



**FIRST PRINCIPLE INVESTIGATION OF
STRUCTURAL AND ELECTRONIC
PROPERTIES OF MONOLAYER TUNGSTEN
DISULFIDE (WS_2)**

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To my mother!

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Abstract

In this thesis the first principle calculation of tungsten disulfide (WS_2) is investigated with density functional theory (DFT) using Quantum Espresso package. Our study is based on Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set implemented in the Quantum-ESPRESSO package. The calculation of the total minimum energy and the total minimum force of WS_2 is calculated as a function of cutoff energy and K-points sampling. The total minimum energy per cell is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-points sampling. Moreover, the equilibrium lattice constant is calculated using results obtained from energy convergence test (i.e., 90 Ry and $7 \times 7 \times 1$). The computational value of the equilibrium lattice constant is 3.23 Å. This result is in good agreement with experimental value which is 3.18 Å. Finally, discussing band structure and density of state of two dimensional WS_2 , the electrical property of two dimensional WS_2 is determined based on energy band gap.

Keywords: Tungsten Disulfide, Density Functional Theory, Electronic and structural properties.

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Chapter 1

Background of the Study

1.1 Introduction

Tungsten disulfide is the chemical compound with the formula WS_2 . It is composed of W and two sulfur atoms which has $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^4 6s^2$ or $[Xe] 4f^{14} 5d^4 6s^2$ and $1s^2 2s^2 2p^6 3s^2 3p^4$ or $[Ne] 3s^2 3p^4$ electron configurations respectively. It occurs naturally as the rare mineral tungstenite. This material is a component of certain catalysts used for hydrodesulfurization and hydrodenitrification. Like the closely related MoS_2 , it exhibits properties of a dry lubricant. It is chemically fairly inert but attacked by a mixture of nitric and hydrofluoric acids, when heated in oxygen-containing atmosphere, WS_2 converts to tungsten trioxide. When heated in absence of oxygen, WS_2 does not melt but decomposes to tungsten and sulfur, but only at $1250\text{ }^\circ\text{C}$ [1].

Density functional theory is an approach for the description of ground state properties of metals, semiconductors, and insulators. The success of density functional theory (DFT) not only encompasses standard bulk materials but also complex materials such as proteins and carbon nanotubes [2]. The main idea of DFT is to describe an interacting system of fermions via its density and not via its many-body wave function.

For N electrons in a solid, which obey the Pauli principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three -the spatial coordinates x , y , and z - rather than $3N$ degrees of freedom [3,4]. Knowledge of the density is all that is necessary for a complete determination of all ground state molecular properties. If one knows the exact electron density, $\tilde{n}(r)$, then the cusps of this density would occur at the positions of the nuclei [5].

1.2 Statement of the Problem

Many of the true breakthroughs in our technology have resulted from a deeper understanding of the properties of materials. Studying the properties of materials plays a crucial role to apply these materials in current technology. Tungsten disulfide is currently being used in industrial, manufacturing, mining, marine, agriculture, and automotive applications to reduce friction and wear.

The aim of this thesis is to investigate structural and electronic properties of WS_2 using DFT.

1.3 Research Questions

What is the total minimum energy of WS_2 per cell with respect to cutoff energy ?

What is the total minimum energy of WS_2 per cell with respect to K-points sampling ?

What is the minimum force of WS_2 per cell with respect to cutoff energy ?

What is the minimum force of WS_2 per cell with respect to K-points sampling ?

What is the lattice constant of WS_2 ?

What is band structure of WS_2 ?

What is density of state of WS_2 ?

1.4 Objectives of the Study

1.4.1 General Objectives

The general objective of this study is to predict the electronic and structural properties of two dimensional WS_2 with respect to density functional theory (DFT).

1.4.2 Specific Objectives

- ▶ To calculate the total minimum energy of WS_2 per cell with respect to cutoff energy ;
- ▶ To calculate the total minimum energy of WS_2 per cell with respect to K-points sampling ;
- ▶ To calculate the minimum force of WS_2 per cell with respect to cutoff energy ;
- ▶ To calculate minimum force of WS_2 per cell with respect to K-points sampling ;
- ▶ To calculate the lattice constant of WS_2 ;
- ▶ To calculate band structure of WS_2 ;
- ▶ To calculate density of state of WS_2 .

1.5 Significance of the Study

The significance of this study is to understand the electronic and structural properties of two dimensional WS_2 (many electron system) using new computational technique known as ab initio technique. Moreover it helps to understand the electrical property of two dimensional WS_2 . It also helps to compare the experimental results with respect to our calculation.

1.6 Scope of the Research

Due to time and budget constraint the scope of the study is limited to determine total minimum energy per cell of WS_2 with respect to cutoff energy and K-points sampling, to find total minimum force per cell of WS_2 with respect to cutoff energy and K-points sampling, the theoretical lattice constant and band structure of WS_2 , and to determine the density of state of WS_2 .

Chapter 2

Review of Related Literatures

2.1 Introduction

Any problem in the electronic structure of matter is covered by Schrödinger equation including the time. In most cases, however, one is concerned with atoms and molecules without time-dependent interaction, so we may focus on the time-independent Schrödinger equation [6]. Solving the Schrödinger equation to obtain energies and forces, require only the atomic numbers of the constituents as input, and should describe the bonding between the atoms with high accuracy [7].

2.2 Schrödinger Equation

The ultimate goal of most approaches in solid state physics and quantum chemistry is the solution of the time-independent, non-relativistic Schrödinger equation.

$$\hat{H}\psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E_i\psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \dots, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) \quad (2.2.1)$$

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_i \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}} \quad (2.2.2)$$

A separable solution of time independent Schrödinger equation has the property that every measurement of the total energy is certain to return the value E . Here, A and B run over the M nuclei while i and j denote the N electrons in the system. The first two terms describe the kinetic energy of the electrons and nuclei. The other three terms represent the attractive electrostatic interaction between the nuclei and the electrons and repulsive potential due to the electron-electron and nucleus-nucleus interactions [8].

2.3 The Variational Principle for the Ground State

When a system is in the state ψ , the expectation value of the energy is given by

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \quad (2.3.1)$$

where, $\langle \psi | \hat{H} | \psi \rangle = \int \psi^* | \psi d\vec{x}$

The variational principle states that the energy computed from a guessed ψ is an upper bound to the ground-state energy E_0 . Full minimization of the functional $E[\psi]$ with respect to all allowed N -electrons wave functions will give the true ground state ψ and energy $E[\psi_0] = E_0$. For a system of N electrons and given nuclear potential V_{ext} , the variational principle defines a procedure to determine the ground-state wave function ψ_0 , the ground-state energy $E_0[N, V_{ext}]$, and other properties of interest [9]. In other words, the ground state energy is a functional of the number of the electrons N and the nuclear potential V_{ext} :

$$E_0 = E[N, V_{ext}] \quad (2.3.2)$$

2.4 Quantum Many-Body Theory

The state of motion can not be solved analytically for systems in which three or more distinct masses interact [10]. To solve this problem we can use different approximation approaches. In general the N-electron Hamiltonian is given by equation (2.2.2) above. We can write equation (2.2.2) as

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee} \quad (2.4.1)$$

2.4.1 Born-Oppenheimer Approximation

Due to their masses the nuclei move much slower than the electrons. We can consider the electrons as moving in the field of fixed nuclei [11]. We can ignore the nuclear kinetic energy and their potential energy is merely constant. Thus, the electronic Hamiltonian (2.4.1) reduces to

$$\hat{H} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} \quad (2.4.2)$$

The solution of the Schrödinger equation with \hat{H} , is the electronic wave function ψ and the electronic energy E_{elec} is then the sum of E_{elec} and the constant nuclear repulsion term E_{nuc} .

$$\hat{H}\psi_{elec} = E_{elec}\psi_{elec} \quad (2.4.3)$$

$$E_{tot} = E_{elec} + E_{nuc} \quad (2.4.4)$$

where, $E_{nuc} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$

2.4.2 The Hartree-Fock Approximation

The Hartree-Fock approximation is the method whereby the orthogonal orbitals ψ_i are found that minimize energy for this determinantal form of ψ_0 :

$$E_{HF} = \min_{(\psi_{HF} \rightarrow N)} E[\psi_{HF}] \quad (2.4.5)$$

The expectation value of the Hamiltonian operator with ψ_{HF} is given by

$$E_{HF} = \langle \psi_{HF} | \hat{H} | \psi_{HF} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \quad (2.4.6)$$

$$H_i \equiv \int \psi_i^*(\vec{x}) \left[-\frac{1}{2} \nabla^2 - V_{ext} \right] \psi_i(\vec{x}) d\vec{x} \quad (2.4.7)$$

defines the contribution due to the kinetic energy and the electron-nucleus attraction and

$$J_{ij} = \int \int \psi_i(\vec{x}_1) \psi_i^*(\vec{x}) \frac{1}{r_{12}} \psi_j(\vec{x}_2) d\vec{x}_1 d\vec{x}_2 \quad (2.4.8)$$

$$K_{ij} = \int \int \psi_i^*(\vec{x}_1) \psi_i(\vec{x}_1) \frac{1}{r_{12}} \psi_{ij}(\vec{x}_2) \psi_j^*(x_2) d\vec{x}_1 d\vec{x}_2 \quad (2.4.9)$$

The integrals are all real, and $J_{ij} \geq K_{ij} \geq 0$. The J_{ij} are called Coulomb integrals, the K_{ij} are called exchange integrals. We have the property $J_{ii} = K_{ii}$.

The variational freedom in the expression of the energy equation(2.4.6) is in the choice of the orbitals. The minimization of the energy functional with normalization conditions $\int \psi_i^*(\vec{x}) \psi_j(\vec{x}) d\vec{x} = \delta_{ij}$ leads to the Hatree-Fock differential equations:

$$\hat{f} \psi_i = \epsilon_i \psi_i, i = 1, 2, \dots, N \quad (2.4.10)$$

These N equations have the appearance of eigenvalue equations, where the Lagrangian multipliers ϵ_i are the eigenvalues of the operator f. The Fock operator \hat{f} is an effective

one-electron operator defined as

$$\hat{f} = -\frac{1}{2}\nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \quad (2.4.11)$$

The first two terms are the kinetic energy and the potential energy due to the electron-nucleus attraction. V_{HF} is the Hartree potential, the average potential experience by the i^{th} electron due to the remaining N-1 electrons, and it is given by

$$V_{HF}(\vec{x}_1) = \sum_j^N (\hat{J}_j(\vec{x}_1) - \hat{K}_j(\vec{x}_1)). \quad (2.4.12)$$

$$\hat{J}_j(\vec{x}_1) = \int (\psi_j(\vec{x}_2))^2 \frac{1}{r_{12}} d\vec{x}_2 \quad (2.4.13)$$

The Coulomb operator \hat{J} represents the potential that an element at position \vec{x}_1 experiences due to the average charge distribution of another electron in spin orbital ψ_j . The second term in (2.4.13) is the exchange contribution to the HF potential. It has no classical analog and it is defined through its effect when operating on a spin orbital:

$$\hat{K}_j(\vec{x}_1)\psi_i(\vec{x}_1) = \int \psi_j^*(\vec{x}_2) \frac{1}{r_{12}} \psi_i(\vec{x}_2) d\vec{x}_2 \psi_j(\vec{x}_1) \quad (2.4.14)$$

The Hartree-Fock potential is non-local and it depends on the spin orbitals. Thus, the Hartree-Fock (HF) equations must be solved self-consistently [12].

2.5 Density Functional Theory (DFT)

DFT is the many body theory based on the idea of using only the density as the basic variable for describing many electron systems. It is widely used in condensed matter theory and computational material science for the calculation of electronic, magnetic and structural properties of solids.

Density functional theory is an extremely successful approach for solving many body problems' i.e., it is an exact reformulation of many-body quantum mechanics in terms of the probability density rather than the wave function. The following are among approximation approaches of density functional theory [13].

2.5.1 The Thomas-Fermi Model

This is the first density functional theory (1927) [14]. Based on the uniform electron gas, they proposed the following functional for the kinetic energy:

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} \quad (2.5.1)$$

The energy of an atom is finally obtained using the classical expression for the nuclear-nuclear potential and the electron-electron potential:

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} - Z \int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1d\vec{r}_2 \quad (2.5.2)$$

Here, the energy is given completely in terms of the electron density.

In order to determine the correct density to be included in equation (2.5.2), they employed a variational principle. They assumed that the ground state of the system is connected to the $\rho(\vec{r})$ for which the energy is minimized under the constraint of $\int \rho(\vec{r})d\vec{r} = N$.

2.5.2 The first Hohenberg-Kohn Theorem

The starting point of any discussion of DFT is the Hohenberg-Kohn (HK) theorem. The Hohenberg-Kohn theorem states that the particle density uniquely determines the

properties of a many-particle system [15]. It represents the most basic of a number of existence theorems which ensure that stationary many-particle systems can be characterized (fully) by the ground state density and closely related quantities. As the reasoning leading to the HK theorem is quite instructive, it is worthwhile to study this prototype of an existence theorem in some detail [16]. The first Hohenberg-Kohn theorem demonstrates that the electron density uniquely determines the Hamiltonian operator and thus all the properties of the system. This first theorem states that the external potential V_{ext} is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn V_{ext} fixes \hat{H} we see that the fully many particle ground state is a unique functional of $\rho\vec{r}$.

proof: Let us assume that there were two external potential $V_{ext}(\vec{r})$ and $V'_{ext}(\vec{r})$ differing by more than a constant, each giving the same $\rho(\vec{r})$ for its ground state, we would have two Hamiltonians \hat{H} and \hat{H}' whose ground-state densities were the same although the normalized wave functions ψ and ψ' would be different. Taking ψ' as a trial wave function for the \hat{H} problem.

$$E_0 \langle \psi' | \hat{H} | \psi' \rangle = \langle \psi' | \psi' \rangle + \langle \psi' | \hat{H} - \hat{H}' | \psi' \rangle = E'_0 + \int \rho(\vec{r}) [V_{ext}(\vec{r}) - V'_{ext}(\vec{r})] d\vec{r} \quad (2.5.3)$$

Where E_0 and E'_0 are the ground-state energies for \hat{H} and \hat{H}' , respectively. Similarly, taking ψ as a trial function for the \hat{H}' problem,

$$E'_0 \langle \psi | \hat{H}' | \psi \rangle = \langle \psi | \hat{H}' | \psi \rangle + \langle \psi | \hat{H} - \hat{H}' | \psi \rangle = E_0 + \int \rho(\vec{r}) [V_{ext}(\vec{r}) - V'_{ext}(\vec{r})] d\vec{r} \quad (2.5.4)$$

Adding equation (2.5.3) and (2.5.4), we would obtain $E_0 + E'_0 < E'_0 + E_0$, a contradiction, and so there cannot be two different V_{ext} that give the same $\rho(\vec{r})$ for their ground state.

Thus, $\rho(\vec{r})$ determines N and $V_{ext}(\vec{r})$ and hence all the properties of the ground state, for example kinetic energy $T[\rho]$, the potential energy $V[\rho]$, and the total energy $E[\rho]$. Now, we can write the total energy as

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r}) V_{Ne}(\vec{r}) d\vec{r} + F_{HK}[\rho], \quad (2.5.5)$$

$$F_{HK}[\rho] = T[\rho] + E_{ee} \quad (2.5.6)$$

This functional $F_{HK}[\rho]$ is the holy grail of density functional theory. If it were known we would have solved the Schrödinger equation exactly. And, since it is a universal functional completely independent of the system at hand, it applies equally well to the hydrogen atom as to gigantic molecules such as, say, DNA! $F_{HK}[\rho]$ contains the functional for the kinetic energy $T[\rho]$ and that for the electron-electron interaction, $E_{ee}[\rho]$. The explicit form of both these lies completely in the dark [17]. However, from the latter we can extract at least the classical part $J[\rho]$,

$$E_{ee}[\rho] = \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{ncl} = J[\rho] + E_{ncl}[\rho] \quad (2.5.7)$$

E_{ncl} is the non-classical contribution to the electron-electron interaction: self-interaction correction, exchange and coulomb correlation. The explicit form of the functionals $T[\rho]$ and $E_{nl}[\rho]$ is the major challenge of DFT.

2.5.3 The Second Hohenberg-Kohn Theorem

The second Hohenberg-Kohn theorem states that $F_{HK}[\rho]$, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density [18]. This is nothing but the variational principle:

$$E_0[\tilde{\rho}] \leq T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \quad (2.5.8)$$

In other words this means that for any trial density $\tilde{\rho}$, which satisfies the necessary boundary conditions such as $\tilde{\rho}(\vec{r}) \geq 0$, $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$, and which is associated with some external potential $V_{ext}^{\tilde{\rho}}$, the energy obtained the functional of equation (2.5.5) represents an upper bound to the true ground state energy E_o . E_o results if and only if the exact ground state density is inserted in equation (2.5.1).

Proof: The proof of equation (2.5.8) makes use of the variational principle established for wave functions. We recall that any trial density $\tilde{\rho}$ defines its own Hamiltonian \hat{H} and hence its own wave function $\tilde{\psi}$. This wave function can now be taken as the trial wave function for the Hamiltonian generated from the true external potential V_{ext} . Thus,

$$\langle \tilde{\psi} | \hat{H} | \tilde{\psi} \rangle = T[\tilde{\rho}] + E_{ee}[\tilde{\rho}] + \int \tilde{\rho} V_{ext} d\vec{r} = E[\tilde{\rho}] \geq E_{0[\rho]} = \langle \psi_0 | \hat{H} | \psi_0 \rangle \quad (2.5.9)$$

2.6 The Kohn-Sham Equation

In 1965 Kohn and Sham introduced a method for calculating these terms. Replace our system of interacting electrons with a fictitious system of non-interacting electrons of the same density [19]. The Kohn-Sham approach is the real break-through in modern DFT. It is tightly linked to the Hartree-Fock-Slater approximation of many fermion theory and considered exchange and correlation energies [20]. We have seen that the ground state energy of a system can be written as

$$E_0 = \min_{\rho \rightarrow N} (F[\rho] + \int \rho(\vec{r}) V_{Ne} d\vec{r}) \quad (2.6.1)$$

Where the universal functional $F[\rho]$ contains the contributions of the kinetic energy, the classical Coulomb interaction and the non-classical portion:

$$F[\rho] = T[\rho] + J[\rho] + E_{ncl}[\rho] \quad (2.6.2)$$

Of these, only $J[\rho]$ is known. The main problem is to find the expressions for $T[\rho]$ and $E_{ncl}[\rho]$. Kohn and Sham accounted for that by introducing the following separation of the functional $F[\rho]$.

$$F[\rho] = T_S[\rho] + J[\rho] + E_{xc}[\rho] \quad (2.6.3)$$

Where E_{xc} , the so-called exchange-correlation energy is defined through equation (2.6.2) as

$$E_{xc}[\rho] = (T[\rho] - T_S[\rho]) + (E_{ee}[\rho] - J[\rho]) \quad (2.6.4)$$

The exchange and correlation energy E_{xc} is the functional that contains everything that is unknown.

Now the question is: how can we uniquely determine the orbitals in our non-interacting reference system? In other words, how can we define a potential V_s such that it provides us with a Slater determinant which is characterized by the same density as our real system. To solve this problem, we write down the expression for the energy of the interacting system in terms of the separation described in equation (2.6.3).

$$E[\rho] = T_s[\rho] + J[\rho] + E_{xc}[\rho] + E_{Ne}[\rho] \quad (2.6.5)$$

$$\begin{aligned} E[\rho] &= T_S[\rho] + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho\vec{r}_2}{r_{12}} d\vec{r}_1 d\vec{r}_2 + E_{xc}[\rho] + \int V_{Ne}\rho(\vec{r})d\vec{r} \\ &= -\frac{1}{2} \sum_i^N \langle \psi_i | \nabla^2 | \psi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \int \int |\psi_i(\vec{r}_1)|^2 \frac{1}{2r_1} |\psi_j(\vec{r}_2)|^2 d\vec{r}_1 d\vec{r}_2 \\ &\quad + E_{xc}[\rho] - \sum_i^N \int \sum_A^M \frac{Z_A}{r_{1A}} |\psi_i(\vec{r}_1)|^2 d\vec{r}_1 \quad (2.6.6) \end{aligned}$$

The only term for which no explicit form can be given is E_{xc} . We now apply the variational principle and ask: What condition must the orbitals ψ_i fulfill in order

minimize this energy expression under the usual constraint $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. The resulting equations are the Kohn-Sham equations.

$$\left(-\frac{1}{2}\nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}\right]\right)\psi_i = \left(-\frac{1}{2}\nabla^2 + V_S(\vec{R}_1)\right)\psi_i = \epsilon_i\psi_i \quad (2.6.7)$$

$$V_S(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \quad (2.6.8)$$

2.7 Exchange-Correlation Energy Functional

In this section we introduce the most frequently used approximations for the xc-energy functional on the basis of a number of rigorous results for $E_{xc}[n]$.

2.7.1 Definition of Exact Exchange within DFT

It is usual to decompose the total xc-energy functional $E_{xc}[n]$ into an exchange part $E_x[n]$ and a correlation functional $E_c[n]$, in analogy to conventional many-body theory. It is nevertheless the natural first choice to define the exchange functional in such a way that the total energy E^{HF} and density n_{HF} of the Hartree-Fock (HF) approximation are reproduced if the correlation functional is completely neglected. The corresponding HF-only ground state energy functional $\tilde{E}[n]$ [21-25],

$$E[n] = T_s[n] + E_{ext}[n] + E_H[n] + E_x[n], \quad (2.7.1)$$

is hence to be minimized by n_{HF} ,

$$E^{HF} = \tilde{E}[n_{HF}], \quad (2.7.2)$$

while for any other density one must have

$$E^{HF} < \tilde{E}[n], \quad (2.7.3)$$

$$\forall n \neq n_{HF}$$

2.8 The Local Density Approximation

The early thinking that lead to practical implementations of density functional theory was dominated by one particular system for which near exact results could be obtained - the homogeneous electron gas. In this system the electrons are subject to a constant external potential and thus the charge density is constant. The system is thus specified by a single number - the value of the constant electron density $r = \frac{N}{V}$ [26].

Thomas and Fermi studied the homogeneous electron gas in the early 1920's. The orbitals of the system are, by symmetry, plane waves. If the electron-electron interaction is approximated by the classical Hartree potential (that is exchange and correlation effects are neglected) then the total energy functional can be readily computed . Under these conditions the dependence of the kinetic and exchange energy on the density of the electron gas can be extracted and expressed in terms of a local functions of the density. This suggests that in the inhomogeneous system we might approximate the functional as an integral over a local function of the charge density. Using the kinetic and exchange energy densities of the non-interacting homogeneous electron gas this leads to [27,28];

$$T[\rho] = 2.87 \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r} \quad (2.8.1)$$

and

$$E_x[\rho] = 0.74 \int \rho^{\frac{5}{3}}(\vec{r}) d\vec{r} \quad (2.8.2)$$

These results are highly suggestive of a representation for E_{xc} in an inhomogeneous system. The local exchange correlation energy per electron might be approximated as a simple function of the local charge density (say, $e_{xc}(r)$). That is, an approximation

of the form;

$$E_{xc}[\rho] \approx \int \rho(\vec{r}) \varepsilon_{xc}(\rho(\vec{r})) d\vec{r} \quad (2.8.3)$$

An obvious choice is then to take $E_{xc}(r)$ to be the exchange and correlation energy density of the uniform electron gas of density r - this is the local density approximation (LDA). Within the LDA $E_{xc}(r)$ is a function of only the local value of the density [29,30]. It can be separated into exchange and correlation contributions;

$$\varepsilon_{xc}(\rho) = \varepsilon_x(\rho) + \varepsilon_c(\rho) \quad (2.8.4)$$

2.9 Beyond the Local Density Approximation

At first sight a very natural extension of the LDA would be to recognise that in many systems the exchange contribution to the energy is dominant over the correlation energy and to compute the non-local exchange potential exactly as in Hartree Fock theory whilst approximating the correlation potential within the LDA [31]. This would yield a functional of the form:

$$E_{xc}(\rho) = E_{Fock} + E_c^{LDA} \quad (2.9.1)$$

The greater complexity associated with the calculation of the non-local exchange potential would be offset by potentially significantly greater accuracy. However, the performance of the LDA is, in part, based on rather delicate cancellations between the exchange and correlation interactions and, in general, the use of the exact exchange interaction produces rather poor results. In the homogeneous electron gas the non-local exchange potential has effectively infinite range and its contribution to the electron-electron interaction diverges at the Fermi surface. In metals we conclude that the non-local exchange potential does not yield the correct physics - indeed this

behaviour was one of the main motivating factors in the early work of Thomas and Fermi, which formed the basis of density functional theory.

The Hartree-Fock potential produces a very reasonable local and semi-local description - which is superior to that of the LDA - but introduces a pathological non-local feature. We can conclude that in order to improve on the LDA approximation semi-local theories which incorporate some of the features of the exact exchange interaction are required and that theories which preserve the analytic properties of the exchange correlation hole are likely to be successful [13,32].

2.10 The Generalized Gradient Approximation

The local density approximation can be considered to be the zeroth order approximation to the semi-classical expansion of the density matrix in terms of the density and its derivatives. A natural progression beyond the LDA is thus to the gradient expansion approximation (GEA) in which first order gradient terms in the expansion are included. This results in an approximation for the exchange hole which has a number of unphysical properties; it does not normalize to -1, it is not negative definite and it contains oscillations at large u .

In the generalized gradient approximation (GGA) a functional form is adopted which ensures the normalization condition and that the exchange hole is negative definite. This leads to an energy functional that depends on both the density and its gradient but retains the analytic properties of the exchange correlation hole inherent in the LDA [33]. The typical form for a GGA functional is;

$$E_{xc} \approx \int \rho(\vec{r}) \varepsilon_{xc}(\rho, \nabla \rho) d\vec{r} \quad (2.10.1)$$

2.11 Meta- GGA Functionals

Recently functionals that depend explicitly on the semi-local information in the Laplacian of the spin density or of the local kinetic energy density have been developed. Such functionals are generally referred to as meta-GGA functionals [34]. The form of the functional is typically;

$$E_{xc} \approx \int \rho(\vec{r}) \varepsilon_{xc}(\rho, |\nabla\rho|, \nabla^2, \tau) d\vec{r} \quad (2.11.1)$$

Where the kinetic energy density τ is

$$\tau = \frac{1}{2} \sum_i |\nabla\varphi_i|^2 \quad (2.11.2)$$

2.12 Hybrid Exchange Functionals

There is an exact connection between the non-interacting density functional system and the fully interacting many body system via the integration of the work done in gradually turning on the electron-electron interactions. The exact energy could be computed if one knew the variation of the density-density correlation function with the coupling constant, l . The LDA is recovered by replacing the pair correlation function with that for the homogeneous electron gas [35]. The adiabatic integration approach suggests a different approximation for the exchange-correlation functional. At $l = 0$ the non-interacting system corresponds identically to the Hartree-Fock ansatz, while the LDA and GGA functionals are constructed to be excellent approximations for the fully interacting homogeneous electron gas - that is, a system with $l = 1$. It is therefore not unreasonable to approximate the integral over the coupling constant as

a weighted sum of the end points - that is, we might set:

$$E_{xc} \approx aE_{Fock} + bE_{xc}^{GGA} \quad (2.12.1)$$

2.13 Self-Consistency in Density Functional Calculations

As mentioned, the Hohenberg-Kohn theorem shows that the total energy is variational, and this is the key to its usefulness. The true ground state density is that density which minimizes the energy. When approximations are made to $E_{xc}[p]$, such as the LDA, there is no longer a true variational principle, and there is no guarantee that the energy obtained by minimizing the now approximate energy functional will be higher than the exact ground state energy. Clearly then, the relative quality of different approximations cannot be determined by determining which of them yields the lower energy [36]. Furthermore, the true ground state density is not in general the density that minimizes the total energy as determined using approximate functionals. There is, in fact, no prescription for determining what the exact ground state density is from approximate functionals.

Accordingly, calculations proceed by minimizing the approximate energy functional, recognizing that, although the resulting energy may be lower (or higher) than the true ground state energy, a good approximation to the energy functional should give a good energy and density and that the procedure is exact for the true energy functional [37].

2.14 Pseudopotential

The Phillips-Kleinman Construction

The pseudopotential approach originated with the orthogonalized plane-wave (OPW) method [38], in which the valence wavefunctions were expanded using a basis consisting of plane-waves that were orthogonalized to the lower lying core states, φ_c .

$$\phi_{OPW}(K + G) = \phi_{PW}(K + G) - \sum_{\alpha,c} \langle \varphi_c | \phi_{PW}(K + G) \rangle \varphi_{\alpha,c}, \quad (2.14.1)$$

where ϕ_{PW} is a plane-wave and ϕ_{OPW} is the corresponding OPW, and the sum is over core states and atoms.

Pseudo-potentials were introduced to model the interaction between ions and valence electrons. They effectively eliminate, from the very start, the true electron-nuclear potential and the inner core electrons, that is, those electronic states which are tightly bound to the nucleus, do not participate in the formation of chemical bonds, and remain approximately unchanged in atoms, molecules, and solids [39,40]. This tremendous conceptual simplification also amounts to a very practical and efficient computational scheme, especially when a plane-wave basis set is adopted to expand the electronic wave functions. After 1980, this method, in connection with a density-functional description of the electron-electron interaction, evolved into a reliable prescription for the first-principles computation of electronic, structural, and

dynamical properties of molecules and solids.

The fundamental idea of pseudopotential is the replacement of one problem with another. The primary applications in electronic structure is to replace the strong Coulomb potential of the nucleus and the effects of the tightly bound core levels by an effective ionic potential acting on the valence electrons. The core states remain almost unchanged (Frozen approximation). Plane wave pseudopotentials are usually employed because of the extreme simplicity. The strong core potential is replaced by a pseudopotential. For many elements the resulting pseudo wave functions are quite smooth.

2.14.1 Orthogonalized Plane Wave (OPW) Method

Orthogonalized plane wave (OPW) begins by explicitly distinguishing between the core electrons and the valence electrons. The core wave functions are well localized about the lattice sites. Valence wave functions are approximated by a few plane waves. The OPW ϕ_k is defined by:

$$\phi_k = e^{i\vec{k}\cdot\vec{r}} + \sum b_c \psi_k^c(\vec{r}) \quad (2.14.2)$$

where, $\psi_k(\vec{r})$ is core wave functions.

Orthogonalized plane wave ϕ_k satisfy the Bloch condition with the wave vector \vec{k} . Therefore, the actual electronic eigenstates of the Schrödinger equation can be expanded as a linear combination of OPW's.

$$\psi_k = \sum c_k \phi_{k+K} \quad (2.14.3)$$

2.14.2 Model Ion Potential

Pseudopotential has become a fertile field for generating new methods and insight for the electronic structure of molecules and solids. There are two approaches:- Ionic Pseudopotential, i.e., for better transferability and total pseudopotential for describing bands accurately.

Pseudopotential has the following goals:

- (1) Pseudopotential should be as soft as possible, meaning that it should allow expansion of the valence pseudo-wave equations using as few plane waves as possible.
- (2) It should be as transferable as possible (meaning that a pseudopotential generated for a given atomic configuration should reproduce others accurately).
- (3) The pseudo-charge density (the charge density constructed using the density-wave functions) should reproduce the valence charge density as accurately as possible [39,40,41].

2.14.3 Norm-conserving Pseudopotential

The pseudo-wave function (and potential) are constructed to be equal to the actual valence wave function (and potential) outside some core wave function radius r_c . Inside r_c , the pseudo-wave functions differ from the true wave function, but the norm is constructed to be the same.

$$\int_0^{r_c} dr r^2 \psi^{*ps}(\vec{r}) = \int_0^{r_c} dr r^2 \psi^*(\vec{r}) \psi(\vec{r}) \quad (2.14.4)$$

The integrated charge density inside r_c for each wave function agrees.

The wave function and eigenvalue depend on the angular momentum l . The pseudo-wave function should be l dependent and is called semi-local. In position of norm-conservation ensures that the logarithm derivative (scattering property) of pseudo and all electron wave functions much of reference energy $[E]$ and the first derivative with respect to E matches as well.

Norm conserving pseudopotential has a special class in the development of ab initio pseudopotential and generated by calculations on atoms and can't be fitted to experiment.

2.14.4 Ultra Soft Pseudopotential

Ultra soft pseudopotential defines an auxiliary function added to the plane waves around each atom and allows fewer plane waves for good description. This is in spirit of OPW but with smooth auxiliary function.

Vanderbilt and co-workers [42,43,44] proposed a radical departure from the concept of norm-conservation. In their approach, the pseudo-wavefunctions are required to be equal to the all-electron wavefunctions outside r_c , as with norm-conserving pseudopotentials, but inside r_c they are allowed to be as soft as possible; the norm-conservation constraint is removed to accomplish this. Although this introduces some complications, it can greatly reduce the planewave cutoff needed in calculations, particularly since quite large values of r_c can be used in their scheme. The complications that result are two-fold. First of all, since the pseudo-wavefunctions are equal to the all-electron wavefunctions (and therefore have the same norm) in the interstitial, but do not have the same norm inside r_c they are necessarily not normalized. This introduces a non-trivial overlap into the secular equation. In fact, the overlap turns out

to be non-diagonal. Secondly, the pseudocharge density is not obtained by computing $\sum \varphi^* \varphi$ as with norm conserving pseudopotentials; among other things this would yield the wrong total charge. Rather, an augmentation term needs to be added in the core region. A third, but less important, complication is that by relaxing the norm conservation, the resulting pseudopotentials can become less transferable. However, Vanderbilt pseudopotentials were proposed for use in large scale calculations, for which the cost of generating pseudopotentials is negligible compared with the cost of the calculations. Accordingly, it is quite feasible to recalculate the pseudopotential as the configuration evolves during the course of the calculation [41].

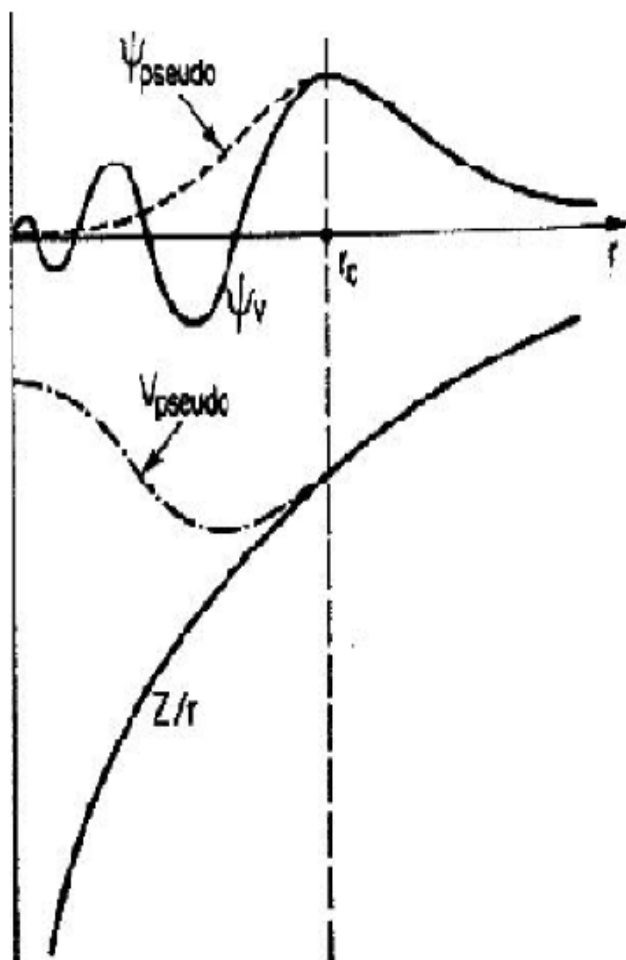


Figure 2.1: Schematic illustration of the replacement of the all-electron wavefunction and core potential by a pseudo-wavefunction and pseudopotential.

Chapter 3

Research Methodology

3.1 Materials

An intensive survey of literature from published articles, books and dissertations is carried out based on the projectile title.

Latex software, Quantum ESPRESSO and computers were additional instruments to accomplish this project.

3.2 Methodology

Our study is based on Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt ultra soft pseudo potentials [45] and the plane wave basis set implemented in the Quantum-ESPRESSO program package. Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling based on density-functional theory (DFT) , plane waves basis sets (PW) and pseudo potentials (PP). It is freely available and distributed as open-source software under the terms of the GNU General Public License (GPL) [46].

At first, an initial guess for the electron density is assumed, which is required for the calculation of $V_{eff}(r)$, the diagonalization of the Kohn-Sham equations, and the subsequent evaluation of $\rho(r)$ along with total minimum energy. As long as the convergence criterion is not fulfilled, the numerical procedure is continued with the last $\rho(r)$ instead of the initial guess. When criterion is satisfied, various output quantities are computed [47].

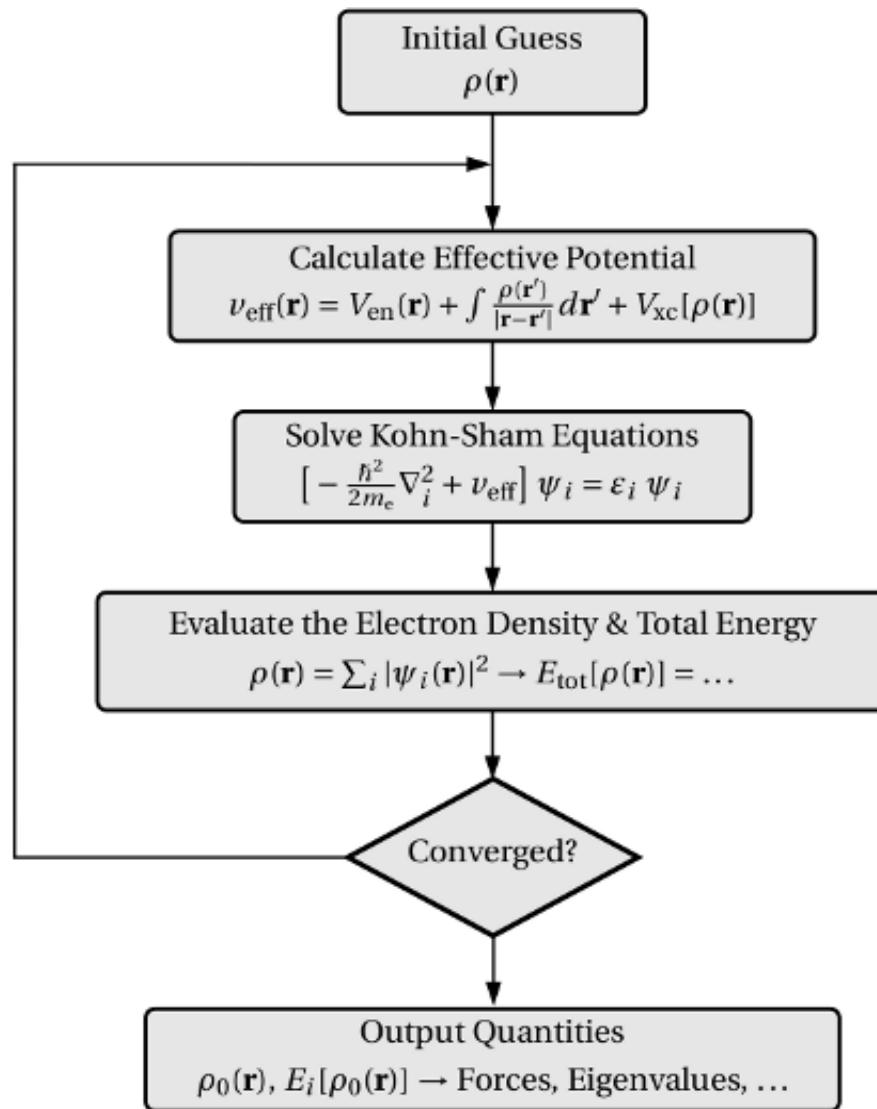


Figure 3.1: *Self Consistent Field of flow chart of the iteration scheme.*

Chapter 4

Results and Discussions

4.1 Introduction

In this chapter, the structural and electronic properties of tungsten disulfide, WS_2 , is calculated within the frame work of the density functional theory. The important aspects in studied tungsten disulfide are the total minimum energy and total minimum force, lattice constant, band structure and density of state of WS_2 . Results are mainly presented in figures. The first results are the total minimum energy per cell with respect to cutoff as well as K-points sampling and second results are total minimum forces values for two dimensional WS_2 with respect to cutoff and K-points sampling. Then comes the results for the equilibrium lattice constants, band structure and density of state of WS_2 . Graphs were plotted to obtain the optimized parameters for WS_2 structure with in the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set.

4.2 Geometrical Structure of Mono-layer WS_2

The primitive cell of WS_2 is shown in Figure 4.1. A single-layer of WS_2 is composed of hexagons with **S-W-S** atoms situated at commutative corners.

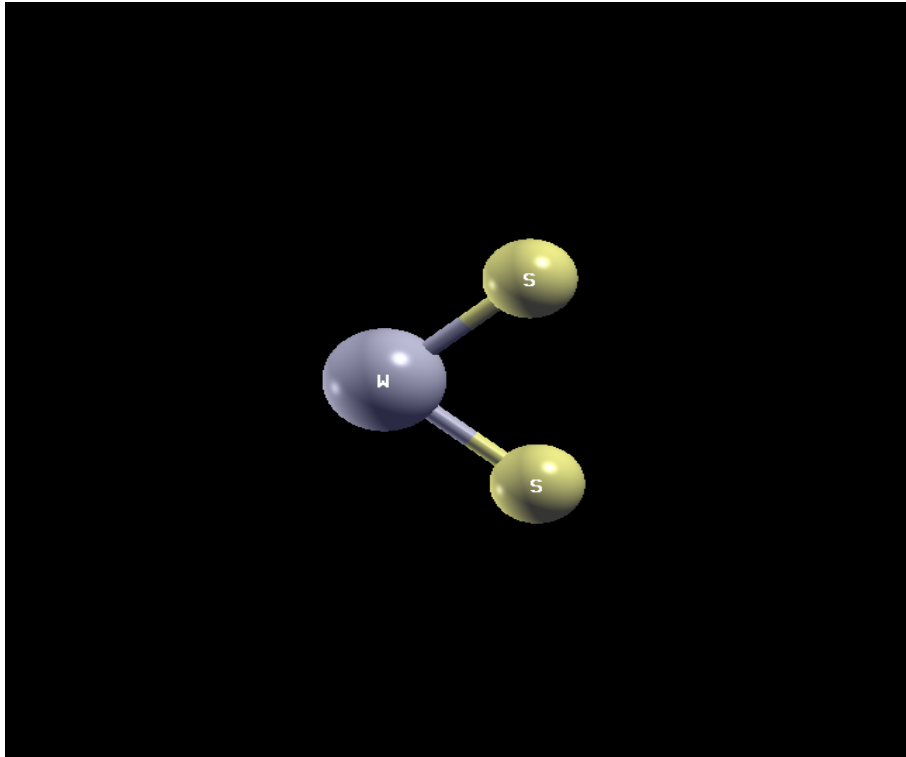


Figure 4.1: *Geometrical Structure of Mono-layer WS_2*

4.3 Convergence Test of Total Minimum Energy of WS_2 with Respect to Energy Cutoff

The total minimum energy of WS_2 is calculated as a function of energy cutoff. In this case the input code has $2 \times 2 \times 1 = 4$ K-points mesh and lattice constant of 3.18\AA . The calculation was done using different cutoff values, from 20 to 150 Ry. An increment of energy cutoff for wave function is made until the convergence is achieved (i.e., the place where the energy becomes nearly constant). As we can see from the Figure 4.2, the total minimum energy converges at 90 Ry plane wave cutoff energy and the total ground state energy had its minimum at -207.45120294 Ry. Moreover,

the total minimum energy is monotonically decreasing with increasing energy cutoffs for wave function. The accuracy of the ground state energy depends on the number of basis functions. However, we can get energy that close to ground state energy as the number of basis functions approaches infinity.

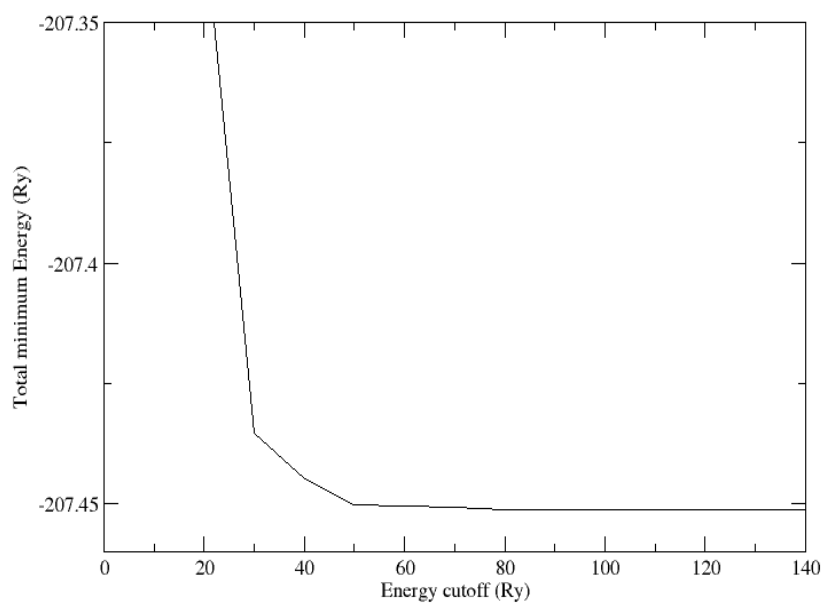


Figure 4.2: *Total minimum energy of WS_2 with respect to energy cutoff*

4.4 Convergence Test of Total Energy of WS_2 with Respect to K-point grid

In this case, the calculation was done using different k-point values from $2 \times 2 \times 1$ to $10 \times 10 \times 1$ k-points. The other variables such as lattice constant, energy cutoff, are kept fixed. The total minimum energy of WS_2 is calculated as a function of k-points grid size using PWSCF code. The total energy of WS_2 versus k-points grid size is shown in Figure 4.3. It can be observed that the total minimum energy of WS_2 converged at $7 \times 7 \times 1$ K-points grid and the total ground state energy has its minimum at -207.39508572 Ry.

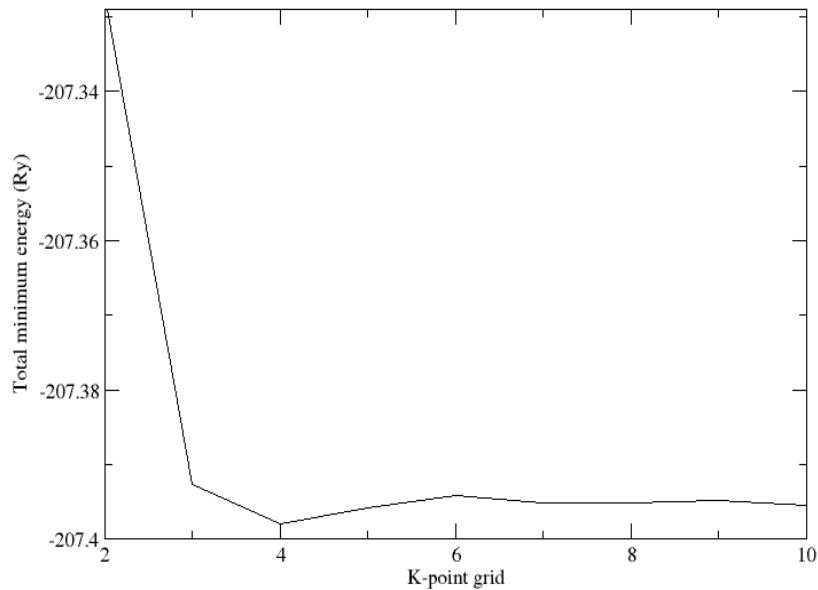


Figure 4.3: *Total minimum energy of WS_2 with respect to k-point sampling*

4.5 Convergence Test of Total Force of WS_2 with Respect to Energy Cutoff

In this calculations, we see that the forces on WS_2 are zero in x, y and z directions. This is because of symmetry, which cancels out forces. However, it is possible to create forces by displacing a W atom $+0.05\text{\AA}$ in the z directions (fractional coordinates). Here we calculated total force on WS_2 as a function of plane wave cutoff energy by keeping other parameters fixed. For this calculation, we used the lattice constants $a = 3.18\text{\AA}$ and $2 \times 2 \times 1$ k-points grid. In this simulation convergence is achieved when the energy cutoff is equal to 80 Ry. A total force value at this energy cutoff is $-0.037684\text{Ry}/\text{\AA}$.

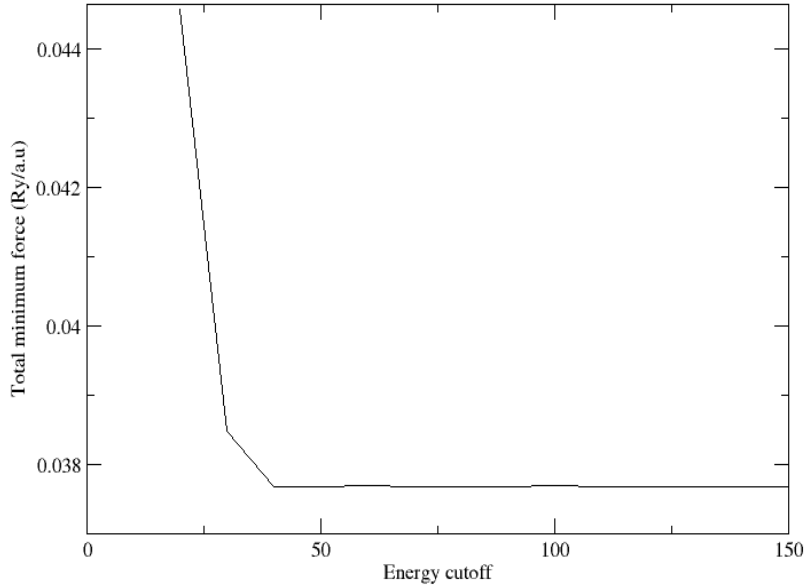


Figure 4.4: *Total force of WS_2 with respect to energy cutoff*

4.6 Convergence Test of Total Force of WS_2 with Respect to K-point grid

In this case, the calculation was done using different k-points value from $2 \times 2 \times 1$ to $10 \times 10 \times 1$. Here the other variables such as lattice constant, energy cutoff are kept fixed. As it is observed in Figure, the total force converges at the grid size of $8 \times 8 \times 1$ k-point mesh; and its value is $0.018640 \text{ Ry}/\text{\AA}$. Generally, it is true that different structural geometries will require different k-point meshes in order to reach convergence.

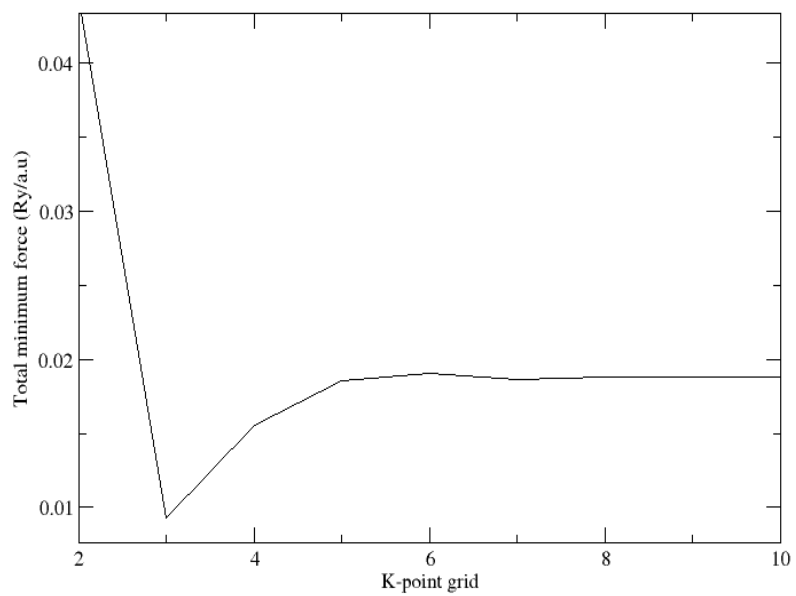


Figure 4.5: *Total minimum force of WS₂ with respect to k-point sampling*

4.7 The Equilibrium Lattice Constant of WS_2

To find the equilibrium lattice constant of WS_2 we estimated series of lattice parameters from 2.8 to 3.6. In this calculation the energy cutoff and the K-points sampling are made fixed (90 Ry, $7 \times 7 \times 1$ k-point) using the cutoff and k-point grid criteria for energy convergence. The numerical calculation shows that the equilibrium lattice constant is 3.23\AA . This result is in good agreement with experimental value.

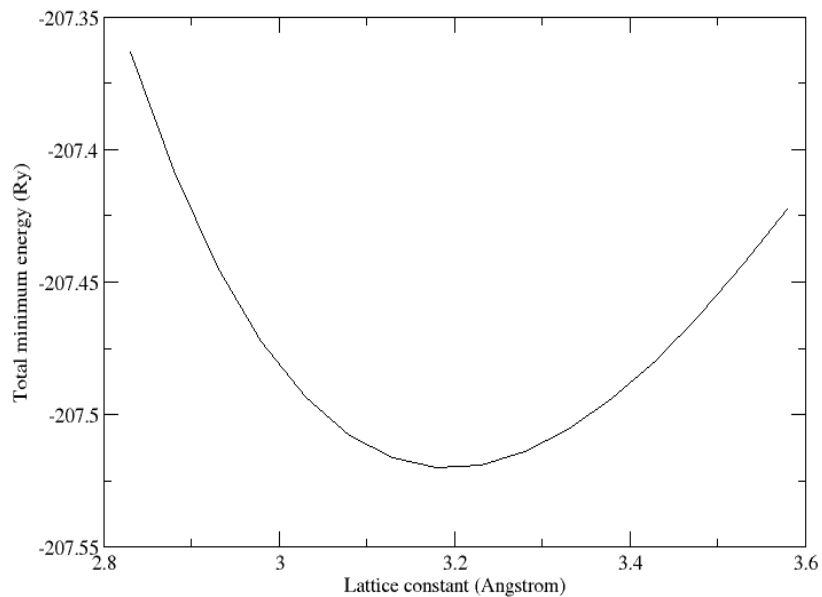


Figure 4.6: *Total energy of WS_2 versus lattice constant*

4.8 Band Structure of Two Dimensional WS_2

In this work, the energy cutoff and the BZ sampling were chosen to converge the total energy with a value of 20 Ry and we generated 36 K-points in crystal coordinate. The energy band structure of the mono-layer WS_2 is presented in Figure 4.7. Energy

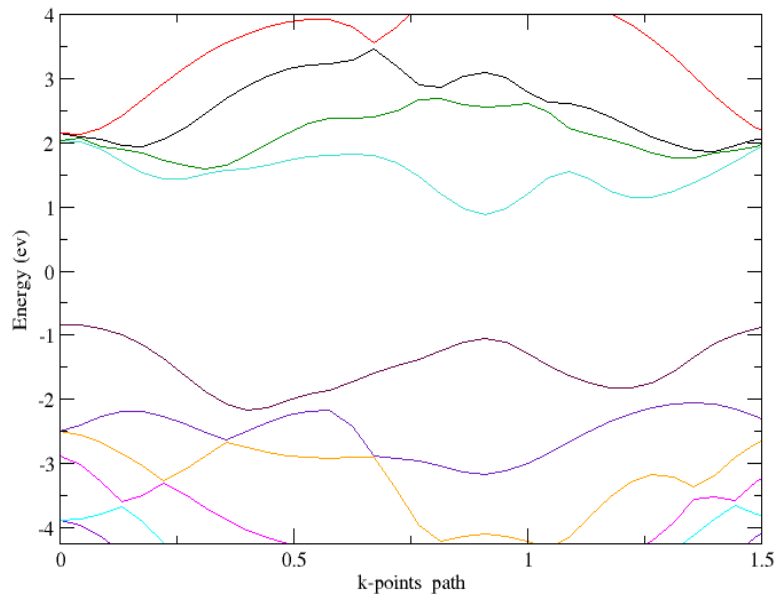


Figure 4.7: *Band Structure of mono-layer 2D WS_2*

gap between occupied and unoccupied energy levels is among the ways that we can determine the difference between electrical properties of metals, semiconductor, and insulator. From band structure of two dimensional WS_2 , we calculated the energy gap which is 1.875 eV. The calculated value has 6.25 percent of error with experimental value (2 eV). The two dimensional mono-layer WS_2 has a direct band gap.

The presence of a direct band gap in WS_2 makes it interesting for applications in optoelectronics.

4.9 Density of State (DOS) of WS_2

The main issue we can see from calculating the DOS of WS_2 is the investigation of electronic transport properties of WS_2 . From the following Figure 4.8, we see that before the Fermi level enters the conduction band, there is an insulating regime. The Fermi level (E_f) was referenced at 0 eV. The calculated energy gap of mono-layer WS_2 between the occupied and unoccupied energy levels was 1.78 eV and has 6.5 percent of error with experimental value. Semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the occupied level (valence electrons) and the energies of unoccupied level. Intrinsic semiconductors has (band gap between 1 eV and 3 eV). Since so, our calculated value shows as our system is semiconductor.

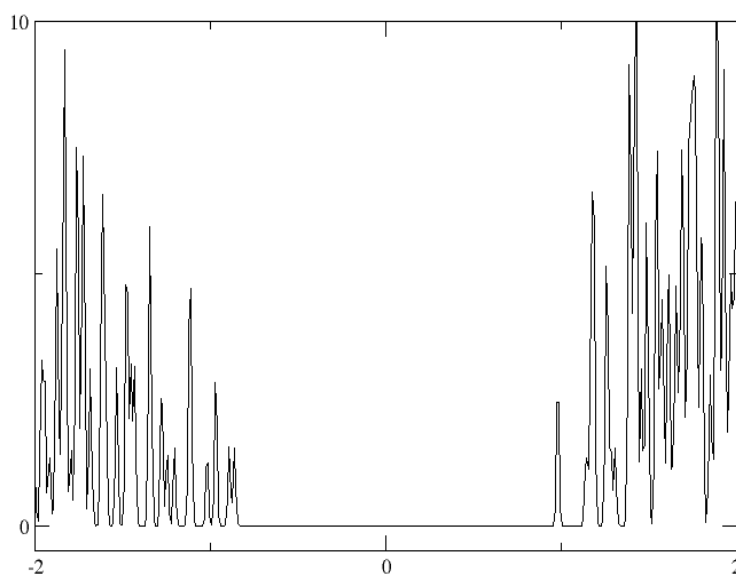


Figure 4.8: *Density of state of WS₂*

Chapter 5

Conclusion

In this thesis, we investigated structural and electronic properties of two dimensional WS_2 using DFT. The electronic and structural properties of Tungsten disulfide WS_2 was investigated within the frame work of the density functional theory (DFT) with the Perdew Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set implemented in the Quantum-ESPRESSO program package. All calculations have been carried out with Quantum Espresso package. The total minimum energy calculation is performed as a function of cutoff energy and Monkhorst pack-grid size (K-points sampling), respectively fixing the other parameters constant. The total energy convergence test is achieved, at the energy cutoff 90 Ry for the energy cutoff case and at $7 \times 7 \times 1$ k-point grid size for the K-point sampling case. The total minimum energy is -207.45120294 Ry for the first case and -207.39508572 Ry for the second case. The total minimum force on WS_2 as a function of cutoff energy and Monkhorst-Pack grid is calculated by displacing W atom by $+0.05\text{\AA}$. Total force convergence test is achieved for the cutoff energy 80 Ry and for Monkhorst-Pack grid at $8 \times 8 \times 1$ k-point grid size. The numerical calculation shows that the equilibrium lattice constant is 3.23\AA .

This value is in good agreement with existing experimental value which is 3.18\AA . In the case of investigating the band gap of WS_2 , we observed that indirect band gap of bulk WS_2 is changed to direct band gap of WS_2 . This change makes it interesting for applications in optoelectronics. Also, experimentally the band gap of 2D WS_2 is about 2.0 eV and our numerical calculation shows 1.875 eV, which has 6.25 percent of error with the experimental value. Finally, the calculated DOS of WS_2 determines its electrical property. The calculated energy gap of mono-layer WS_2 between the occupied and unoccupied energy levels in case of DOS is 1.78 eV and has 6.5 percent of error with experimental value. This value shows as this system is semiconductor.

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JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
PERFORMANCE CERTIFICATE FOR MASTER'S
DEGREE

Name of Student: **Gadaa Wako Gacha** ID No. **RM1035/10**

Graduate Program: **Regular, M.Sc.**

1. Course Work Performance

Course Code	Course Title	Cr. hr	Number Grade	Rank **	Remark
Phys799	M.Sc. Thesis	6		V.good	

** Ecellent, Very Good, Good, Satisfactory, Fail.

Thesis Title

First principle calculation of Tungsten disulfide using Density Functional Theory

2. Board of Examiners decision Mark in one of the boxes. Pass Failed

If failed, give reasons and indicate plans for re-examination.

3. Approved by: Name and Signature of members of the examining Board, and Department Head

<u>Committee member</u>	<u>Name</u>	<u>Signature</u>	<u>Date</u>
Chairman	_____	_____	_____
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Major Advisor	_____	_____	_____
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We the undersigned, member of the Board of Examiners of the final open defense by **Gadaa Wako Gacha** have read and evaluated his/her thesis entitled “**First principle calculation of Tungsten Disulfide using Density Functional Theory**” and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfilment of the requirements for the degree Master of Science in **Physics (Condensed Matter Physics)**.

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DECLARATION

I hereby declare that this M.Sc thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the dissertation have been duly acknowledged.

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This M.Sc dissertation has been submitted for examination with my approval as University advisor.

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