

FIRST PRINCIPLES STUDY OF QUANTUM CONFINEMENT EFFECT IN MoS₂ ELECTRONIC STRUCTURE

Submitted in partial fulfillment of the requirements for the award of
Master of Science degree in Physics

By

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**DEPARTMENT OF PHYSICS
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SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Accredited with “A” grade by NAAC | 12B Status by
UGC Approved by AICTE**

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BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of K. Nila (41590013) who carried out the project entitled "FIRST PRINCIPLES STUDY OF QUANTUM CONFINEMENT EFFECT IN MoS₂ ELECTRONIC STRUCTURE" under my supervision from November 2022 to May 2023.

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ABSTRACT

The three-dimensional materials possess great unique properties such as electronic, optical and thermoelectric properties. This leads in making very thin devices. The (TMDs) Transition Metal Dichalcogenides gained captivity among researchers since it has fascinating properties which leads to play specific role in certain applications. It is mainly used for semiconductor devices. It is composed of a metal (M) and two chalcogens (X₂). Among the TMDs, MoS₂ (Molybdenum Disulphide) has specific properties which can be studied theoretically in any of the structures. Each structure gives different property as a result.

In the present work, we study the structural, electronic, optical and thermoelectric properties of cubic and hexagonal structure of MoS₂ using DFT calculations. And also found that for cubic structure the bandgap is 0; hence it is a metal. On the other hand, the hexagonal structure is a semiconductor with energy gap of 0.891 eV. The main objective of the work is to study the properties which related to thermoelectric applications of Molybdenum Disulphide using wein2k software.

The lattice parameters are calculated using Birch-Murnaghan equation of states. The density of states (DOS) and the band gap diagrams are analyzed and studied. The graph has been plotted using the calculations.

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LIST OF SYMBOLS AND ABBREVIATIONS

$a.c$	-	lattice constant
B	-	Bulk modulus
ρ_{core}	-	core density
ρ_{val}	-	valence density
ρ_{tot}	-	total density
ϵ	-	Eigen values
E_F	-	Fermi energy
F_L	-	Fermi level
$F_{HK}[\rho]$	-	Hohenberg Kohn density functional
$N(E_F)$	-	DOS Fermi level
$n(r)$	-	electron density
V_H	-	Hartree potential
λ	-	electron-phonon coupling constant
Z_X	-	Variable positional parameter
BZ	-	Brillouin Zone
DFT	-	Density Functional Theory
DOS	-	Density of states
EFG	-	Electric Field Gradient
FP-(L)APW	-	Full Potential - (Linearized) Augmented Plane Wave
GGA	-	Generalized gradient Approximation
GUI	-	Graphical User Interface
KS	-	Kohn Sham
KKR	-	Koringa Kohn Rostoker
LDA	-	Local Density Approximation
LMTO	-	Linear Muffin Tin Orbital
LO	-	Local orbitals
LSDA	-	Local Spin Density Approximation

LCAO	-	Linear Combination of Atomic Orbitals
OPW	-	Orthogonalized Plane Wave
RMT	-	Radius of Muffin Tin spheres
EPM	-	Empirical Pseudo potential Method

GREEK LETTERS

Ω	Ohm
K	Thermal conductivity
K_e	Electronic, thermal conductivity
K_l	Lattice thermal conductivity
ρ	Density
ψ	Wave function

CHAPTER 1

INTRODUCTION

1.1 HISTORY OF THERMOELECTRICS

By the end of 18th century, the direct conversion of thermal to electrical energy was affirmed. The impact of electricity on animals was studied by Luigi Aloisio Galvani (Bologna, September 9,1737-Bologna, December 4,1798) at University of Bologna during those years. He is an Italian physician, physicist, philosopher and biologist. The temperature difference between the junctions of two dissimilar conducting materials, termed as the thermoelectric effect which was entrenched by an Italian physicist, Alessandro Volta.

This transpired beyond couple of decades before Johann Seebeck who is a German physicist from a Baltic German business family. A thermocouple deflects a compass magnet kept closer to the circuit, the angle of deflection depending on the temperature difference between the junctions. Seebeck disclosed his discovery in 1821, [1] presumed by mistake that the phenomena were because of the magnetism generated by temperature variations, which made him to decide that the observable Earth's magnetic field was prompted by the temperature variation between the two cold poles and the hot equator.

The electrical currents interact with magnetic materials, which was manifested in 1820 [2] by Danish scientist Hans Christian Oersted (Rudkbing, August 14,1777-Copenhagen, March 9,1851) this has started to happen.

In addition, even with Ampere, Laplace, Savart, Biot, and other scientists determined the interaction of electrical currents with magnetic fields. Seebeck opposed the phenomenon's electrical basis and termed the observed effect as thermos-magnetism [1]. Even though Seebeck distorted the phenomenon's physical basis, he measured the deflection of angle of the

magnetic compass because of variation in temperature difference in series of thermocouple by designing a setup that was almost similar to the one shown in Fig (1.1). Later it was understood that it was induced electrical current. Therefore, it paved a way for the further development of thermoelectricity.



Fig.1.1 The instrument used by T.J. Seebeck during his experiment

1.2 THERMOELECTRIC MATERIAL

As the world population increases drastically, the clean and renewable energy source becomes the essential requirement for human survival. We tend to face an energy challenge of climate in today's world in order to find new, clean and renewable energy sources [1].

By using the green and renewable energy sources we can control the utmost changes given raised by global warming and to stabilize the living condition on earth. Many articles have been published, studied and examined about the renewable energy sources such as biomass, hydropower, wind energy, solar energy, thermoelectricity etc in the context of energy crisis and environmental pollution [2-10]. Some well accepted renewable energy sources are biomass, hydropower, wind energy, solar energy, thermoelectric

energy etc. The important global problem is the unwanted heat which effects the global climate system. A majority household to industrial heat wastes are greater than 50% [2,3].

Due to the lack of moving components, lack of chemical reactions long life span etc, thermoelectric energy conversion technology has obtained large interests. Thermoelectric devices lay out a path to retain energy from implementation with enormous amount of waste heat. In energy conversion, heat energy is converted into electricity using thermoelectric generators which plays a significant part. In order to generate good electric power without utilising non-renewable resources, several experimentalists and theoretical physicists are examining for and fabricating new thermoelectric materials.

By utilising thermoelectric generators, which transforms heat energy into electricity and have a wide advantage such as moderate performance, a simple system structure and no moving parts, which can help improve the prolonged sustainability of power generated from waste heat. Solid-state devices such as refrigerators and thermoelectric generators transform heat energy into electricity [5]. Thermoelectric generators have been utilised in various applications besides remote power generation and electricity storage. Thermoelectric refrigerators are eco-friendly, working duration is large and can be used instead of usual refrigerators. Semiconducting alkaline earth metal compounds have grasped a great interest on implementing it in the thermoelectric devices [6].

$ZT = S^2 \sigma T / \kappa$ is the dimensionless figure of merit ZT [11], in which σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is the absolute temperature. These are the parameters that analyses the execution of thermoelectric materials. Power factor (PF) can be given by taking product of Seebeck coefficient and electrical conductivity (σ). The dimensionless figure of merit can determine the efficiency (η) [12] of any thermoelectric generator or refrigerators. The high Seebeck coefficient (thermo power) and low thermal conductivity determines the good thermoelectric material [7].

1.3 CONSTITUENT PARAMETERS INVOLVED IN FIGURE OF MERIT

It is contemplated that the main hindrance for the development of thermoelectric devices to large scale production is getting higher ZT value. The parameter to find the value of ZT extremely correlated.

$ZT = S^2 \sigma T / K$ is the dimensionless figure of merit ZT in which for a greater value of ZT, we depend on higher Seebeck coefficient (thermo power) and electrical conductivity whereas decreased value of thermal conductivity.

This section shares out of each quantity that aims towards enhancing constituent factors [8].

1.3.1 Seebeck coefficient (thermopower)

Seebeck coefficient otherwise termed as thermopower which is given as the ratio of voltage difference to the temperature difference. It can be given as $S = \frac{\Delta V}{\Delta T}$, holding the unit V/K. In which ΔV is the voltage difference,

ΔT is the temperature difference and S is the Seebeck coefficient. $S = \frac{8\pi^2 k^2 B T}{3 e h^2}$

$m_s^* (\pi/3n)^{2/3}$ is the Seebeck coefficient which is equivalent of the effective mass of electrons and concentration of charge carriers.

1.3.2 Thermal conductivity

Electrons and phonons have the capability of conducting heat. The addition of thermal conductivity owing to electrons and thermal conductivity owing to phonons is equal to the net thermal conductivity, which can be given as,

$$k = k_L + k_E$$

In which k_L determines the phonon induced heat conductivity

And k_E determines the thermal conductivity of electrons in which the electrons result thermal conductivity.

1.3.3 Electrical conductivity(σ)

The materials ability to pass the flow of current is the electrical conductivity which can be given as

$$\sigma = 1/\rho = ne\mu \quad [13]$$

μ -mobility

It can be denoted using the unit Siemens per metre ($S.m^{-1}$)

The materials ability to oppose the flow of current is the electrical resistivity(ρ) which is totally a reciprocate of electrical conductivity.

1.3.4 Figure of Merit

Thermoelectric materials can be determined by the important criterion called figure of merit [14]. Thermoelectric materials efficiency can be expressed using it.

$$ZT = \frac{S^2 \sigma T}{k}$$

Is the figure of merit, in which

S determines the Seebeck coefficient(V/K), σ determines the electrical conductivity(S/m), k determines the thermal conductivity(W/Mk) and temperature(K) as T . Power factor (PF) can be given as by taking product of Seebeck coefficient (S^2) and electrical conductivity($S^2\sigma$) [11].

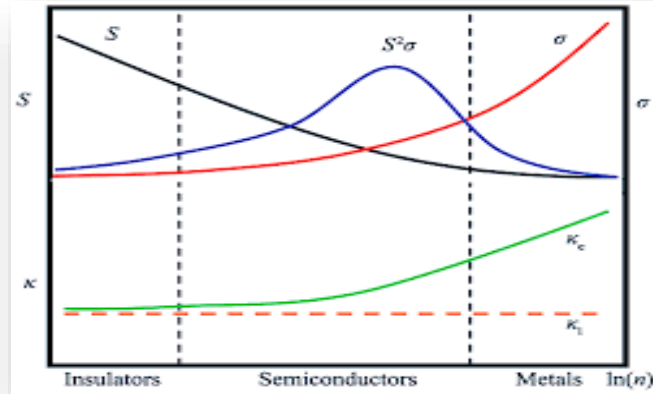


Fig. 1.2 Thermoelectric figure of merit

In order to acquire a high figure of merit, the following parameters should be needed such as a high Seebeck coefficient, low thermal conductivity and high electrical conductivity. From the above graph it is clear that all the parameters correspond one another. ZT is otherwise termed as thermoelectric efficiency since it is correlated to the device efficiency and single element.

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1 + ZT}}{\sqrt{1 + ZT} \frac{T_C}{T_H} + 1}$$

is the thermoelectric efficiency in which ΔT is the temperature difference between hot side T_H and cold side T_C [13].

1.4 APPLICATIONS

1.4.1 Solar energy application

Basically, solar panels are eco-friendly to the environment and are renewable source of energy. The phenomenon here is the sun rays emitted from the sun or thermal energy or heat is directly converted into electrical energy. Studies reveal that thermoelectric panel can be a best replacement for photovoltaic panels which can compete. They are more advantageous than PV panels [15]. About 80 percentage of incident solar radiation can be absorbed by PV panels. There is a large amount of waste heat which results in the lowering the efficiency rate, thus it is required to implement a cooling system for PV panels [16].

To avoid those circumstances and to increase the efficiency the PV systems can be integrated to the thermoelectric (TE) devices [17,18].



Fig 1.3 Thermoelectric solar panel

The combination of p and n type semiconductors and conductors imposes thermoelements which gives basic structure for thermoelectric module. They are connected electrically and thermally in series and parallel

respectively. This module is based on the principle of Seebeck effect [15].

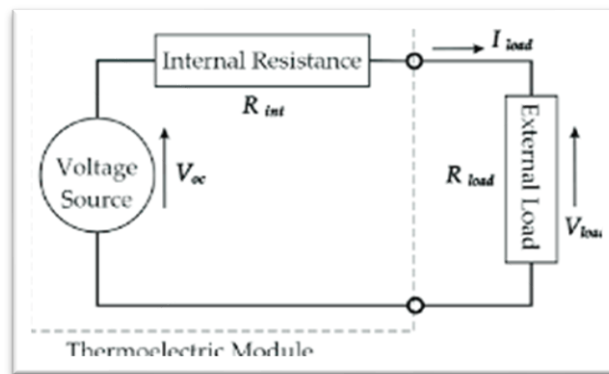


Fig 1.4 Thermoelectric Module

1.4.2 Solar thermal water purification

As there is a rapid growth in population, there rises scarcity in clean fresh water and we are in a need of water treatment processes. we use solar steam generation on the phenomenon of photoelectric effect. So far, we have been using carbon-based materials such as graphene, graphene oxide and carbon nanotubes for the process which can reduce the efficiency. Molybdenum disulphide overcomes the shortcomings of the other materials and gives good scalability and high efficiency [19].

This purifier system is generally refined from the electricity produced by solar PV, solar UV light collection and solar thermal. This solar thermal disinfectant absorbs heat from the sun and heats the water for optimum temperature [22].



Fig 1.5 Solar powered water purification

1.4.3 Photocatalyst for CO_2 reduction

CO_2 is one of the major causing constituents of global warming and other environmental related changes which leads to several health issues and mortality [20]. By photocatalytic activity we can produce fuel from hydrogen and CO_2 which is referred as e fuels. Because of the atomic arrangement and structure of metal dichalcogenides, they are implemented in catalytic activities in HER, OER and CO_2 reduction [21].

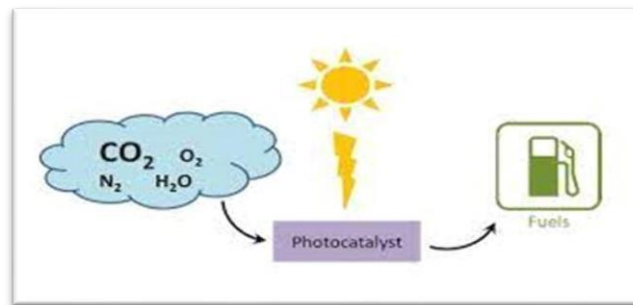


Fig 1.6 Photocatalytic CO_2 reduction

1.4.4 OPTOELECTRONIC DEVICES

Based on semiconductor junction electronics some types of devices such as Photodiodes, Light emitting diode, Laser diodes in which the optical radiation is emitted, converted or modified to other useful forms. Photodiodes transform incoming light into current which is a optoelectronic device based on semiconductor junction. Recently the atomic layers of TMD's have been used as a gate dielectric in the fabrication of Field Effect Transistors (FET) for electronic and optoelectronic devices [46].

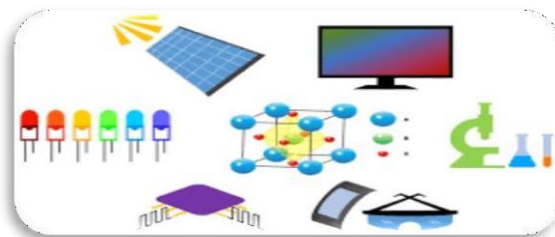


Fig 1.7 Optoelectronic functional devices

1.5 COMPOUND

In recent years, scientists have a strong interest in doing researches using TMDs. They have a very unique properties and wide range of applications. They are the class of materials which has the chemical formula of MX_2 , in which M corresponds to the transition metal atom which belongs to group 4 to 12 and X corresponds to chalcogen which belongs to group 16 in the periodic table respectively. Here one layer of M is sandwiched with two layers of chalcogens. From the periodic table, the transition metals are such as Ti, V, Co, Ni, Zr, Nb, Mo, Tc, Rh, Pd, Hf, Ta, W, Re, Ir, Pt and the chalcogens such as S, Se and Te.

MoS_2 , WS_2 , $MoSe_2$ and WSe_2 are some recently implemented TMDs in various applications. MoS_2 has many promising peculiarities and wide range of applications in several fields. It is an inorganic compound, composed of Molybdenum and Sulphur. The solubility nature in water is insoluble. It is obtained in black or lead grey crystal or in powder form. The boiling point of MoS_2 is $2375^\circ C$. Its molar mass is around 160.07 g/mol [47]. Experimentally it can be synthesised in various methods. Their properties get varied according to their different structures.



Fig 1.8 Molybdenum disulphide

CHAPTER 2

LITERATURE REVIEW

In 2022, Wei sun investigated the recent advances in MoS₂-based materials synthesis and their applications especially on batteries, catalysts and gas sensors.

In 2021, Omnia Samy, successfully made the different MoS₂ structures and their synthesizing techniques in expansion and given a comprehensive comparison between the three different structures providing the main optical, lattice and electrical properties and applications.

In 2021, Hakon Eidsvåg, Murugesan Rasukkannu, a Dhayalan Velauthapillaia and Ponniah Vajeeston studied the in-depth first-principle study on novel MoS₂ polymorphs.

In 2021, Abdel maksoud carried out the synthesis, electronic structure and properties, calculations of state, bandgap and charge density profiles, and applications in energy storage and water remediation of MoS₂.

In 2019, Nuria Aguilar and Santiago Aparicio studied the properties of MoS₂ based nanomaterials gaseous CO₂ using theoretical approach.

In 2018, Nguyen N. Hieu ^a, Victor V. Ilyasov ^b, Tuan V. Vu ^c, Nikolai A. Poklonski ^d, Huynh V. Phuc ^e, Le T.T. Phuong ^f theoretically studied the optical properties of molybdenum disulfide using first principles calculations.

In 2018, Peng fei lui and bao tian wang studied face-centered cubic MoS₂: a novel superconducting three-dimensional crystal more stable than layered T-MoS₂.

In 2018, Basant A. Ali studied the composite of MoS₂, CNT and GNF with ratio of 1:1:1. And examined that the charge storage is dependent on structure and carbon materials content. Also successfully demonstrated the fabrication of 2H MoS₂.

In 2017, Imam Abdul Rahman and Acep Purqon studied the characteristic, electronic structure and unique bandgap properties of MoS₂. density functional theory approach: a first principle study.

In 2017, M. Javaid, Daniel W. Drum studied the size dependent properties of MoS₂ monolayer nanoflakes using density-functional theory.

In 2016, Qasim Mahmood demonstrated the fast and reversible extrinsic surface charge-storage behavior of MoS₂ that rises from nano scaling and hybridization, which is given by measuring the electrokinetic parameters and dynamics. Such unique capacitive features of the 2D RM hybrids such as a high specific capacitance, high-rate capability, and long-cycle stability, which were not observed in the bulk and 2D MoS₂.

In 2015, Xiao Li provides the trending development of optical and electronic properties, synthesis and potential applications of 2D molybdenum disulphide. A pathway for fabricating hybrid structures based on MoS₂ and graphene has been highlighted.

In 2015, Muharrem Acerece examined and concluded as per results that TMDs other than MoS₂ can exhibit electrochemical properties, by chemically a fitting metallic phase is achieved.

In 2015, Nitin Choudhary fabricated a high-performance superconductor electrode using MoS₂ thin films experimentally using the direct magnetron sputtering technique.

In 2014, A. Ramadoss synthesized the mesoporous molybdenum disulphide (MoS₂) nanostructure using facile hydrothermal way for the application of

supercapacitor. The images from SEM and TEM characterization confirmed certain mesoporous morphology.

In 2012, Hao Qui reported the performance and environmental on bilayer MoS₂ field effect transistor. Also showed that the devices are sensitive to water and oxygen in ambient. And demonstrated to remove the absorbates to restore its efficiency.

In 2011, Yan Guang Li, developed a selective solvothermal synthesis of molybdenum disulphide nanoparticle on RGO sheets put up in a solution. The resulting RGO hybrid material has nanoscopic few layer MoS₂ structures with an abundance of exposed edges stacked onto graphene like structure.

In 2011, Goki eda reported structural and electronic properties of chemically exfoliated molybdenum disulphide. The chemically exfoliated MoS₂ exhibit prominent band gap photoluminescence, similar to mechanically exfoliated monolayers showing the semiconducting properties are greatly retained.

CHAPTER 3

AIM AND SCOPE

3.1 AIM

The aim of the project is to study theoretically the properties of transition metal dichalcogenides MoS_2 . The properties such as structural, electronic property, thermoelectric property and optical property of my chosen material MoS_2 is studied. Each property differs according to their material structure. The above-mentioned properties are theoretically studied using Wien2k software.

There are many research papers out there on the properties, application and synthetization of MoS_2 . Here my objective is to study different MoS_2 structures property such as hexagonal and Cubic structure of MoS_2 . From the literature survey so far, I have studied, we lack a comprehensive comparison of different structures of MoS_2 . This work gives a clear out look of comparison on each property of these two structures.

As of my literature review the cubic structure of MoS_2 lacks experimental research work so far. As per the band gap acquired the properties have been studied. The comparative results have been discussed and graphs have been stimulated and attached for clear understanding. The values obtained from the stimulation and some manual calculations applied through the formulas have been tabulated in the tables. The graphs have been analysed and interpreted in the conclusion part. Few applications of MoS_2 have been focused based on their property.

3.2 SCOPE

For the past several decades silicon plays a revolution over semiconducting based devices. It is abundant on earth. Although researches are in the nook for the replacement of silicon over other materials.

MoS₂ has such promising peculiarities for the replacement of silicon. Some applications which can be implemented in future can be semiconductor, transistor, chips and other fields which are advanced. MoS₂ comes under the transition metal dichalcogenides which plays a vital role in energy storage devices such as solar panels, photovoltaic cells etc. As the world population gets increased there is a need for the conservation of energy and lacking of natural resources occur. Thus, we are in an urge of developing the energy storage devices to face the challenges in future.

It can be a future revolutions best outcome and development for the micro and nanoelectronics industry. On the other hand, it is quite difficult to synthesis. There is a wasted heat category in using silicon-based devices, but MoS₂ overcomes such conditions, even they are faster and conduct large current without heated is one of the best reasons for the alternative of silicon.

By doping MoS₂ with other reliable materials gives excellent outcome which can be implemented in several fields. Thus, utilizing it in a proper way it can be implemented in wide applications.

CHAPTER 4

COMPUTATIONAL METHODOLOGY

4.1 DENSITY FUNCTIONAL THEORY

Density functional theory (DFT) is a quantum mechanical modelling method used in Physics and Chemistry to investigate the electronic structure of many-body systems, in particular atoms, molecules, and the condensed phases [23-26]. An analytical solution of the many-electron Schrödinger equation is not available, and a numerical solution, while perfectly possible in theory, is effectively impossible in practice for more than a handful of electrons due to the finite speed and memory of computers. In this section we will introduce density functional theory (DFT) as a mean of circumventing solution of the many-electron Schrödinger equation, since the properties of a many-electron system can be determined by using just functional of the electronic density.

Density functional theory Ground state properties of metals, semiconductors, and insulators have been successfully described by DFT. DFT has been not only applied for standard bulk materials, it has been quite 74 successful for complex materials such as proteins and carbon nanotubes. The main idea of DFT is to describe a many body problem of interacting system of electrons and nuclei by mapping on to a one electron reference system that leads to same density as real system.

According to Hohenberg and Kohn theorem all observable quantities can be retrieved in a unique way from the density alone and can be written as a functional of density. Therefore, the basic variable of a system depends only on three (spatial coordinates x , y , and z) rather than $3N$ degrees of freedom. Spin densities $\rho\sigma(r)$ are the key quantities here and total energy can be written as

$$E_{\text{tot}}(\rho\uparrow, \rho\downarrow) = T_s(\rho\uparrow, \rho\downarrow) + E_{ee}(\rho\uparrow, \rho\downarrow) + E_{Ne}(\rho\uparrow, \rho\downarrow) + E_{xc}(\rho\uparrow, \rho\downarrow) + E_{NN}$$

Where T_s , E_{ee} , E_{Ne} , E_{xc} , E_{NN} are the kinetic energies of the non-interacting particles, electron-electron repulsion, nuclear-electron attraction, exchange-correlation and repulsive Coulomb energy of fixed nuclei respectively. Out of infinite

number of possible densities the one which minimizes energy is the ground state density. The problem therefore is to solve the Kohn-Sham (KS) equation.

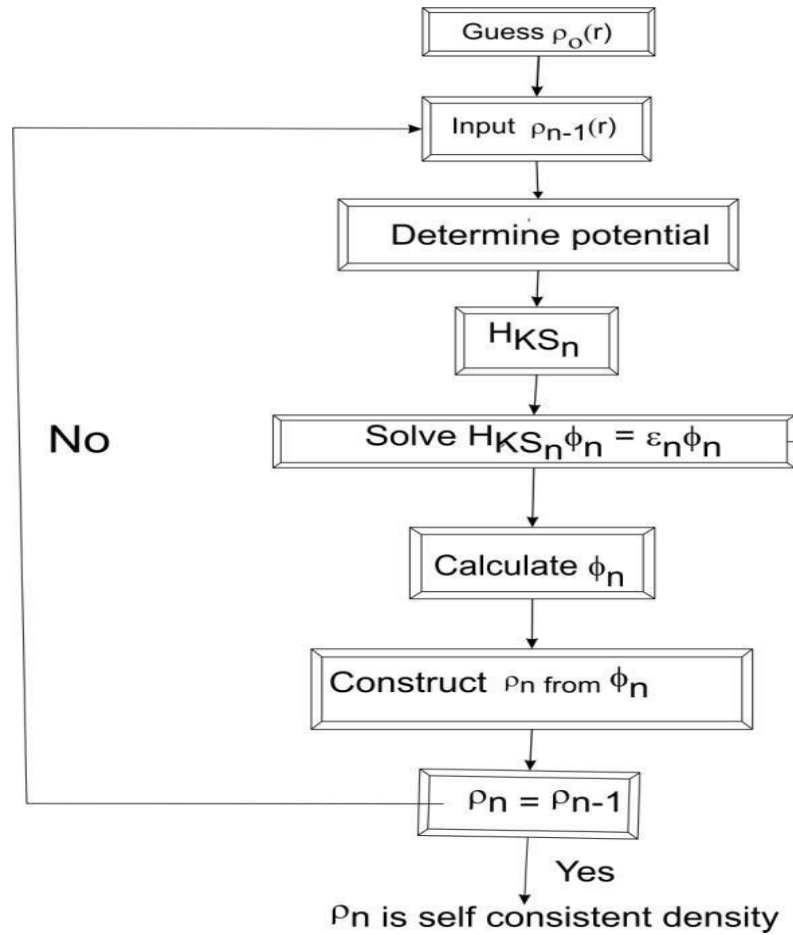


Fig.4.1. Flow chart to solve the Kohn-Sham equation

The spin densities can be written by summing over the orbitals as (3.10) are the occupation numbers such that, where is the symmetry-required weight of point k . Orbitals are wave functions of single particle (quasiparticle) but not the wave function of electrons. Overall density of these quasiparticles is equal to true electron density [27].

Kohn-Sham equation must be solved self-consistently in an iterative process as finding the orbitals require knowledge of the potentials which themselves depend on density and thus on the orbitals again. The flow chart to solve the KS equation is shown below. Fig.4.1 Flow chart to solve the Kohn-Sham equation. Practical applications of DFT are based on approximations and one must choose the functional that is used to represent exchange and correlation (xc) effects. But after this approximation one can solve the effective Hamiltonian with high

precision. A common approximation is the so-called local density approximation (LDA) [28].

4.2 MANY BODY SYSTEMS

From the microscopic point of view, a solid can be seen as a collection of heavy, positively charged nuclei (n) and lighter, negatively charged electrons (e). The nuclei and electrons are treated as electromagnetically interacting point charges and the exact non relativistic many-body Hamiltonian for this system becomes:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_i^2}{M_i} - \frac{\hbar^2}{2} \sum_i \frac{\nabla_i^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{r}_j|} \quad (4.1)$$

M_i is the mass of the nucleus at $\vec{R}_i$ and m_e is the mass of the electron at $\vec{r}_i$. The first and second term correspond to the kinetic energy operator of the nuclei and of the electrons respectively. The remaining terms describe the Coulomb interaction between electrons and nuclei respectively. Unfortunately, due to the high degree of complexity it is impossible to solve this equation without introducing some approximations [29].

4.2.1 THE BORN-OPPENHEIMER APPROXIMATION

Mass of the electrons is much smaller than the nuclei while the electromagnetic forces acting on them are of comparable magnitude. Consequently, the electronic motion is considerably faster than the nuclear motion. Since the nuclei move so slowly on the scale of velocities of relevance to the electrons, it is justified to assume that at any moment, the electrons will be in their ground state with respect to the instantaneous nuclear configuration. The assumption of instantaneous electronic equilibrium for every nuclear configuration implies that the electron wave function is a solution of the Schrodinger equation for Hamiltonian (4.1) with fixed nuclear positions:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_i \frac{\nabla_i^2}{m_e} - \frac{1}{4\pi\epsilon_0} \sum_{i,j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \frac{1}{8\pi\epsilon_0} \sum_{i \neq j} \frac{e^2 Z_i Z_j}{|\vec{R}_i - \vec{r}_j|} \quad \mathcal{W}_{ext} \quad \mathcal{W}_{NN} \quad (4.2)$$

This Hamiltonian corresponds to the electronic motion in the external potential produced by the nuclei. Where, $\hat{T}$ represents the kinetic energy of the electrons, $\hat{V}$ is the electronic repulsion and $\hat{V}_{ext}$ is the electron-nucleus interaction. Important to note here is that the nuclear repulsion ($\hat{V}_N$) contributes to the total energy by augmenting it with a constant. As a consequence, removing this term from the Hamiltonian will not affect the corresponding wave function.

The resulting Hamiltonian can be written as:

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_N \quad (4.3)$$

This decoupling of the electronic and nuclear motion is known as the Born-Oppenheimer or adiabatic approximation [30].

4.2.2 HOHENBERG AND KOHN THEOREM

According to Hohenberg and Kohn theorem [27], all observable quantities can be retrieved in a unique way from the density alone and can be written as a functional of density. In 1964, Hohenberg and Kohn stated two theorems on which DFT has been built.

First theorem: There is a one-to-one correspondence between the ground state density $\rho(r)$ of a many-electron system and the external potential V_{ext} . An immediate consequence is that the ground state expectation value of any observable $\hat{O}$ is a unique functional of the exact ground state electron density:

$$\langle \Psi | \hat{O} | \Psi \rangle = \hat{O}[\rho(r)] \quad (4.4)$$

Second theorem: For $\hat{O}$ being a Hamiltonian $\hat{H}$, the ground state total energy functional,

$H[\rho] \equiv E_{V_{ext}}$ is of the form,

$$\begin{aligned} E_{V_{ext}[\rho]} &= \langle \Psi | \hat{T} + \hat{V} | \Psi \rangle + \langle \Psi | \hat{V}_{ext} | \Psi \rangle \\ &= E_{HK}[\rho] + \int \rho(r) V_{ext}(r) dr \end{aligned} \quad (4.5)$$

where the Hohenberg-Kohn density functional $F_{HK}[\rho]$ is universal for any many-electron system. $E_{V_{xt}}[\rho]$ reaches its minimal for the ground state density corresponding to $\hat{V}_{xt}$. The one-to-one correspondence between the ground state density and the external potential has some important implications. It is obvious that, with the given external potential of the system, it is possible to find a unique ground state density for the system [31].

Solving the Schrodinger equation yields the ground state wave function out of which the ground state density can be calculated. Intuitively, the ground state density seems to contain less information than the ground state wave function. If this were true, the inverse correspondence from ground state density to external potential would not hold.

The first theorem of Hohenberg and Kohn, however, states that this correspondence holds as well. In other words: the density contains as much information as the wave function. As a consequence of the second theorem, it is understood that the ground state density minimizes ground state total energy functional ($E_{V_{xt}}[\rho]$). The Rayleigh-Ritz Variational method can be used to obtain the ground state density. It is important to note that $E_{V_{xt}}[\rho]$ evaluated for the ground state density corresponding to external potential ($\hat{V}_{xt}$), equals the ground state energy. Only this value of $E_{V_{xt}}[\rho]$ has a physical meaning. Also in the second theorem, the Hohenberg-Kohn-functional (F_{HK}) contains no information on the nuclei and the nuclear positions. Consequently, the functional is the same for all many-electron systems [32]. Moreover, the expressions for the kinetic energy and exchange-correlation functional are unknown. Hence density-functional theory in the Hohenberg-Kohn form is found to be impractical for most of the time.

4.3 KOHN-SHAM EQUATIONS

In 1965, Kohn and Sham [28] showed that it is possible to reduce the many-body quantum mechanical problem to an exactly equivalent set of one-electron equations, solved self-consistently. Inspired by the idea of the Hohenberg-Kohn theorems, Kohn-Sham derived total energy functional including

kinetic, Hartree, exchange-correlation energy, for a set of doubly occupied orbitals ψ_i and is rewritten as

$$E[\psi_i] = 2[\hbar^2/2m] \sum_i \psi_i \nabla^2 \psi_i dr + E_H[n] + E_{XC}[n] + \int V_{ext} n(r) dr \quad (4.6)$$

where the kinetic energy functional has been replaced by its exact analytical expression acting on the set of orbitals ψ_i . The electron density $n(r)$ is then given as

$$n(r) = 2 \sum_i |\psi_i(r)|^2 \quad (4.7)$$

In the case of a crystalline solid, the external potential is simply equal to the ionic interaction between the nuclei and the electrons,

$$V_{ext} \equiv V_{ion}$$

Then according to Kohn-Sham energy functional, in order to determine the ground state total energy of the electronic system, one has to determine the set of orbitals $\psi_i(r)$ that minimizes it. This is done by self-consistently solving the Kohn-Sham equations:

$$[-\hbar^2 / 2m_e] \nabla^2 + V_{ion}(r) + V_H(r) + V_{xc}(r) \psi_i(r) = \epsilon_i \psi_i(r) \quad (4.8)$$

where ϵ_i is the Kohn-Sham Eigen value associated with electronic state i , V_H is the Hartree potential given by

$$V_H(r) = e^2 \int |\rho(r')| / |r - r'| d^3r' \quad (4.9)$$

V_{ion} is the ionic potential describing the attractive interaction between electrons and nuclei and V_{xc} is the exchange-correlation potential given by the functional derivative

$$V_{xc}(r) = \delta E_{xc}[n(r)] / \delta n(r) \quad (4.10)$$

The Kohn-Sham equations are in fact a reformulation of the Hohenberg-Kohn problem [33].

4.4 THE FULL POTENTIAL APW METHODS

The development of the Augmented Plane Wave (APW) method from Slater's APW (1937), to Linearized Augmented Plane Wave (LAPW) and the new APW+ local orbital (LO) was described by Schwarz et al., (2002).

4.4.1 The LAPW Method

The linearized augmented plane wave (LAPW) method is one among the most accurate methods available for performing electronic structure calculations of crystals. It is based on the density functional theory for the treatment of exchange and correlation and uses the local spin density approximation (LSDA). Several forms of LSDA potentials exist in the literature, but recent improvements were made by using the generalized gradient approximation (GGA). The LAPW method is a procedure for solving the Kohn-Sham equations for the ground state density of a many-electron system by introducing a basis set which is especially adapted to the problem. This adaptation is achieved by dividing the unit cell into (I) non-overlapping atomic spheres (centred at the atomic sites) and (II) an interstitial region. In the two types of regions different basis sets are used.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW's according to the linear variation method

$$\psi_k = \sum_{\mathbf{k}_n} c_{\mathbf{k}_n} \phi_{\mathbf{k}_n} \quad (4.14)$$

and the coefficients are determined by the Rayleigh-Ritz variational principle. $\phi_{\mathbf{k}_n}$ is the radial basis function. The convergence of this basis set is controlled by a cut off parameter $R_{mt}K_{max} = 6 - 9$, where R_{mt} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of the largest $\vec{K}$ vector in equation (4.14).

Singh (1994) described that in order to improve upon the linearization and to make possible a consistent treatment of semi core and valence states in one energy window, additional basis functions can be added. They are called "local orbitals (LO)" and consist of a linear combination of two radial functions at two different energies and one energy derivative (at one of these energies):

$$Y_{lm}\hat{r}\phi_{lm}^{LO} = [A_{lm}u_l(r, E_{1,l}) + B_{lm}\dot{u}_l(r, E_{1,l}) + c_{lm}u_l(r, E_{2,l})] \quad (4.15)$$

The coefficients A_{lm} , B_{lm} and C_{lm} are determined by matching the value and derivative on the sphere boundary to the plane waves as usual.

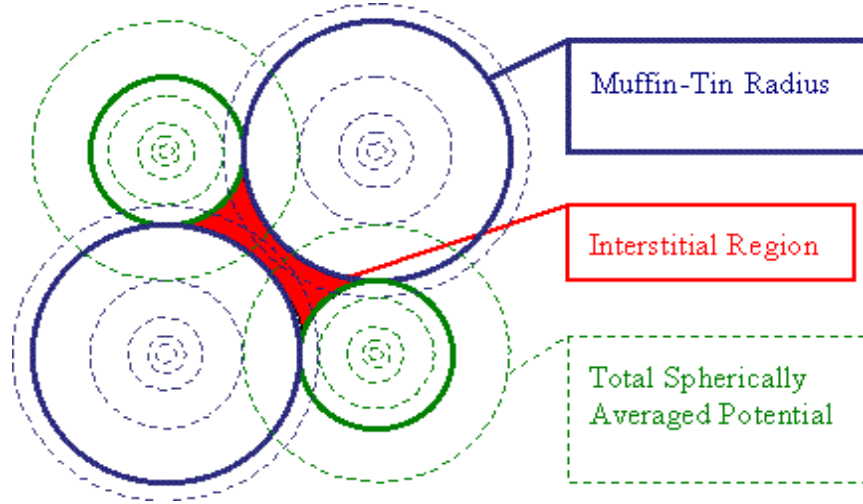


Fig.4.2. The unit cell divided into muffin-tin region and interstitial region

4.4.2 The APW+LO Method

The standard LAPW method with the additional constraint on the plane waves of matching in value and slope to the solution inside the sphere is not the most efficient way to linearize Slater's APW method (Sj ostedt et al., 2000). It can be made much more efficient when one uses the standard APW basis, but of course with $u_l(r, E_l)$ at a fixed energy E_l in order to keep the linear eigen value problem. One then adds a new local orbital to have enough variational flexibility in the radial basis functions.

The new basis-functions, here after referred to as APW+LO, will differ in some important aspects from the LAPW basis functions inside the MT-region. Most important is that APW+LO set uses both in its original APW form and in a linear combination with $\dot{u}_l(r, E_{1,l})$.

$$\phi_{k_n} = \sum_{lm} [A_{lm,k_n} u_l(r, E_l)] Y_{lm}\hat{r} \quad (2.16)$$

$$\phi_{lm}^{LO} = [A_{lm}u_l(r, E_{1,l}) + B_{lm}\dot{u}_l(r, E_{1,l})]Y_{lm}\hat{r} \quad (2.17)$$

This new ‘LO’ looks almost like the old “LAPW” basis set, but here the A_{lm} and B_{lm} do not depend on k_n and are determined by the requirement that ‘LO’ should be zero at the sphere boundary and normalized. In this new scheme corresponding computational time is drastically reduced. i.e., the APW+LO basis functions have no restriction on their derivatives at the MT-boundaries as in LAPW. Once the standard local orbitals scheme is implemented into a LAPW code, the changes for adding the APW+LO [33] basis is straightforward. All the computations within the LAPW code, work equally well for APW+LO, with the exception that the kinetic energy needs to be treated differently. Hence, basis functions that have “kinks” at the sphere boundary are constructed which makes it necessary to include surface terms in the kinetic energy part of the Hamiltonian. However, the total wave function is of course smooth and differentiable.

4.5 WIEN2k CODE

WIEN2k is one of the fastest and reliable simulation codes among computational methods. All the computational work presented on lanthanide intermetallic compounds has been performed by using this code [34]. WIEN2k is a full-potential all-electron code developed by *Blaha et al.* at the Institute for Materialchemie, Technical University at Wien, Austria. WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts. The code is based on the Kohn-sham formalism of DFT [34].

In the previous chapter, we have described how to reduce the complex problem of many interacting particles to a Schrodinger wave equation. In order to solve these equations, we have to construct the effective Hamiltonian operator which depends on the electron density of the electronic system. The manner through which the Schrodinger wave equation solved within Code WIEN2k is represented by the flow chart [35].

4.5.1 Properties of WIEN2K:

Following are the considerations which are essential for a modern computer code and were made in the development of new Wien2k package.

a) Accuracy

It is achieved by well-balanced basis set, which contains numerical radial functions that are calculated in each iteration cycle. Thus, these functions adapt to effects due to charge transfer or hybridization, are accurate near the nucleus. It is a full-potential and all electron method. Relativistic effects (including spin orbit coupling) can be treated with a quality comparable to solving Dirac's equation. All atoms in the periodic table can be handled.

b) Efficiency and Good Performance

The new mixed basis APW+lo/LAPW optimally satisfies this criterion. Smaller matrix size helps to save computer time and thus larger systems can be studied.

c) Parallelization

The program can run in parallel, either in a coarse grain version where each k-point is computed on a single processor or in a fine grain scheme if the memory requirement is larger than that available on a single CPU.

d) Architecture

Depending on the given architecture, optimized algorithms and libraries are used during installation of the program package.

e) Portability

It requires the use of standards as far as possible, such as FORTRAN90, MPI, BLAS, SCALAPACK, etc.

f) User friendliness

It is achieved by a web based graphical user interface (GUI), called w2web. The program package provides an automatic choice of default

options and it is also complemented by an extensive User's Guide [36].

4.5.2 APPLICATIONS OF WIEN2K

The problems considered so far in QM calculations using the LAPW method (employed in various versions of the Wien code) have covered a wide spectrum, including in particular insulators, semiconductors, (transition) metals up to f -electron systems or intermetallic compounds. A variety of applications are briefly introduced below

i) Band structure and density of states (DOS) calculations

The energy band structure and corresponding density of states are prominent quantities that determine the electronic structure of a system. Their inspection provides information about the electric property (metal, insulator or semiconductor) and gives insight into the chemical bonding [37].

By looking at site decomposed partial densities of states one can find a hint for the strength of interactions between the orbitals of the constituting atoms. The band structure is also useful in connection with photoelectron spectra.

ii) Electron densities

The electron density is the key quantity in DFT. By taking its Fourier transform the static structure factors can be determined easily, and it can be compared with the experimental X-ray diffraction data.

iii) Electric field gradients (EFG)

Since the EFG is uniquely defined by charge distribution and thus electron density, it can be calculated from first principles. The EFG is sensitive to anisotropy of charge density distribution close to the nucleus which can be determined by the nuclear quadrupole interaction (NQR) and can be measured by nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR), Mossbauer or by perturbed angular correlation (PAC) measurements.

iv) Total energy and phase transitions

With the knowledge of total energy, the relative stability of different phases can be computed by keeping as many parameters constant as possible in order to have a cancellation of systematic errors.

v) Forces and structural optimization

In cases where the atoms occupy general positions that are not fixed by the crystal symmetry, the knowledge of the forces acting on atoms helps to optimize the structure parameters. Forces can be computed in Wien2k and are crucial for such optimizations.

vi) Spectra

The photoelectron spectra, X-ray emission and absorption spectra can be calculated using partial densities of states and the transition probabilities between a valence and a core state. Such spectra provide useful information on local binding situation of the atom, whose core state is involved. Optical spectra and related quantities e.g., energy dependence of real and imaginary parts of the dielectric constant can be calculated from electronic response which is further used to determine absorption coefficient, refractive index, electron energy loss spectrum and reflectivity by using the Kramers-Kroening relation.

vii) Others:

Many properties using WIEN2k have been investigated for a large variety of structures, such as chemical bonding, structural stability, high-pressure phases, Jahn–Teller distortions, charge disproportionate, phase transitions, ferroelectric, ferroelectric or elastic properties etc. The roles of spin and orbital magnetic moments, magnetic ordering (ferro-, ferri-, antiferro-magnetic) or meta-magnetism were investigated in magnetic solids (including intermetallic compounds). LAPW calculations have helped to understand optical, core-level, photoelectron, Mossbauer, NMR spectra [38].

It also provides information on hyperfine or crystal fields, the magneto-optical Kerr effect or electric field gradients. It is possible to represent defects, e.g., an impurity, by studying a super-cell 2x2x2 (or larger), i.e., doubling the original unit cell in all the three dimensions. When one atom in this large unit cell

is replaced by an impurity atom, the neighbouring atoms can relax to new equilibrium positions [39].

By periodical repetition of such a super-cell an isolated impurity can be represented approximately. Super-cells can also be used to simulate surfaces and their interaction with atoms or molecules. Hypothetical or artificial structures can be considered and their properties can be calculated, irrespective of whether they can be made in reality or not. Such calculations can predict the property of a system (e.g., insulator or metal) or find its magnetic structure.

The changes in a system with deformations, under pressure or substitutions can be simulated. In the present work density of states (DOS), partial density of states (PDOS) of constituent atoms, electronic band structure and frequency dependence of linear optical properties viz. real and imaginary part of dielectric constant, refractive index, reflectivity, electron energy loss spectra (EELS) etc. have been calculated for PbMoO_4 , BaWO_4 and $\text{NaBi}(\text{WO}_4)_2$ using WIEN2k program.

4.6 FLOW OF COMPUTATIONAL WORK

In the present work, the Full Potential Linearized Augmented Plane Wave method as implemented in the WIEN2k code is employed for calculating electronic structure of solids. The exchange and correlation energy are determined by using generalized gradient approximation (GGA) and by local density approximation (LDA). The integration in the Brillion zone was done by using Monkhorst Pack 10 x10x10 k-points. In order to achieve convergence, the basis function it expanded up to $R_{\text{MT}} \times K_{\text{max}} = 7$. The maximum value for partial waves inside the atomic sphere is $l_{\text{max}} = 10$ while the charge density is Fourier expanded upto $G_{\text{max}} = 12$. The self-consistent calculations are carried out to an accuracy of 0.0001 eV energy and 0.001 mRy charge.

Computations are performed to find the total energy of given system and obtained total energies are then fitted into Birch–Murnaghan equation of state proposed by Birch (1947) to get the ground state properties.

Structure file generation, initialization and self-consistent field cycle performance will be carried using calculated lattice parameter. In order to do the band structure calculations for ternary cubic compounds, initially a structure file is generated using its optimized lattice constant. Then, $2 \times 2 \times 2$ supercell is created and the ternary addition is made with parent binary compound. Now the flow of calculations is carried for ternary compound as depicted in flowchart as shown in Figure 4.3.

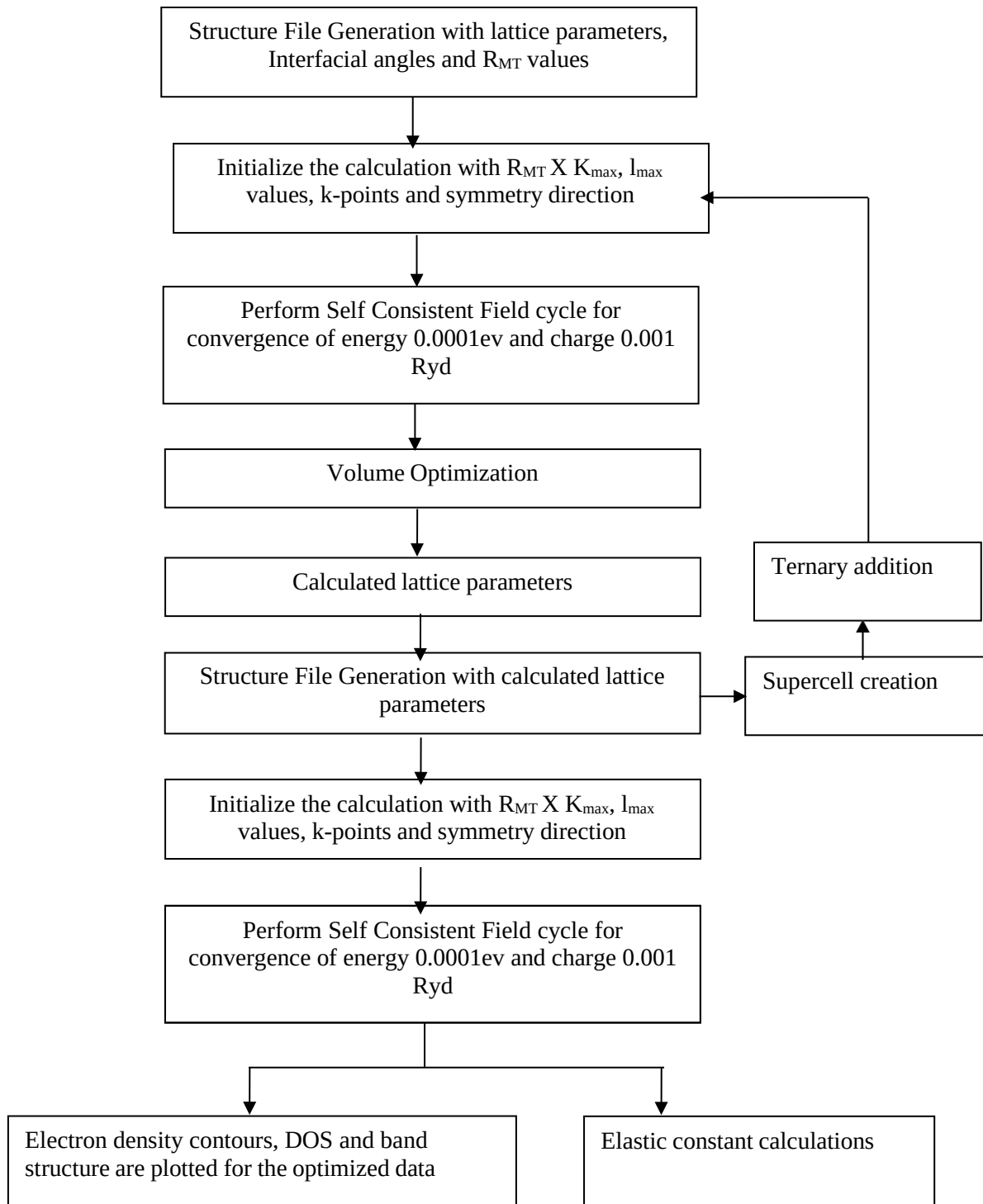


Fig.4.3. Flowchart of computational work to perform the band structure study

CHAPTER 5

RESULT AND DISCUSSION

5.1 STRUCTURAL PROPERTIES

In DFT calculations the first step to be carried out is the structural optimization. From the experimental data we can obtain the primary structure in most of the occurrences. For favourable outcome, the DFT energy E_{TOT} can be determined. Crystal symmetry do not control the atoms in general positions, concerning the forces acting on it leads in the optimization of structural parameters. WEIN2k is capable of calculating forces, which are essential for similar optimizations. The atoms muffin tin radius (R_{MT}) is optimized in addition since function of cell volume energy.

Smallest atomic sphere radius is represented as R_{MT} and K_{MAX} represents the largest k vector in which the cut-off parameter $R_{MT} K_{MAX} = 8.5$ approximately [40]. As the lowest muffin tin radius is enlarged, the nearest point a plane wave will reach near a nucleus step far off.

➤ *CUBIC structure of MoS_2*

- ❖ R_{MT} values: Mo - 2.3
S - 2.0
- ❖ Convergence parameters: Energy - below 0.0001Ry
Charge - below 0.001Ev
- ❖ K-Points: 1000
- ❖ Lattice type: Cubic
- ❖ Space group: F-43m
- ❖ Space group number: 216

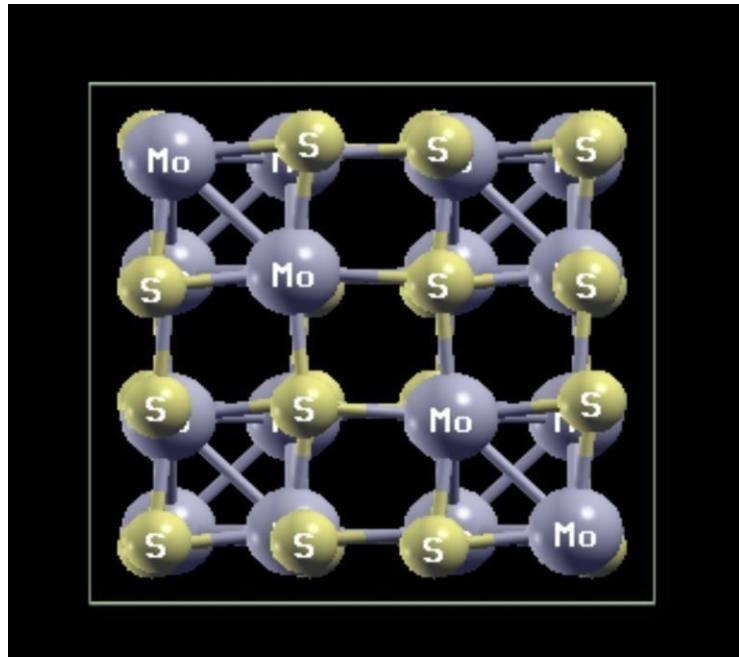


Fig.5.1. Cubic structure of MoS₂

- *HEXAGONAL structure of MoS₂*
- ❖ R_{MT} value: Mo – 2.4100
S – 2.08
- ❖ Convergence parameters: Energy - below 0.0001Ry
Charge – below 0.001Ev
- ❖ K-points: 1000
- ❖ Lattice type: Hexagonal
- ❖ Space group: P63/mmc
- ❖ Space group number: 194

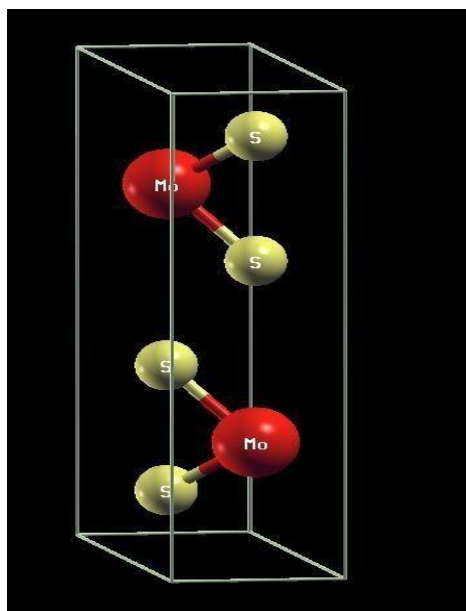


Fig.5.2. Hexagonal structure of MoS₂

5.2 K-POINTS

SCF charge density defines the substantially applicable Hamiltonian operator is the execution of SCF. For any set of k-points using the Hamiltonian operator, we can excerpt the one particle energies and wave functions. Between the high symmetry points, the first BZ's k-point set which includes the points of the paths mentioned. By using the Monkhorst-Pack method the k-point meshes for Brillouin zone sampling was generated. The number of k-points is alternated in relation to total electronic capacity to establish the k-point concurrence. The Fermi levels complexity of the band structure and the systems size is dependent on the number of k-points. The number of k-points accustomed for the cubic and hexagonal structure of MoS₂ is k-point=1000.

5.3 VOLUME OPTIMIZATION AND BULK MODULUS

The total energy (E) can be calculated and determined as the sum of electron kinetic energy, Hartree energy, XC energy, ion-electron energy and ion-ion energy by utilizing the self-consistent run. The lattice constant of a solid is almost equal to the size of the conventional unit cell length at equilibrium volume. By minimizing total energy as a function of cell volume it can be attained

computationally.

We use optimize job to optimize the lattice parameter. As we change the lattice parameter to certain percentage, we can observe the variation in its energy. Further energy versus volume graph is plotted. We have carried out various calculations of the total energy of several lattice constants to attain the value of lattice constant whose total energy comes to the least. The volume optimization sticks to Birch Murnaghan's equation of state [41]. The cubic and hexagonal structural parameters have been determined for MoS₂ compound and volume optimization curve have been generated and given.

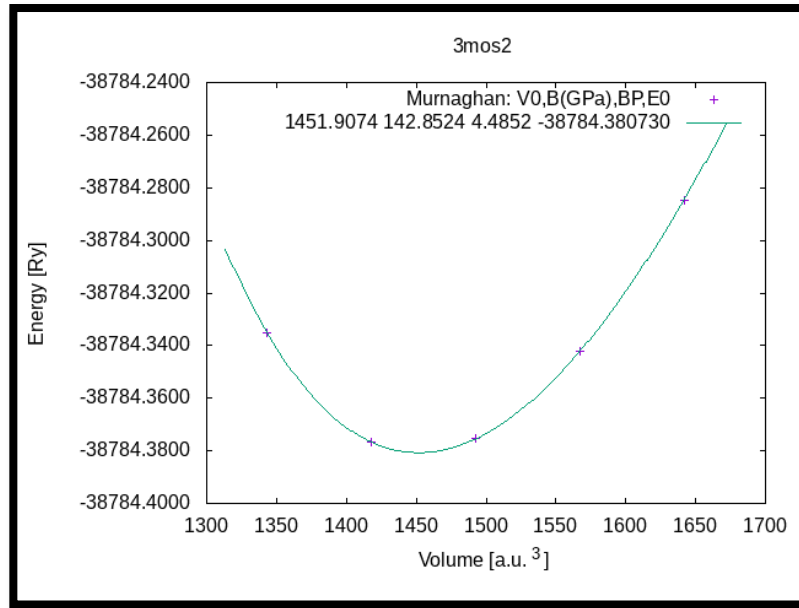


Fig.5.3. Volume optimization curve of Cubic structure of MoS₂

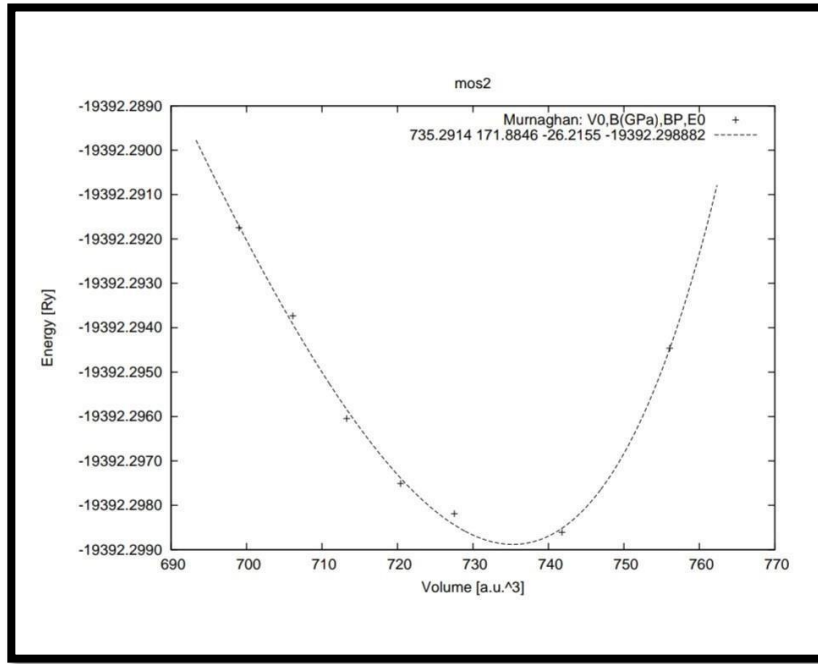


Fig.5.4. Volume optimization curve of hexagonal structure of MoS₂

Table 5.1 and table 5.2 represents the calculated lattice parameter, bulk modulus, total energy, fermi energy and band gap value for cubic and hexagonal structure of MoS₂.

Table 5.1: Calculated lattice parameters, Bulk modulus(B) and its derivative (B') of cubic and hexagonal structure of MoS₂

Structure of MoS ₂	Present study		Lattice parameter		V ₀ (bohr ³)	B (GPa)	B _p
Cubic	a(Å)	9.60	α	90°	1451.8464	142.6589	4.5341
	b(Å)	9.60	β	90°			
	c(Å)	9.60	γ	90°			
Hexagonal	a(Å)	6.069385	α	90°	734.2897	174.0705	-16.6136
	b(Å)	6.069385	β	90°			
	c(Å)	23.699504	γ	120°			

Table 5.2: Calculated total energy (Ry), bandgap(eV) and fermi energy (eV) of cubic and hexagonal structure of MoS₂

Structure of MoS ₂	Total energy E ₀ (Ry)	Fermi energy	Band gap (eV)
Cubic	-38784.380722	0.53338	0
Hexagonal	-19392.298854	0.51584	0.891

From these values it is clear that there is no bandgap for cubic structure whereas there is a small band gap energy for hexagonal structure which can be perfectly fit for the thermoelectric materials as its nature is semiconducting.

5.4 ELECTRONIC PROPERTIES

5.4.1 DENSITY OF STATES (DOS)

Density of state is the number of different states the electron can occupy at a particular energy level. The DOS is obtained by FP-LAPW method corresponding to GGA is represented in the following figures. The unoccupied state is called the conduction band which is above the fermi level whereas below the fermi level is called the valence band which is fully filled [42].

A) DOS of cubic MoS₂

The total and partial density of states(DOS) of cubic structure of MoS₂ is shown in Fig.5.5 and Fig.5.6 respectively.

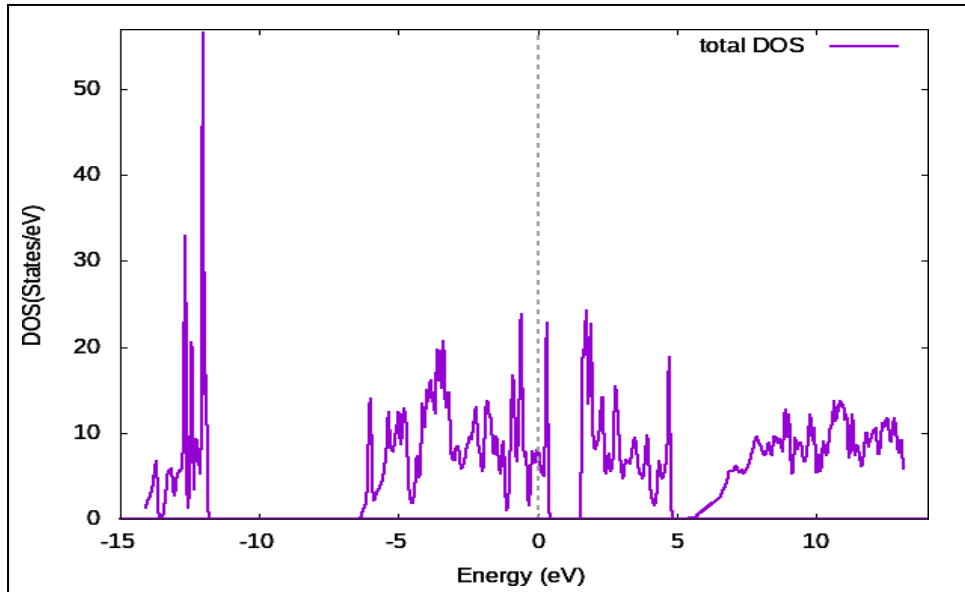


Fig.5.5 Total Density of states of cubic MoS₂

From the Fig. 5.5, there is a transition of states from valence band to conduction band. The core electrons are nothing but nearer to nucleus which has the contribution above the Fermi level. There is more contribution of the states below the Fermi level.

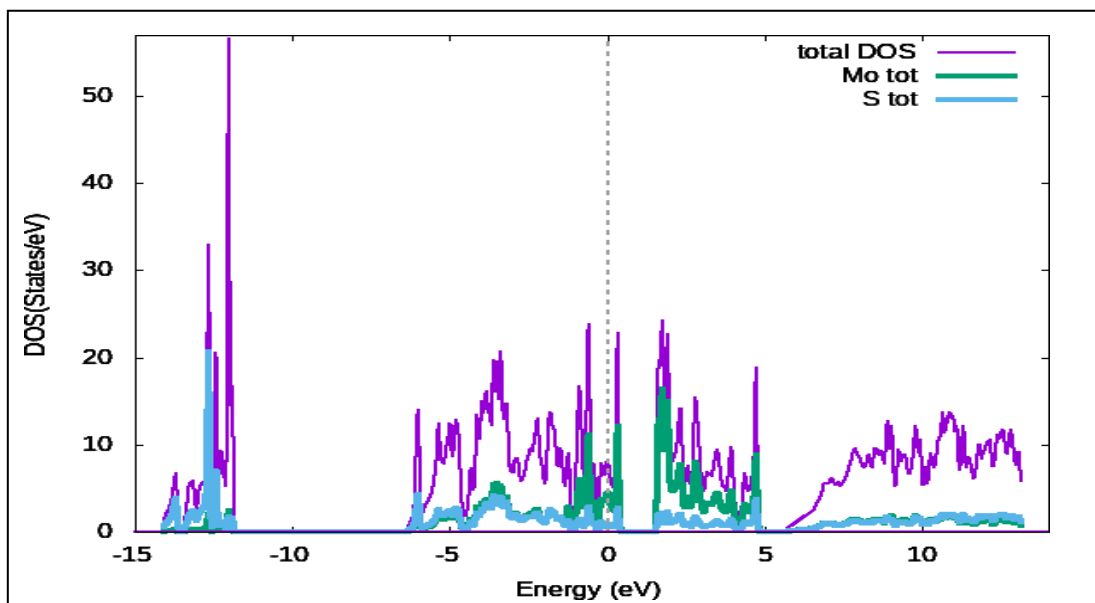


Fig.5.6 Partial density of states of cubic structure of MoS₂

From the Fig.5.6, S has the higher contribution over Mo in both above and below the fermi level. Among the states of Mo d-state has the great contribution comparatively. Various for S, p-state has the higher contribution over the other states. Thus, S has more contribution overall.

B) DOS of hexagonal MoS₂

The total and partial density of states(DOS) of hexagonal structure of MoS₂ is shown in Fig.5.7.

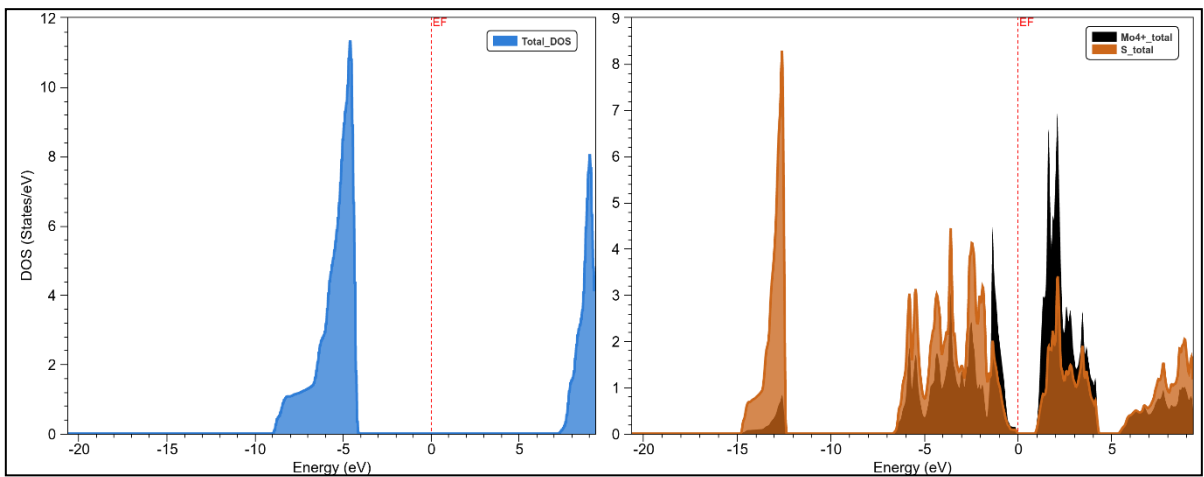


Fig.5.7 Density of states of hexagonal structure of MoS₂

The total density of states (DOS) of hexagonal structure of MoS₂ is presented in Fig.5.7. There is contribution of states from valence to conduction band with small band gap. Both below and above the fermi level is mainly contributed by S and less contribution of Mo is seen overall in the partial DOS.

5.4.2. BAND STRUCTURE

Band structure helps to reveal the materials property which specifies the electronic property of the material. The electronic band structure of MoS₂ is presented in the below figure and the gap of two structures is compared.

A) Band structure of cubic MoS₂

With the optimized structure, we calculated the band structure of cubic

MoS₂. From the Fig.5.8, it is clear that there is no bandgap due to the overlap of valence band and conduction band in the fermi level region. Thus, we can conclude that the cubic structure of the material (MoS₂) is metallic in nature since there is zero bandgap energy.

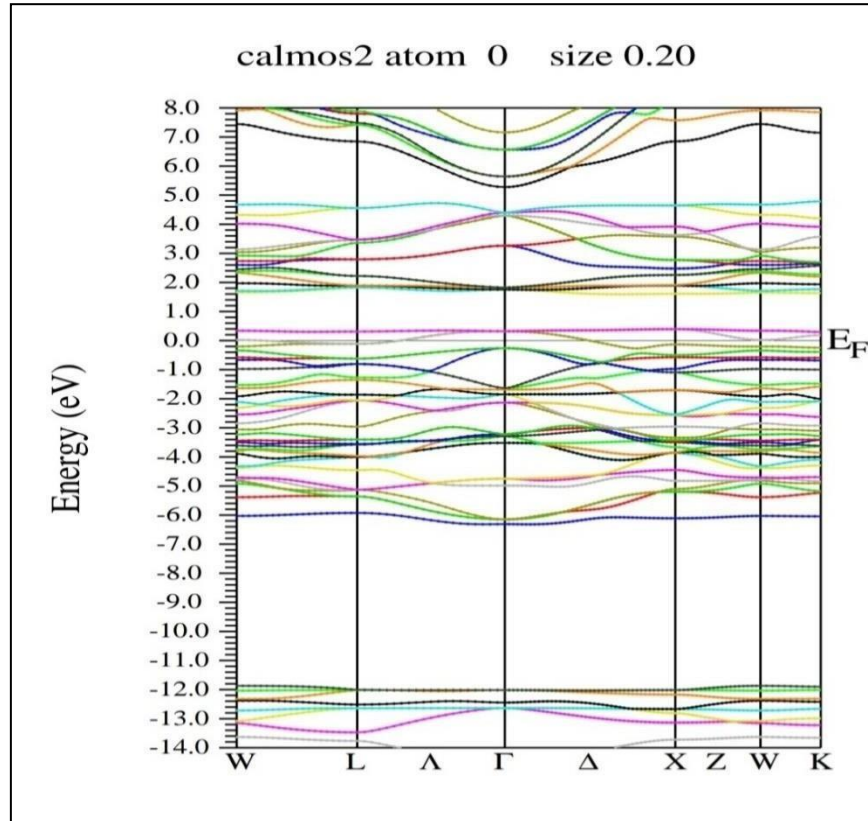


Fig.5.8 Band structure of Cubic MoS₂

Since the minima and maxima of conduction and valence band respectively lie in the same line Γ point, the band structure of cubic MoS₂ shows the direct band gap.

B) Band structure of hexagonal MoS₂

With the optimized structure, we calculated the band structure of hexagonal structure of MoS₂. From the Fig.5.9, it is clear that there is a bandgap of 0.891 eV of energy gap at the fermi level. Thus, we can conclude that the hexagonal structure of the material (MoS₂) is semiconductor in nature since there is an optimum bandgap energy over the conduction band and valence band.

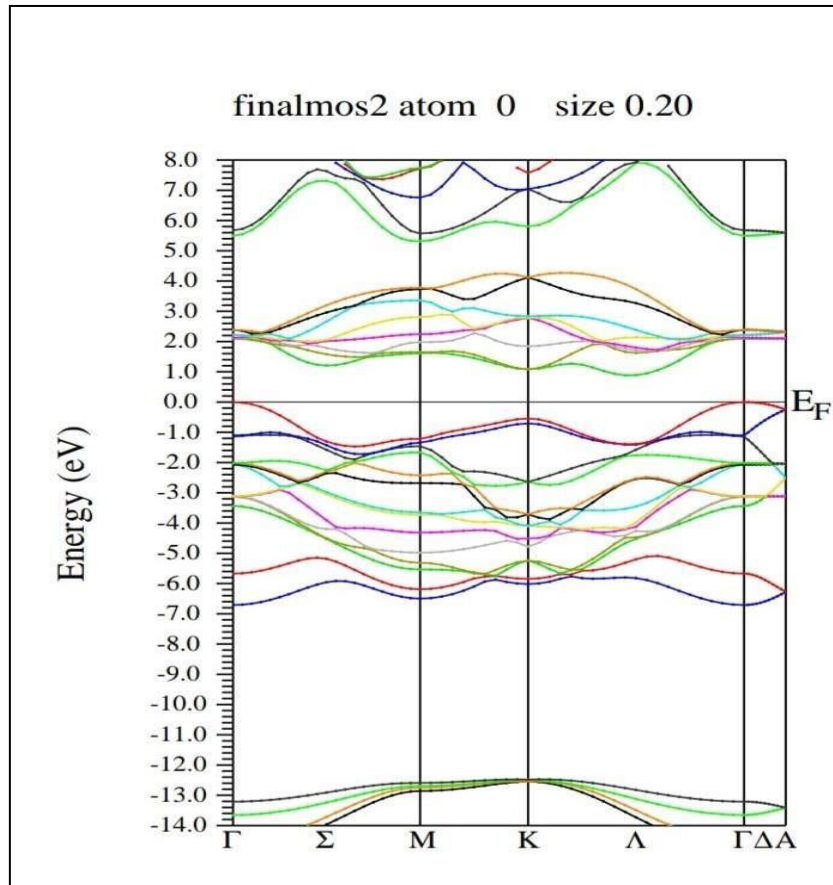


Fig.5.9 Band structure of hexagonal structure of MoS₂

5.5 THERMOELECTRIC PROPERTIES

Thermoelectric properties of cubic and hexagonal structure of MoS₂ were calculated. The Seebeck coefficient (thermopower) and power factor have been calculated. Using these calculated values a graph has been generated and the results are tabulated.

$$\text{Power Factor, PF} = S^2\sigma$$

Where S- Seebeck Coefficient

σ - Electrical conductivity

If the value of power factor is greater, the efficiency of the thermoelectric material is improved greater.

Table 5.3 Transport properties of cubic structure of MoS₂ for temperature 100k to1000k

Structure of MoS ₂	Temperature (K)	Seebeck coefficient (10 ⁻⁴)	Power Factor (10 ¹⁶)
Cubic	100	-17.76	2.245
	200	-29.61	6.356
	300	-35.0	8.63
	400	-35.62	8.71
	500	-33.90	7.72
	600	-31.14	6.37
	700	-27.83	5.003
	800	-24.07	3.66
	900	-19.90	2.45
	1000	-15.36	1.43

Table 5.5 Transport properties of hexagonal structure of MoS₂ for temperature 100k to1000k

Structure of MoS ₂	Temperature (K)	Seebeck coefficient	Power Factor
Hexagonal	100	-65.71	6.433
	200	-18.54	4.639
	300	-0.215	6.421
	400	1.952	5.410
	500	2.558	9.421
	600	4.084	2.401
	700	6.147	5.440
	800	8.230	9.685
	900	10.070	1.43
	1000	11.588	1.892

5.5.1 SEEBECK COEFFICIENT

In Fig.5.10. and Fig.5.11, the Seebeck coefficient (S) versus Temperature graph is shown. The thermoelectric power is otherwise called as Seebeck coefficient. Majority of charge carriers determines the convention of the Seebeck coefficient. If the value of the Seebeck coefficient is negative then the majority charge carriers is electrons whereas if the Seebeck coefficient is positive then the majority charge carriers are holes [43].

A) Cubic MoS₂

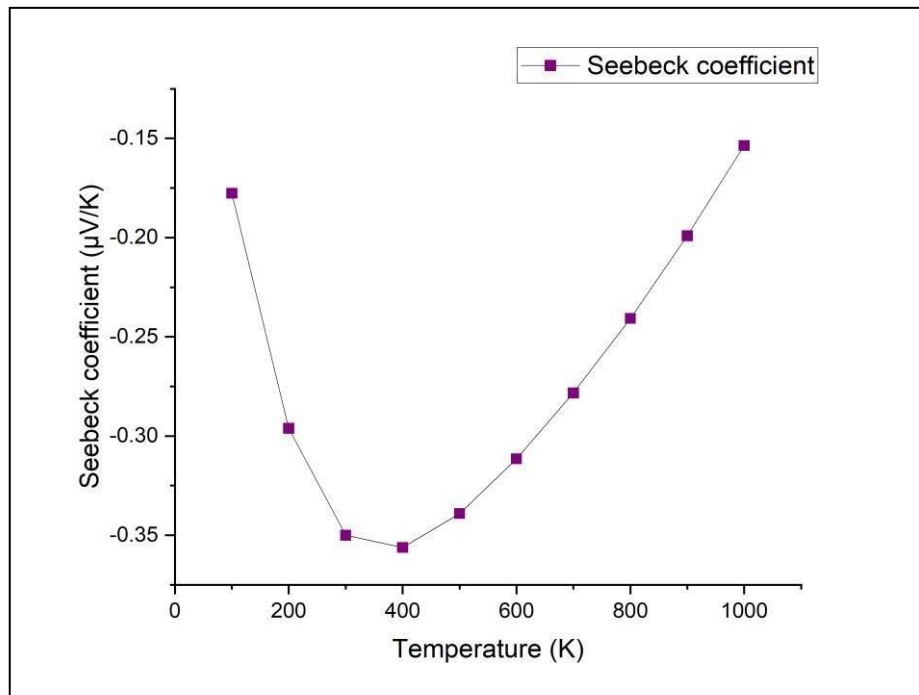


Fig.5.10. Variation of Seebeck coefficient with temperature of cubic structure of MoS₂

From the Fig.5.10. it is clear that the Seebeck coefficient gets decreased from 100-400K and gets gradually increased above 400K. i. e, 400K to 1000K. So, at certain point, as the temperature increases the Seebeck coefficient gets increased. Also, the Seebeck coefficient value here is negative hence the majority charge carriers are electrons.

B) Hexagonal MoS₂

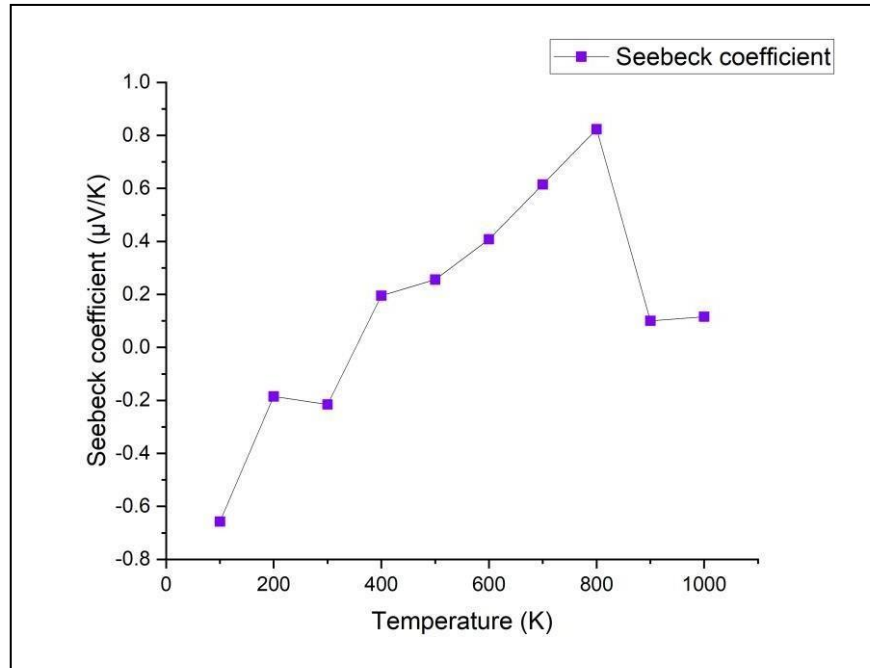


Fig.5.11. Variation of Seebeck coefficient with temperature of hexagonal structure of MoS₂

From the Fig.5.11. it is clear that the Seebeck coefficient gets increased from 100-800K and gets gradually decreased above 800K. So, at certain point, as the temperature increases the Seebeck coefficient gets increased. Also, the Seebeck coefficient value here is comprised of both positive and negative hence the majority charge carriers are holes and electrons respectively to their types. This is one of the major advantages over cubic structure.

5.5.2. POWER FACTOR

In Fig.5.12 and 5.13, the Temperature versus Power Factor graph is shown. The higher the power factor greater will be the efficiency of the thermoelectric material. The Figure of Merit (ZT) is dependent on the Seebeck coefficient, electrical conductivity, thermal conductivity and temperature. A material is considered as a good efficient thermoelectric material if the Seebeck coefficient, electrical conductivity and power factor are higher.

A) Cubic MoS₂

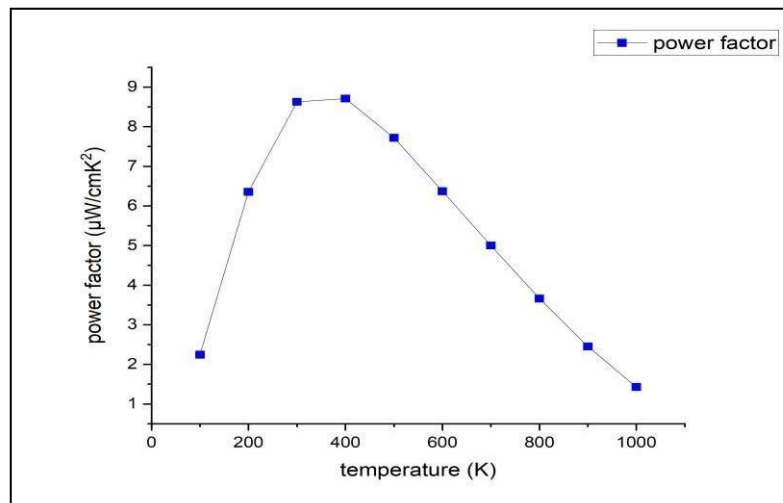


Fig.5.12 Variation of Power Factor with temperature of cubic structure of MoS₂

From the Fig.5.12. it is clear that the Power Factor gets increased from 100-400K and gets gradually decreased above 500K. So, at certain point, as the temperature increases the power factor gets decreased. So, let's go for particular temperature like 300K (room temperature). The highest peak obtained is at 300K where the efficiency is higher too.

B) Hexagonal MoS₂

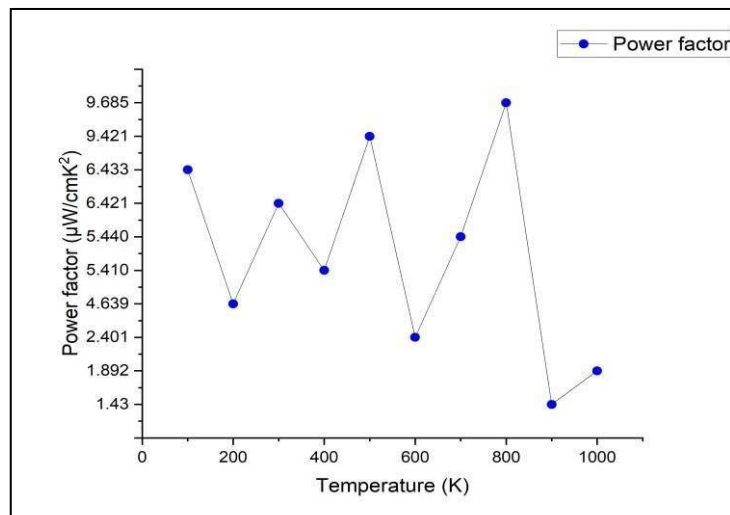


Fig.5.13 Variation of Power Factor with temperature of hexagonal structure of MoS₂

From the Fig.5.13., it is clear that the Power Factor is not in a stable state. The values of power factor are getting fluctuated as the temperature gets increased. So, let's go for particular temperature like 800K which is the highest peak obtained, where the efficiency is higher too. Thus, for higher temperature applications we can go for hexagonal structure of MoS₂ whereas for low temperatures such as room temperature's cubic structure of MoS₂ is opted.

5.6. OPTICAL PROPERTIES

The calculated static and maximum values of absorption coefficient, reflectivity, refractive index and energy loss function of cubic and hexagonal structure of MoS₂ is shown in the Table 5.5.

Table 5.5 Maximum optical values for cubic and hexagonal structure of MoS₂

Structure of MoS ₂	$\alpha(\omega)$	$n(\omega)$	$R(\omega)$	$L(\omega)$
Cubic	220.782	3.962	0.586	0.269
Hexagonal	231.898	5.484	0.553	0.508

5.6.1. ABSORPTION COEFFICIENT

Absorption coefficient is the measuring of the lowering rate in of electromagnetic radiations intensity as light, when passing through any of the substance.

The absorption coefficient is given by

$$A(\omega) = 2 \omega k(\omega)/C$$

K is extinction coefficient [48].

A) Cubic MoS₂

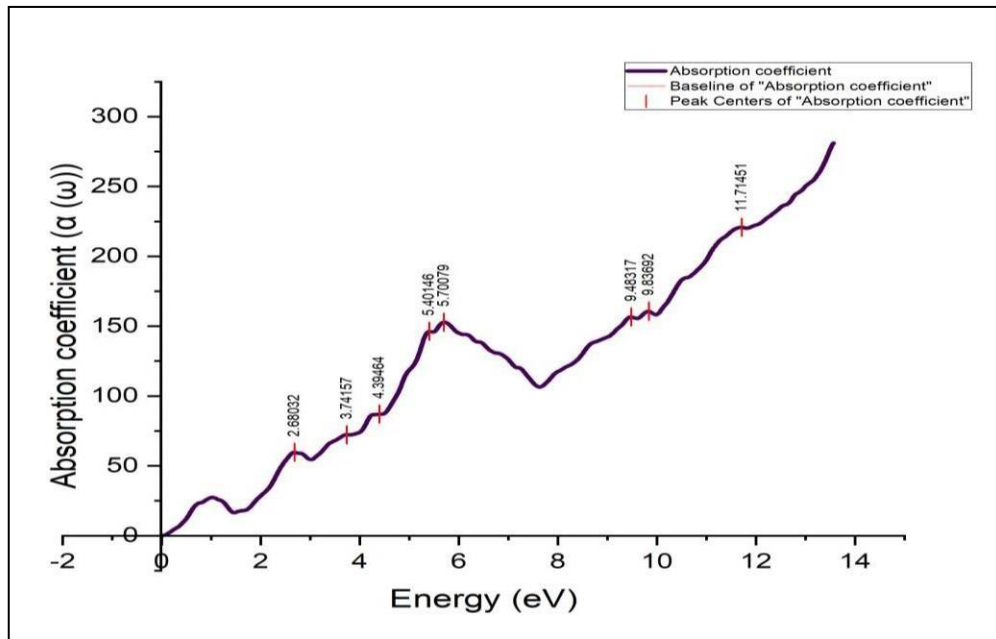


Fig.5.14 Calculated absorption coefficient of cubic MoS₂

The absorption coefficient is a major parameter in optoelectronic materials [44]. From the Fig.5.14, the absorption spectra initialize from zero photon energy for cubic structure of MoS₂ due to the metallic nature of the material and increase when energy increases. The highest peak of absorption coefficients at 11.71451 eV and 5.70079 eV. Due to the transition of valence band and conduction band the intense peaks are seen. Even lower energy peaks are observed. The absorption peaks are there in visible and UV regions. Thus, these materials are suitable for optoelectronic, solar cell, infrared detectors, in LEDs and fiber-optic telecommunications [44].

B) Hexagonal MoS₂

From the Fig.5.15, the absorption spectra initialize from zero photon energy and decreases at certain point of energy above 7 eV and then increase when energy increases of around 10 eV. The highest peak of absorption coefficients at 11.6065 eV and 12.3675 eV. The higher absorption is observed in UV region.

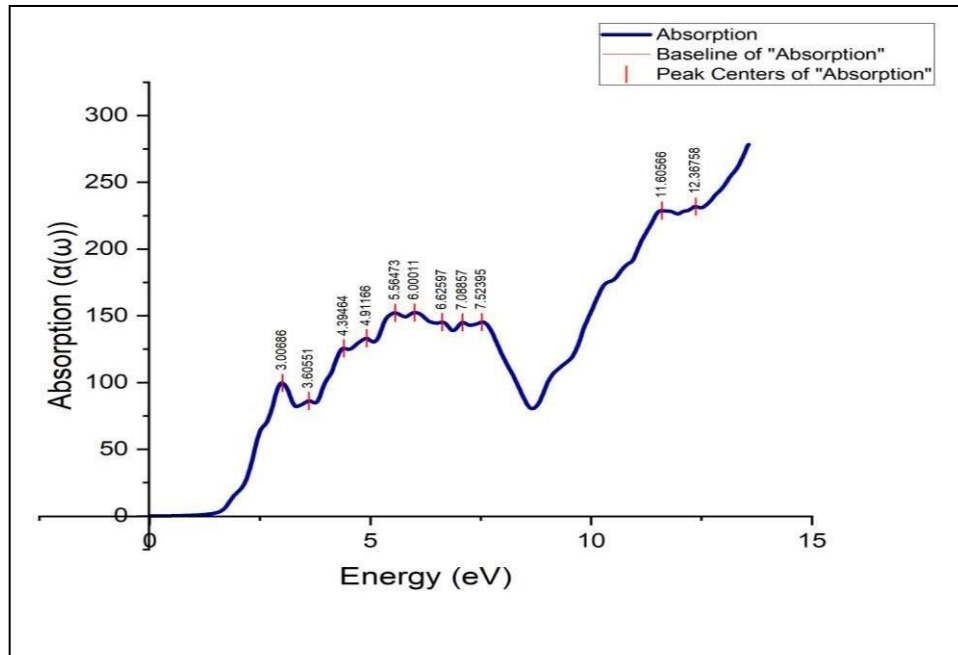


Fig.5.15 Calculated absorption coefficient of hexagonal MoS₂

5.6.2. REFLECTIVITY

Reflectivity can be defined as the ratio of the optical reflected power to the incident optical power. In simple terms it can be given as the ability to reflect light waves or radiation from its surface.

The reflectivity of material is given by [49],

$$R(\omega) = \frac{[n(\omega) - 1]^2 + k(\omega)^2}{[n(\omega) + 1]^2 + k(\omega)^2}$$

A) Cubic MoS₂

Fig.5.16 shows the reflectivity spectra of cubic structure of MoS₂ as a function of photon energy. The maximum reflectivity peak is observed in the IR region which is 0.09524 eV and 0.61226 eV. Very less reflectivity is observed at 6eV which is in the UV region. Although the visible region has continuous reflectivity peaks at a gradual increase of energy.

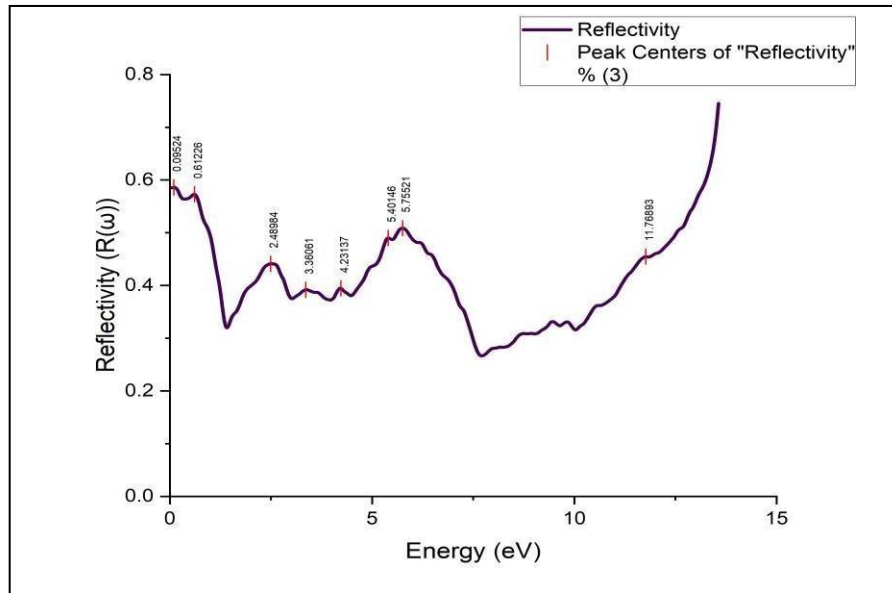


Fig.5.16 Calculated reflectivity of cubic MoS₂

B) Hexagonal MoS₂

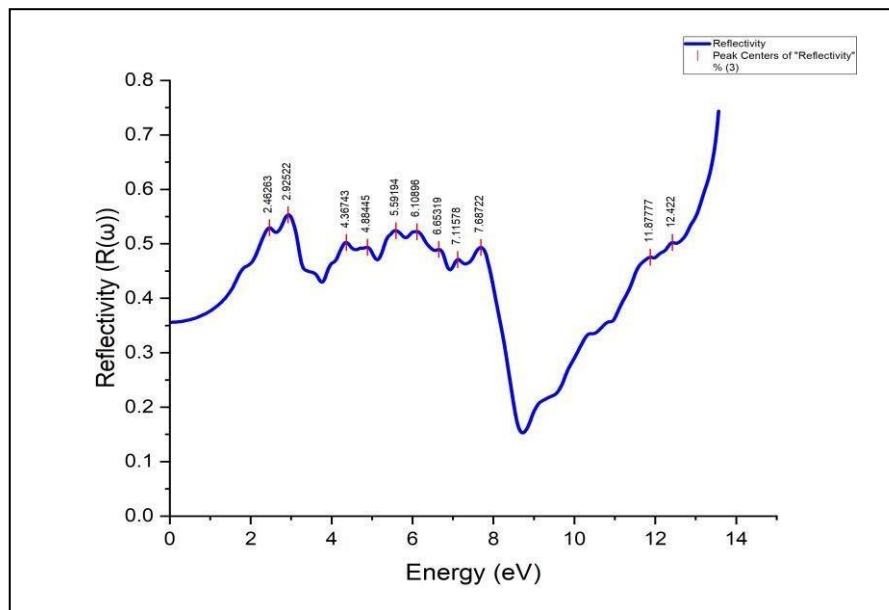


Fig.5.17 Calculated reflectivity of hexagonal MoS₂

Fig.5.17 shows the reflectivity spectra of hexagonal structure of MoS₂ as a function of photon energy. The maximum reflectivity peak is observed in the visible region which is 0.5531 eV and 0.5294 eV. Very less reflectivity is observed at 9eV which is in the UV region.

5.6.3. REFRACTIVE INDEX

The bending of light rays when passing from one medium to the other can be determined by refractive index. $n=c/v$ is the ratio of the speed of light in the medium to the speed of light in vacuum in which n is the refractive index, v is the speed of light in material and c is the speed of light in vacuum.

The formula for refractive index is [44],

$$n(\omega) = \sqrt{\frac{\epsilon^2(\omega) + \epsilon^2(\infty)}{2}}$$

A) Cubic MoS₂

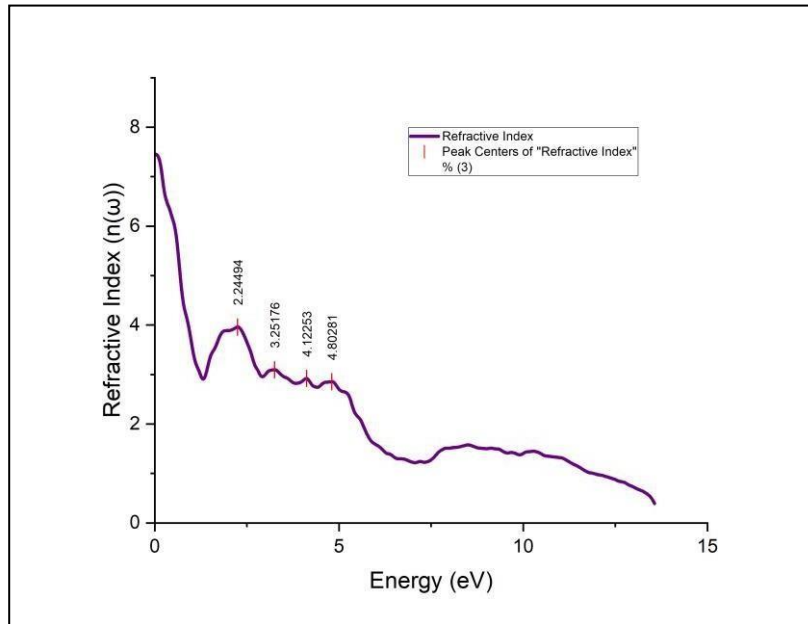


Fig.5.18 Calculated refractive index of cubic MoS₂

The refractive index of the cubic structure of MoS₂ is given in the Fig.5.18. The real part of the refractive index represents the phase velocity of the electromagnetic wave in the samples inner side. The refractive index is the optical properties fundamental parameter. Since it is correlated to electronic polarizability of ions and the local field inside the material [45]. It determines the transparency of the material. The highest peak is at 2.24494 eV and 3.25176eV which is at the visible region of the spectra. The lowest refractive index is at the UV region.

B) Hexagonal MoS₂

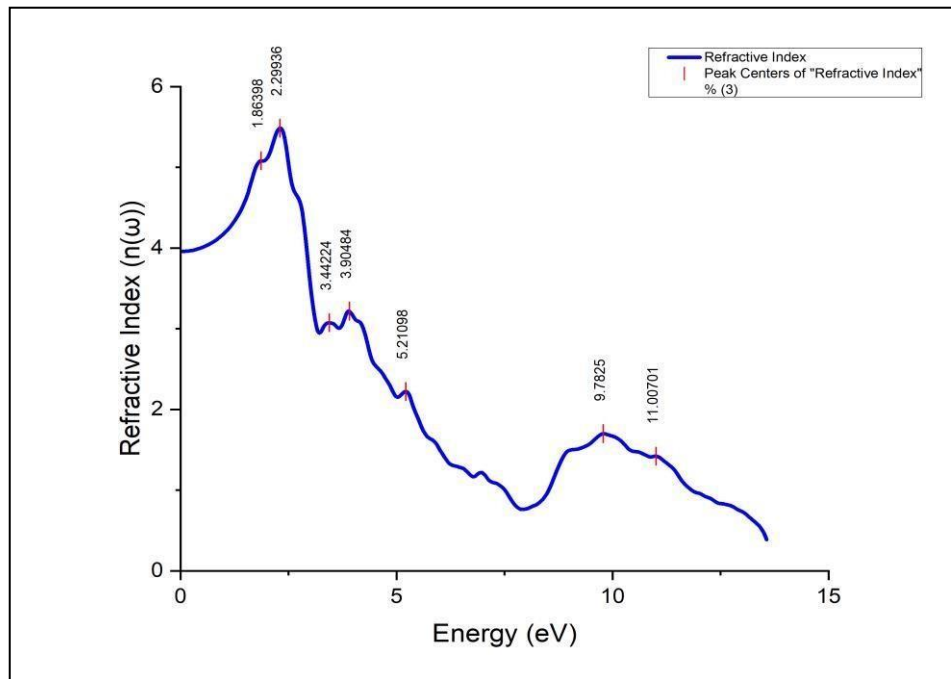


Fig.5.19 Calculated refractive index of hexagonal MoS₂

The refractive index of the hexagonal structure of MoS₂ is given in the Fig.5.19. The highest peak is at 2.29936 eV and 1.86398 eV which is at the visible region of the spectra. The lowest refractive index is at the UV region of around 11.00701 eV. The maximum value corresponds to the covalent bond while the minimum is ionic bond.

5.6.4. ENERGY LOSS FUNCTION

Energy loss function relates the electron and matters interaction in solids. It determines the energy loss due to the fast-moving electrons through matter. Using dielectric function, it can be calculated as,

$$L(\omega) = \ln \{-1/\epsilon(\omega)\}$$

A) Cubic MoS₂

The calculated energy loss function is given in fig.5.20 for the cubic structure of MoS₂. The maximum value of eloss is at 7.55116eV which is in the UV region. But in the visible region the lower peaks are observed. Thus, less energy loss of the material occurs. Since less eloss is observed in visible region, it is very much suitable for the solar cell applications.

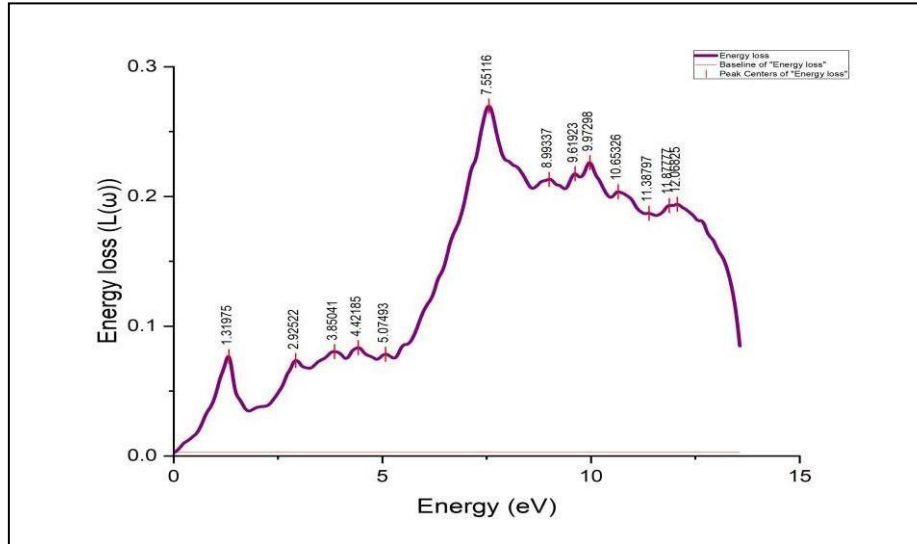


Fig.5.20 Calculated energy loss function of cubic MoS₂

B) Hexagonal MoS₂

The calculated energy loss function is given in fig.5.21 for the hexagonal structure of MoS₂. The calculated energy loss function is given in fig.5.21 for the hexagonal structure of MoS₂. The maximum value of eloss is at 8.50356eV which is in the UV region which shows a sharp peak. Comparing with the cubic structure this has large value of energy loss about 0.508346.

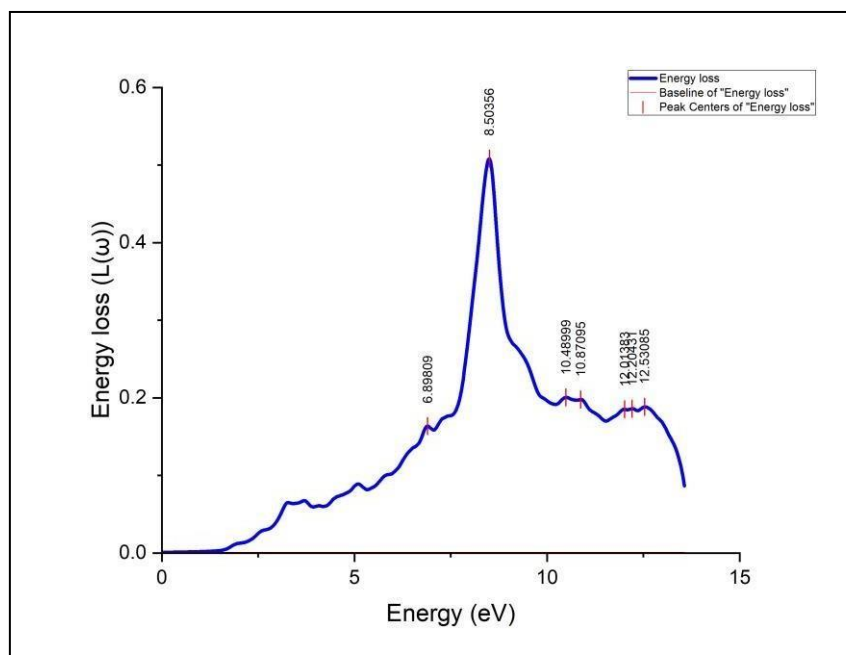


Fig.5.21 Calculated energy loss function of hexagonal MoS_2

CHAPTER 6

CONCLUSION

In the present study, structural, electronic, thermoelectric and optical properties of cubic and hexagonal structure of MoS₂ have been established. Using FP-LAPW technique the calculations were carried out using the density functional theory as the main frame by PBE-GGA exchange-correlation method. Every calculated value well suits with the other theoretical and experimental results. The band structure, total density of states and partial density of states has been reported individually for the two structures.

From the band structure, it can be concluded that the cubic structure is a metal since zero bandgap of energy whereas hexagonal structure is semiconductor since it has 0.891eV of energy gap. Thus, hexagonal structure of MoS₂ is more suitable for the thermoelectric applications. Also, the from the graphs we interpreted that for higher temperatures, we can go for hexagonal structure and for low temperatures like room temperature cubic structure is suitable in accordance with their power factor value.

From the Seebeck coefficient versus temperature graph, as the temperature decreases the Seebeck coefficient gets decreased for both the structures. Hexagonal structure can be used for both p type and n type since it has both positive and negative Seebeck coefficient value.

The calculated values of optical properties such as absorption coefficient, reflectivity, refractive index and energy loss have been reported. The absorption coefficient, refractive index and energy loss are comparatively high for the hexagonal structure of MoS₂. The energy loss is comparatively less for the cubic structure which is reported in the visible region. Hence it can be used for the solar cell applications.

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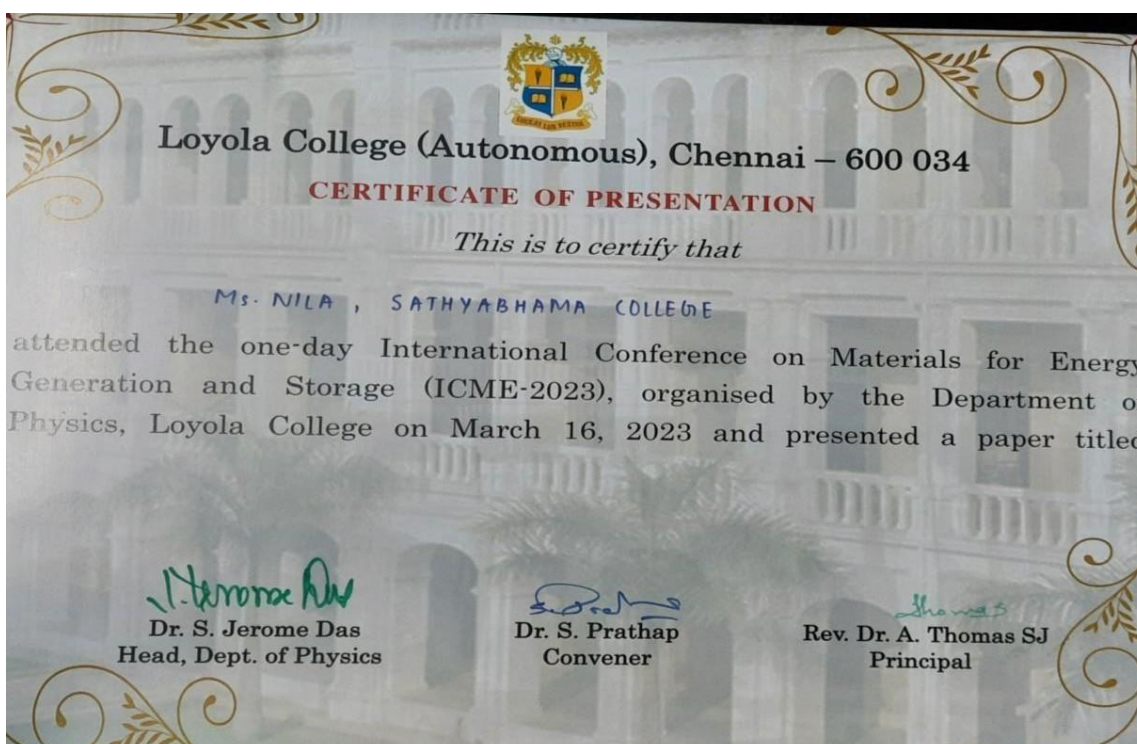
LIST OF CONFERENCES

Authors	Conferences	Date	Title	Presentation
K. Nila ¹ , M. Manjula ^{2*} and M. Muthumari ³	MCGPD 2023	6-8 March 2023	First principle study of quantum confinement effect in cubic molybdenum disulphide electronic structure	Oral presentation on 07-03-2023
K. Nila ¹ , M. Manjula ^{2*} and M. Muthumari ³	ICME 2023	16 th , March 2023	First principle study of quantum confinement effect in hexagonal molybdenum disulphide electronic structure	Oral presentation on 16-03-2023

Conference 1



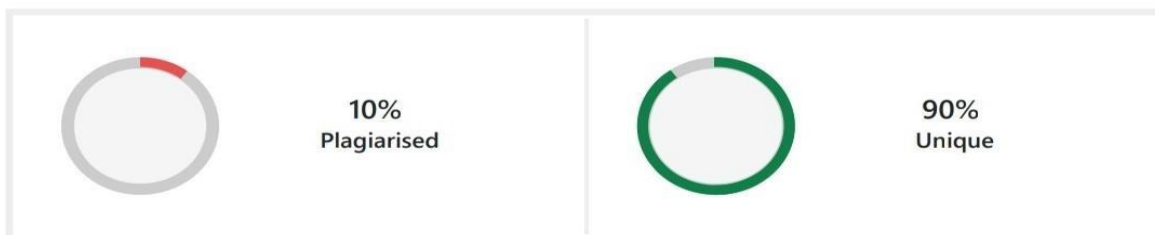
Conference 2



PLAGIARISM REPORT



PLAGIARISM SCAN REPORT



**Signature of internal guide
(Dr.M. MANJULA)**