\rangle V_i \langle \chi_i|$

Relativistic Treatment:-

The various relativistic schemes used in this work are as follows.

Schrodinger - Schrodinger treatment used for electrons and it is a non-relativistic equation. First introduced by Schrodinger in 1926. Schrodinger treatment used to calculate the wave function and probability of finding the particle in a region. [23-28]

Koelling-Harmon- Koelling-Harmon is a scalar relativistic treatment used to study the electronic properties of solid. Here valence electrons are of linear combination of atomic wave functions. [29,30]

ZORA – Zeroth-Order Regular Approximation is relativistic Dirac equation describe the relativistic motion of electrons. The approximation contains two parts one is the nonrelativistic part and another one is the relativistic effects [31-35].

Generalized Gradient Approximation (GGA)

GGA is one of the approximations used to solve the exchange- correlation potential in DFT. GGA approximation improve the calculations including both electron density and its gradient that provide better explanation of spatial variation of electron density. In electronic properties calculation using these conventional DFT calculated band gap value is underestimated as compared to the experimental value. Using GGA functional calculated band gap ranges from 1.0eV-2.0 eV (Table-2). This result is mainly due to the limitation of GGA, the underestimation of the repulsion between O-2p and Sn-5s,5p electronic states resulting in an increase in the valence band and decrease in the band gap.

Hubbard (U) Scheme:-

DFT+U is a method in computational materials science that combines density functional theory and the Hubbard U correction to account for the effects of electron-electron interaction. The calculations involve solving the Kohn-Sham equations of DFT with an additional term added to the effective potential to account for the Coulomb repulsion between electrons in the same atomic orbital. The value of U is a parameter that is fit to experimental data or other more accurate theoretical data and can be used to describe the local electronic properties. Hubbard parameter for GGA is given by

$$E_{GGA} + U[n(\mathbf{r})] = E_{GGA}[n(\mathbf{r})] + E_U[n(\mathbf{r})] - E_{dc}$$

Where, E_{GGA} : the energy in GGA formalism, $n(r)$: is the probability of finding electrons, E_U : is the Hubbard energy, E_{dc} : is the double counting of energy correction.

In order to overcome calculation error of Band gap using both LDA and GGA in SnO_2 system, Hubbard-U method is usually used due to it's simple procedure and reliable nature. We added Hubbard (U) parameter at both d- state (U_d) and p- state (U_p) which increase the band gap. Value of U_d , varies from 6-9 eV and U_p in between 3-7 eV. One of the most popular methods in DFT+U method is GGA+U method, which is slightly computationally heavier compared to conventional DFT methods. Out of the different configuration of U (p,d) using ultrasoft pseudopotential with Schrodinger relativistic treatment the band gap is calculated as 3.628eV for the Hubbard parameter $U_p=7\text{eV}$ and $U_d=9\text{eV}$ and it is nearer to the experimental data as shown in Table-1. Again, for more validation, GGA and GGA+U approximations having different pseudopotentials, cutoff energy with different relativistic treatment for band gap are calculated and are shown in table-2. So, for the further calculation for total density of states, Partial density of states of SnO_2 using GGA+U functional these parameters are used.

Table-1:- Cutoff energy, K-point, Hubbard U value and corresponding band gap calculated for SnO₂ is presented here.

Cut off energy in eV	K-point	Hubbard U in eV		Band Gap in eV
		U _p	U _d	
375	3×3×3	0	0	1.002
375	3×3×3	3	6	2.136
375	3×3×3	4	8	2.505
375	3×3×3	6	9	3.251
375	3×3×3	7	9	3.628

Table-2: Band gap obtained with different relativistic treatment with different pseudopotentials is presented here.

Relativistic Treatment	Pseudopotentials	Cutoff energy in electron volt	Band Gap without U in electron volt	Hubbard U in electron volt	Band Gap with U in electron volt
Schrodinger	OTFG ultra-soft	650		U(7,9)	
	OTFG norm-conserving	950	2.016		4.624
	Ultra-soft	375	1.002		3.628
	Norm-conserving	750	1.692		4.367
Koelling Hermon	OTFG ultra-soft	650	1.229	U(7,9)	3.787
	OTFG norm-conserving	950	1.138		3.691
	Ultra-soft	375	1.002		3.628
	Norm-conserving	750	1.692		4.367
ZORA	OTFG ultra-soft	650	1.235	U(7,9)	3.794
	OTFG norm-conserving	950	1.145		3.698
	Ultra-soft	375	1.002		3.628
	Norm-conserving	750	1.692		4.367

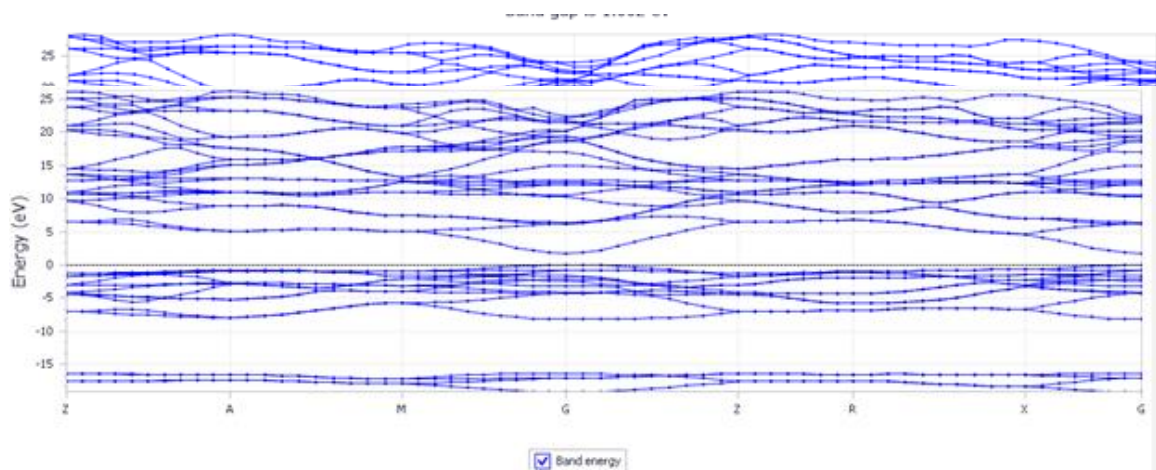
**Fig-3: Band plot of SnO₂ using DFT, Ultra-soft (Schrodinger/ Koelling Harman/ZORA)**

Fig-4: Band plot of SnO₂ using DFT, Norm conserving (Schrodinger/ Koelling Harman/ZORA)

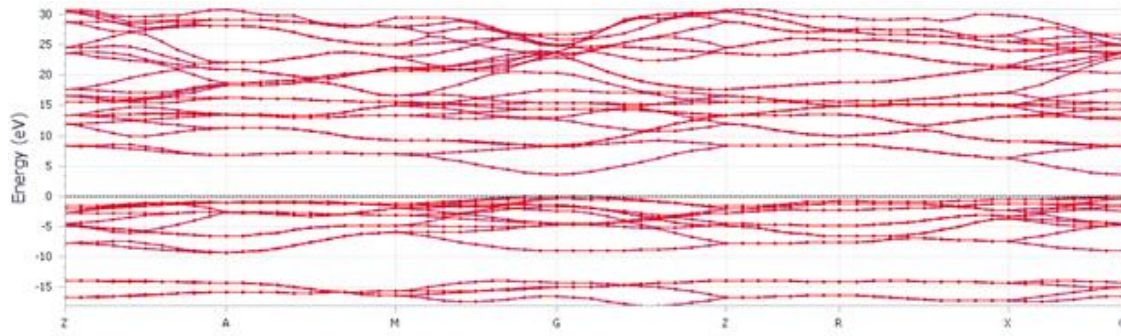


Fig-5: Band plot of SnO₂ using DFT+U, Ultra-soft (Schrodinger/ Koelling Harman/ZORA) with $U_P=7\text{eV}$ and $U_d=9\text{eV}$

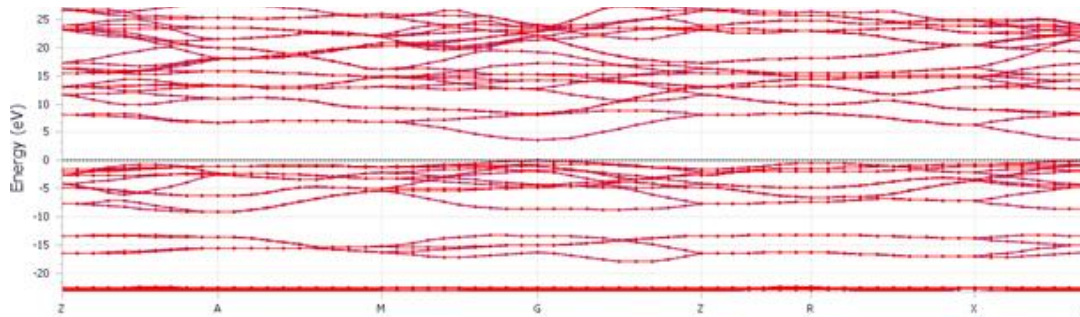


Fig-6: Band plot of SnO₂ using DFT+U, OTFG norm conserving (Koelling Harman) with $U_P=7\text{eV}$ and $U_d=9\text{eV}$

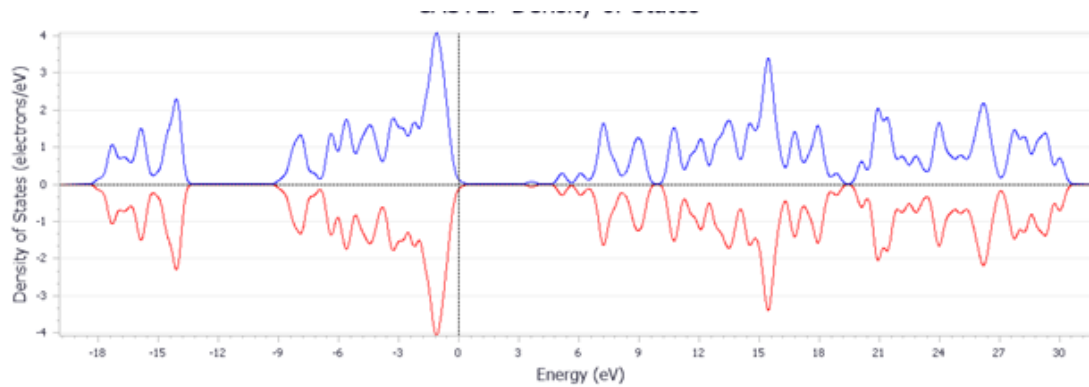


Fig-7: DOS plot of SnO₂ using DFT+U, Ultra-soft (Schrodinger) with $U_P=7\text{eV}$ and $U_d=9\text{eV}$

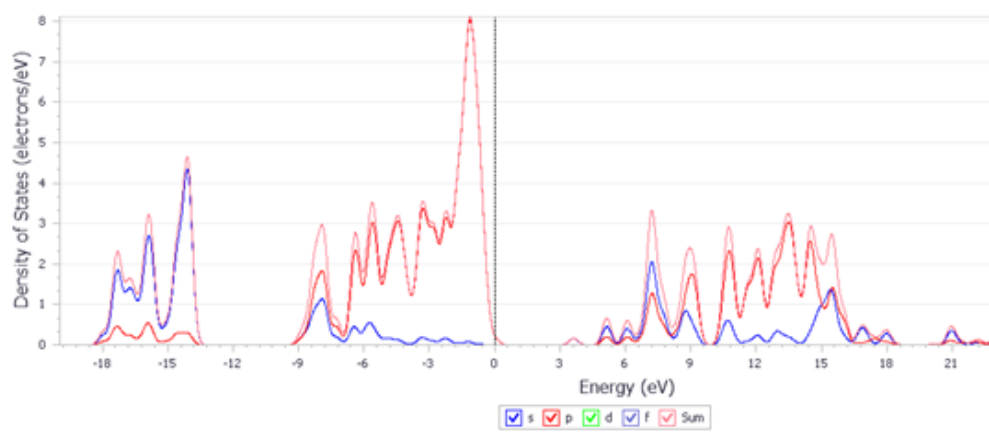


Fig-8: PDOS plot of SnO₂ using DFT+U, Ultra-soft (Schrodinger) with $U_P=7\text{eV}$ and $U_d=9\text{eV}$

Electronic Properties: -

The electronic configuration of Sn is $[\text{Kr}] 4d^{10} 5s^2 5p^2$ and of O is $[\text{He}] 2s^2 2p^4$. For these calculations, valence electrons of Sn and O are considered. All the calculations are done after geometry optimization. The Hubbard U parameter for p- orbital as 7eV and for d-orbital as 9eV taken for the multiple atom configuration. After geometry optimization the lattice parameters are obtained as $a=b=4.7372 \text{ \AA}$, $c=3.1863 \text{ \AA}$ with $\alpha=\beta=\gamma=90^\circ$ which are in good agreement with the experimental values $a=b=4.74 \text{ \AA}$ and $c=3.19 \text{ \AA}$ [21, 22]. Unit cell of SnO₂ is shown in Fig-1 and the BZ sampling of SnO₂ primitive cell shown in Fig-2. Ultra-soft pseudopotential with Schrodinger relativistic treatment is considered for calculation of band plot and DOS and PDOS plot. The calculated energy band structure of SnO₂ along the direction of high symmetry is shown in Fig -5. The zero of the energy axes coincides with the highest value of the valence band. Highest position of VB and lowest position of CB indicates a direct wide band gap of 3.628eV with calculated error of 0.77% in comparison to the experimental value. The TDOS of SnO₂ making use of DFT calculation, accompanied by GGA+U and Ultra-soft pseudopotential appeared in Fig-7. The dotted line represents Fermi level in the graph for density of states and energy. The left side of the dotted line represents VB and right side is the CB. In DOS plot more no of electrons are in valence band compared to conduction band and this indicates semiconducting property of SnO₂. The contribution of electron towards the density of states can be seen by partial density of state (PDOS) plots (Fig- 8). The PDOS plot indicates 's' and 'p' states contribute more both in valence band and in conduction band. The VB has two parts with an energy gap of around 3.9eV with many peaks and the maximum peak is at -1.32eV of the energy axis. The conduction band has four energy gaps of around 2.58eV, 0.6eV, 1.32eV, 0.18eV with the maximum peak is at 7.2eV of the energy axis. Some vacant energy states are present both in the VB and CB. GGA+U calculation shows near Fermi level of VB p-states (-9.3eV to 0.5eV) and s-states (-13.32eV to -18.42eV) contributes more, whereas for Fermi level energy region of CB both s-and p-states (4.8eV to 18.04eV) contributes more. Both in the VB and CB there is no contribution from d-states. Symmetry nature of both alpha and beta plots also explains the SnO₂ has no magnetic behavior.

Conclusion: -

Electronic properties of SnO₂ with DFT using GGA+U approximation with different pseudopotentials with different relativistic treatment having different cutoff energy and different Hubbard values are studied. From all the calculation ultrasoft pseudopotential with Schrodinger relativistic treatment having Hubbard U values $U_P=7\text{eV}$ and $U_d=9\text{eV}$ improved the electronic properties. So these parameters are used for further calculation of Band structure, TDOS and PDOS plots. DOS plot indicate no of electrons more in valence band than the conduction band indicating semiconductor nature of it. PDOS of it using GGA+U approximation shows contribution from 's' and 'p' states are more in both valence and conduction band. Again the symmetry shape of both alpha (for up spin electrons) and beta (for down spin electrons) in DOS plot explains it has no magnetic

behavior. The research can be extended either by doping/ co-doping transition metals or by creating O-vacancy or, by Sn-vacancy, so that it's magnetic property can be enhanced. If, it becomes possible then it will be a potential candidate for spintronic applications as both semiconducting property and magnetic behavior are the basic requirements for spintronics applications.

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