FIRST PRINCIPLE STUDY ON ELECTRONIC AND STRUCTURAL PROPERTIES OF CADMIUM TELLURIDE (CdTe) USING DENSITY FUNCTIONAL THEORY

A Thesis Submitted to the Graduate School of Jimma University Department of Physics in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Physics (Condensed Matter Physics)

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July, 2022

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Dated: July, 2022

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JIMMA UNIVERSITY

Date: July, 2022

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Title: First principle calculation of Cadmium Telluride using density functional theory

Department: Physics

Degree: M.Sc. Convocation: July, Year: 2022

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Contents

List of Tables

List of Figures

Abstract

CdTe is a wide band gap semiconductor belonging to group II-VI. It is commonly used in light emitting diodes (LED) and many optoelectronic devices fabrications. It is obvious that many body problems are complex and a piece challenging to solve. Due to this the state of motion cannot be solved analytically for systems in which three or more masses are interact. To solve this many body problems, the Density Functional Theory is preferred as an accurate and reliable tool. The first principle calculation based on density functional theory (DFT) was employed to investigate the electronic and structural properties of hexagonal(wurtzite) and zincblende CdTe using quantum ESPRESSO package. A number of convergence test were performed to establish the optimal value of various parameters in the numerical calculations. Firstly, the total minimum energy of CdTe per atom was calculated as a function of cutoff energy and k-points sampling. Secondly, the optimal lattice constants of CdTe was calculated for a series of possible parameters using the results obtained from energy convergence test (i.e, for wurtzite 110 Ry and 7×7×7 k-points, for zincblende 110 Ry and 4×4×4 k-points). Moreover the band structure and density of states of CdTe have been calculated based on the frame work of density functional theory. The results of calculations show that the total minimum energy of CdTe per atom is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-point sampling. The computational value of the equilibrium lattice constant for wurtzite was A = 4.684 Å, C = 7.684 Å and for zincblende was 6.60 Å. The obtained result was over estimated as compared to the experimental result.

The computed values of band structure and density of states of wurtzite Cadmium Telluride was 0.595 eV and 0.58 eV respectively. The computed values of band structure and density of states of zincblende Cadmium Telluride was 0.605 eV and 0.79 eV respectively.

keyword: Cadmium Telluride, density functional theory, pseudopotentials, plane wave self-consistent field and Quantum Espresso Package.

Acknowledgements

I would like to express my great thanks to Almighty God for his help through out my study. First and foremost, I would like to express my deep gratitude to my advisor, Dr. Menberu Mengesha (Associate professor) who is a wonderful mentor. I am extremely thankful for his support, guidance, patience and precious encouragement the whole time during my study. I would like to thank also my co-Advisor Dr. Nebiyu Gemechu for his valuable support, encouragement and advice. Finally I would like to express my deepest thank to my wife for her motivation and endless support throughout my study.

1

Introduction

1.1 General Background

Semiconductors are classes of materials that are playing significant role in the area of optoelectronic devices fabrications. For the past several years, the binary compounds have been studied extensively to find a new absorber material for solar cells. In addition, lots of research efforts have been devised for the development of low cost and high efficiency thin film solar cells. In this aspect, group II–VI semiconductors are largely studied because of their potential use in photoconductive devices and solar cells. As a group II-VI semiconductor material, CdTe has a direct band gap of 1.5 eV at room temperature [1, 2], high average atomic number (50), good transport property, high resistivity, and the type of conductivity Cadmium Telluride is a crystalline compound formed from Cadmium and Tellurium. Because of its optimum energy band gap (1.5 eV) at room temperature and high absorption coefficient ($> 10^{+5}cm^{-1}$) in the visible region, CdTe can act as a good candidate for solar energy conversion [3, 4].

It is sandwiched with Cadmium Sulfide to form a p-n junction photovoltaic solar cell. It has very low solubility in water and is etched by many acids such as hydrobromic and hydrochloric acids. It is commercially available as powder or crystals. It can also be made into nanocrystals.

As a consequence of the direct band gap, the absorption edge of CdTe is very sharp and more than 90% of the incident light is absorbed in a few micrometers, while a 20μm thick layer of Si is required to absorb the similar radiation intensity [5].

The state of motion of particles cannot be solved analytically for systems in which three or more distinct masses interact. To solve this problem, the density functional theory was appeared in different principles or approaches. First principle pseudo potential calculations have been performed on CdTe in the wurtzite and zincblende structures. The mixed basis approach is employed due to the localized nature of valence charge

3

density in this material. Over the past decade, first principles calculations based on the DFT with local density approximation (LDA) have been developed and made the accurate prediction of ground state properties of solids available. DFT has gained great success particularly in condensed matter electronic structure calculation. One reason for this is that calculation can be done for large systems at modest computational costs [6, 14]. There is no doubt that DFT is exact in principle, however DFT relies on approximation to the exchange correlation functional in practice. Although DFT has been to be very careful, still it is encountered with some deficiencies. One common example in surface physics is that DFT with LDA and GGA predict wrong adsorption site for CO on Pt(111) and other close-packed metal surfaces [7, 8, 9].

The convergence of total minimum energy per atom was calculated with respect to cutoff energy and k-point samplings. The band structure, density of states (DOS) and lattice constants also have been calculated using DFT.

In general the focus of this thesis was, determining electronic and structural properties of CdTe with the help of first principle calculation using Quantum Espresso package.

1.2 Statement of the Problem

It is obvious that many body problems are complex and a piece challenging to solve. Due to this the state of motion cannot be solved analytically for systems in which three or more masses are interact. To solve this many body problems, the Density Functional Theory is preferred as an accurate and reliable tool. The primary reason of DFT is that any property of the interacting structures can be considered as a functional of the ground state density $n_0(r)$. The semiconductor material, Cadmium Telluride (CdTe) plays significant role in the production of light emitting diodes (LEDs) and different optoelectronic devices. It is also promising material for new generations to operate many microelectronic components in the future. But its electronic and structural properties on density functional theory are not well studied. So it is aimed to investigate the electronic and structural properties of CdTe with the help of DFT using Quantum ESPRESSO package.

1.3 Research questions

The following quations have been answered in this study:

1. What is the total minimum energy of CdTe per atom with respect to cut-off energy?

2. What is the total minimum energy of CdTe per atom with respect to K-point sampling?

3. What is the equilibrium lattice constant of CdTe?

4. What is the band structure of CdTe?

5. What is the density of state of CdTe?

1.4 Objectives

1.4.1 General Objective

The general objective of this study is to investigate the electronic and structural properties of Cadmium Telluride (CdTe) using Density Functional Theory with the help of Quantum ESPRESSO package.

1.4.2 Specific Objectives

The specific objectives of this study were:

1. To calculate the total minimum energy of CdTe per atom with respect to cut-off energy.

2. To investigate the total minimum energy of CdTe per atom with respect to k-points sampling.

3. To compute the lattice constant of CdTe with respect to cut-off energy and k-points sampling.

4. To determine the band structure of CdTe using density functional theory and compare it with experimental band gap.

5. To describe the density of states of CdTe using density functional theory.

1.5   Significance of the Study

The major significance of this study was to understand the electronic and structural properties of many electron system (in particular CdTe) helps to know about the system in detail. Moreover, it helps to develop computational skill for solving many body problems.

1.6   Scope of the study

The scope of this study is calculations of electronic and structural properties of Cadmium Telluride. However Cadmium Telluride has zincblende, wurtzite and rocksalt structures. The total minimum energy and the equilibrium lattice constants of Cadmium Telluride were calculated with respect to cut-off energy and k-point samplings, while the band gap and density of states of Cadmium Telluride were calculated based on density functional theory (DFT). We can perform DFT calculations, using Quantum-ESPRESSO, to calculate the crystal structure of CdTe. In this case the optimization procedure was repeated for hexagonal(wurtzite) and zincblende(FCC) .

1.7   Organization of the study

The thesis is organized and separated to five chapters. Chapter one is introduction part which discusses background of the study, problem statement, objectives of the study, its significance and the scope. Chapter two reviews of related literature. Chapter three discusses research methodology. Chapter four discusses the results of the study and includes, explains the results and discusses the findings of the study. Chapter five concludes the results of the study.

2

Review of related Literature

Introduction

This chapter focusing on the basic Quantum mechanical description of many-body system up to the theoretical background of the electronic and structural calculations methodologies. For approximately solving many electron problems, the Hartree-Fock, Hohenberg-Kohn, Thomas-Fermi, the Kohn-Sham, the modern DFT and whatever theories are discussed in detail. Finally to perform calculations of a system, a plane wave basis set and pseudo-potential can be reviewed.

2.1 Applications of CdTe

The successful development of a technique for the production of p-n type CdTe has resulted in the fabrication of blue light emitting diodes (LEDs) and different microelectronic devices [10]. CdTe is very important semiconductor material which is widely applied in different areas for several functions.
CdTe is used:

- As an infrared optical material for optical windows and lenses and is proven to provide a good performance across a wide range of temperatures.

- X-ray and gamma ray detectors: Among the compound semiconductors, CdTe have attractive growing interests in the development of X-ray and gamma ray detectors. Due to its, high atomic number, high density and wide band gap, CdTe detector ensure high detection ratio, at room temperature performance and are very attractive for X-ray and gamma ray applications [11].

- Electro-optic modulator/non-linear optics: One important application of CdTe will most certainly be as an electro-optic modulator in both the near and the far infrared. Because CdTe is a semiconductor with an energy gap of 1.5 eV, it is opaque in the visible range of the spectrum.

- As gunn effect, piezoelectric and similar devices. CdTe, like GaAs, exhibits the Gunn effect ; that is, above a certain threshold aplied field, high frequency current oscillations are produced.

- To make thin film solar cell :its near ideal bandgap, CdTe has a high optical absorption coefficient.

- In nuclear detectors: Due to combination of high average atomic number, high bandgap and reasonable mobility lifetime products for both electrons and holes yield CdTe a quite unique combination of properties for the purpose [4].

2.2   General Properties of Cadmium Telluride

CdTe has arguably the lowest production cost per watt and compete to energy generations using fossil matter. In general, thin films have inherent benefit in manufacturing, as they can be manufactured in large areas with high speeds of fabrication. Power Consumption and materials usage during fabrication is little for thin film deposition (order of $2g/m^2$). For higher band gap CdTe, the decrease in power generation at high operating temperature is to a lesser extent. In research, CdTe technology have achieved Cell-level performance over 22٪ and full-sized panels performance around 18.6٪. CdTe being thin film semiconductors, are polycrystalline in nature, i.e, within the material there are very small crystallites about a micron and in between the crystallites are grain boundaries [12]. Cadmium Telluride (CdTe) forms crystals in zincblende structure with a lattice parameter of 6.482Å. Each Cd atom is tetrahedrally surrounded by four Te atoms and vice versa. In theory semiconductors with a band gap of 1.5 eV are ideally suited for solar cell applications. A 1-2 μm thick film of CdTe is enough for conversion of sunlight into electricity. CdTe is a defect semiconductor with a dielectric constant of 10.2. It can be doped both p and n-type [13]. Cadmium Telluride is a wide band gap semiconductor belonging to the group II-VI and used commonly for optoelectronic applications. It is a very hard material with high heat capacity, thermal conductivity and has resistance to chemical assault. In addition, Cadmium Telluride is mechanically stable extensive band gap compound with melting point 1041^0C, boiling point 1050^0C [5],

average molar mass: 240.01g/mol and density 5.85g/cm^3. CdTe is insoluble in water and its clothing rate increases as humidity increases. Various research articles repeatedly pointed that it is exceedingly stable energy band gap (1.5 eV), it is also an excellent candidate for devices operation in high temperature, high power, high frequency and caustic situation. As mentioned above, CdTe is an attractive material, which is now in an accelerated developing stage. In this work, general properties of CdTe is stated as basic idea, including chemical, electrical and structural properties. As a consequence of the direct band gap, the absorption edge of CdTe is very sharp and more than 90% of the incident light is absorbed in a few micrometers, while a 20μm thick layer of Si is needed to absorb the similar radiation intensity [5].

2.3   Crystal structure of CdTe

2.3.1   Zincblende structure of CdTe

Cadmium Telluride (CdTe) forms a Zincblende lattice with $2.94 \times 10^{22} atoms/cm^3$. Zincblende CdTe has drawn big interest for a long time due to its many important applications in optoelectronics. The Zincblende structure is two interpenetrating face-centered cubic (FCC) structures with Cd at (0,0,0) and Te at (¼, ¼, ¼), as shown in figure 2.1 b displaced from each other along the body diagonal by $\frac{a}{4}$, a being the lattice constant for the Zincblende structure [14, 15]. These results into two different stacking sequences: ABCABC along [111] direction. The ZB structure corresponds to the staggered conformation of atomic arrangement along [111] body diagonal. The closest neighbor (tetrahedral bond) arrangements in the ZB structure and in the ideal WZ structure are the same. The main difference starts to come in the relative position of 3rd nearest neighbors and beyond. The lattice parameter for ZB CdTe is $6.482 \mathring{A}$ [16].

2.3.2 Wurtzite structure of CdTe

Under certain conditions, CdTe can be found in a metastable hexagonal phase (the wurtzite structure)[17]. A perfect WZ structure consists of two interpenetrating hexagonal closed packed (HCP) sublattices, one of atom A, the other of atom B, displaced from each other by $\frac{3}{8}c$ along the c-axis. These result into two various stacking sequences ABAB. . . along c-axis. The arrangement of the distant atoms along the four different tetrahedral bonds are different for a WZ structure. The lattice parameter for Wurtzite CdTe is 4.57Å [16].
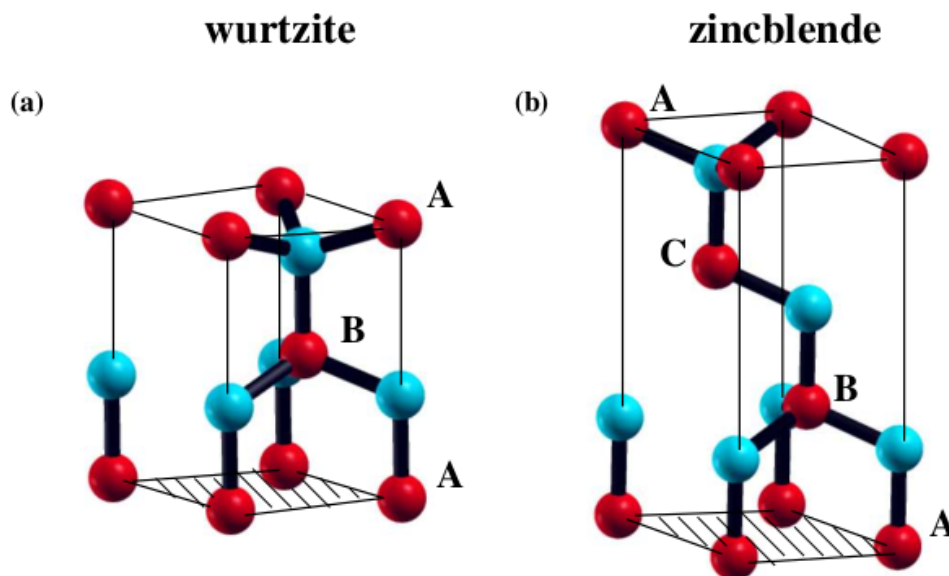
Figure 2.1: Structure of wurtzite and zincblende CdTe

Table 2.1: Structural parameters of WZ and ZB phases for CdTe

Compuond	WZ		ZB
	a(Å)	$\frac{c}{a}$	a(Å)
CdTe	4.57	1.637	6.482

2.4 Chemical properties of CdTe

CdTe is insoluble in water. It has a high melting point of 1041°C with evaporation starting at $1050^0 C$. CdTe has a vapor pressure of zero at ambient temperatures. CdTe is more stable than its parent compounds Cadmium and Tellurium and most other Cd compounds, due to its high melting point and insolubility [5, 18]. Cadmium Telluride

is commercially available as a powder, or as crystals. It can be made into nanocrystals. The compound CdTe has distinct features than the two elements, Cadmium and Tellurium, taken one by one. Toxicity examinations show that CdTe is much less toxic than elemental Cadmium [18]. CdTe has low acute inhalation, oral, and aquatic toxicity, and is poor in the Ames mutagenicity check. CdTe is no longer classified as harmful if ingested nor harmful in contact with skin, and the toxicity type to aquatic lifestyles has been decreased. Once properly and securely captured and encapsulated, CdTe used in manufacturing procedure may be rendered harmless [18].

2.5 Density Functional Theory (DFT)

Density Functional Theory (DFT) is a computational quantum mechanical modeling method which is widely practical in all areas of Physics and chemistry, wherever properties of systems need to be calculated [19, 20, 21]. Using this theory, a many electron system can be determined by using functional, i.e, functions of another function, which in this case is the spatially dependent electron density. It gives a theoretical account to obtain the total energy, total minimum energy, cut- off energy, k-points, crystal structural properties and etc [20, 22]. The DFT has its roots in Thomas-Fermi model for the electron structure of materials [23]. It became first put on a firm theoretical footing with the aid of Walter- Kohn and Pierre Hohenberg within the framework of the two Hohenberg-Kohn theorems (H-K) which states that:

(i) All ground –state properties of a system, including the total energy are some functional of the ground-state charge density and

(ii) The correct ground state charge density minimizes the energy functional, i.e,

$$E[n] = T[n] + U[n] + \int V(r)n(r)\delta^3 r \tag{2.1}$$

Where n is the charge density, T is the kinetic energy, V is the potential energy from the external field (typically due to positively charged nuclei of crystal), U is the electron-electron interaction energy and r is the position. The formulation is applied to any system of interacting particles in an external potential $V_{ext}(r)$ [24]. As mentioned above, DFT follows different formulation to come through its central target. Some of theories or formulation were encountered with some drawbacks. One of these is the Thomas-Fermi theory, which is the poor approximation of kinetic energy functional. There are significant advantages to a computational theory based on electron densities.

The first is in relation to efficiency; the electron density depends on the three spatial variables in contrast to the 4N variables that wave functions depends on (three spatial and one spin per electron). Therefore, large system can be theoretically modeled. In addition, electron correlation is conceptually easier to include in DFT [23]. It has achieved a certain status as a standard first method. This the first principle calculations have gained great success in studying the equilibrium properties of matter, though there are still many challenges to DFT [24]. One of the big issues is how to solve the problems when encountering with electronic degeneracy. Such an issue usually does not pose a problem to the equilibrium conditions. It is well known that electronic degeneracy cannot exist in the ground state of a nonlinear atomic geometry. In DFT we only need to find the charge distribution throughout our system. We can describe only single electron moving in a crystal mean field of all ions and other electrons. In this way we can compute solids up to a few thousand atoms. DFT is a formally exact representation of the N electrons Schrödinger equation. The extent to which DFT has contributed to the chemical, physical and biological sciences is reflected by the 1998 Nobel prize in chemistry, which was awarded to Walter Kohn for the development of DFT, along with John Pople for the development of quantum chemistry [24, 25]. The major problem in DFT is that the exact functional for exchange and correlation are not known, except for the free electron gas. The other well known difficulty met by DFT calculation was the underestimation of the bandgap of the materials (specially semiconductors and insulators). However approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local density approximation (LDA), where the functional depends only on the density at coordinate where the functional is evaluated [26, 27, 28]. However in this study the generalized gradient approximation (GGA) was used because of its better approximate nature.

2.6 Many Electron system

The ultimate goal of most formulation in solid state physics, quantum chemistry and in this electronic structural calculation of CdTe is the solution of the time independent, non relativistic Schrödinger equation. It is eigenvalue equation for the total energy operator, the Hamiltonian $\hat{H}$. The Hamiltonian contains all 3M coordinates of the nuclei $\vec{R}$ and the 3N coordinates of the electrons $\vec{r}$. The electron mass is m_e, the masses of the nuclei are named M, and proton numbers are Z. The electronic Schrödinger [29] of a

system of N electrons reads,

$$H\Psi(r_1, \ldots, r_N) = E\Psi(r_1, \ldots, r_N) \tag{2.2}$$

In the above equation, H is Hamiltonian of the system, E is energy, r_N is coordinate of the electron with index N and $\Psi(r_1, \ldots, r_N)$ is the many particles wave function [30].

$$H = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{T}_n + \hat{V}_{nn} \tag{2.3}$$

$$\hat{T}_e = \sum_i^{N_{elec}} -\frac{1}{2}\nabla_i^2 \tag{2.4}$$

$$\hat{V}_{ne} = \sum_a^{N_{nuc}} \sum_i^{N_{elec}} \frac{Z\alpha}{[R_a - r_i]} \tag{2.5}$$

$$\hat{V}_{ee} = \sum_i^{N_{elec}} \sum_{j>i}^{N_{elec}} \frac{1}{\mid r_i - r_j \mid} \tag{2.6}$$

$$\hat{T}_n = \sum_a^{N_{nuc}} -\frac{1}{2}\nabla_\alpha^2 \tag{2.7}$$

$$\hat{V}_{nn} = \sum_a \sum_{b>a} \frac{1}{\mid R_a - R_b \mid} \tag{2.8}$$

In atomic units.

Where, $\hat{T}_e$ is the electronic kinetic energy, ∇_i^2 is the Laplacian acting over the electronic coordinates r_i. $\hat{T}_n$ is the energy corresponding to the motion of the nuclei, ∇_α^2 is the Laplacian acting over the nuclues coordinates. $\hat{V}_{ee}$ and $\hat{V}_{nn}$ are the pairwise electrostatic electron-electron and nucleus-nucleus interactions respectively, where $\mid r_i - r_j \mid$ and $\mid R_a - R_b \mid$ are the electron-electron and nucleus-nucleus separations of the pairs which are being considered, and $Z\alpha$ represents the charge of the αth nucleus [31].

2.7 The Electron Density

The electron density $n(r)$ is defined as the number of electrons per volume at the point r in space. It is a physical quantity it can (at least in theory) be measured [32]. The integral of the electron density gives the total number of electrons,

$$\int n(r)dr = N$$

The relation between $n(r)$ and the many-electron wave-function Ψ_e is

$$n(r) = N \iint ... \int |\Psi_e(r\sigma_1, X_2, ..., X_N)|^2 d\sigma_1 dX_2...dX_N \qquad (2.9)$$

2.8 Thomas-Fermi Theory

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 [33]. Thomas Fermi Theory is the simple model of DFT. It come out when we ignore the exchange energy and make the simplest possible approximation for the kinetic energy [23, 28]. For a solely varying density function the kinetic energy density will only depend on the number of density at the same position. Taking the specific function from the Fermi gas, we get the kinetic energy functional.

$$T[n(\vec{r})] = \int \frac{3}{10} \frac{(3\pi^2)^{\frac{2}{3}}}{m} [n(r)]^{\frac{5}{3}} d^3r \qquad (2.10)$$

And the sum of the kinetic energy and potential energy terms will yield us the total energy within the Thomas Fermi approximations [24].

$$E[n(\vec{r})] = \int \frac{3}{10} \frac{(3\pi^2)^{\frac{2}{3}}}{m} [n(r)]^{\frac{5}{3}} d^3r +$$

$$\int \frac{e^2}{2} \int \frac{n(\vec{r})n(\vec{r'})}{|\vec{r} - \vec{r'}|} d^3\vec{r} d^3(\vec{r'}) + n(r)V_N(r)d^3r \qquad (2.11)$$

The first term of the right hand side of equation 2.11, is the kinetic energy of the non-interacting electrons in a homogeneous electron gas, the second term is the potential energy of the electrons due to their mutual electron repulsion and the third term is

the potential energy of an atom's electrons, due to the electric attraction of positively charged nucleus. Note that the expression only depends on density $n(r)$. Unfortunately, this theory has limited validity due to its poor approximation of kinetic energy functional [21].

2.9 Hartree-Fock Theory

The Hartree-Fock equations are determined by assuming that, the interactions of electrons can be solved using a Slater determinant (derived using Pauli's exclusion principle). Hartree-Fock theory is essential to much of electronic structure theory. It is the basis of molecular orbital (MO) theory, which posits that each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. Hartree-Fock theory was developed to solve the electronic Schrödinger equation that results from the time-independent Schrödinger equation after invoking the Born-Oppenheimer approximation [34]. Hartree-Fock Theory is the Variational theory obtained by the expectation value of the Hamiltonian, allowing all wave functions that can be represented as Slater determinants. This theory was formulated by two individuals, Hartree and Fock. Fock applied the slater determinant to the Hartee method and proposed the Hartree-Fock method and involves antisymmetric natures of waves(derived using Pauli's exclusion principle), spin orbital (slater determinant), orthogonality and angular momentum [35]. One of the strategies of Hartree-Fock is, the self-consistent solutions are obtained by employing variational principle, which is given by;

$$\delta \langle \Psi^{(N)} \mid H \mid \Psi^{(N)} \rangle = 0 \tag{2.12}$$

2.10 The Hohenberg-Kohn Theorem

The foundation of the DFT method is the Hohenberg-kohn theorem, which states that for each given electronic density $n(r)$, there is one and only one corresponding potential. All properties of the many body system are determined by ground state density. The Hohenberg-Kohn theorem implies that the ground state for any system can be determined by varying the charge density until the global minimum in the energy functional is found[33].

2.10.1 First Theorem of Hohenberg-Kohn

If E is the lowest possible energy of the system, i.e. the energy of the ground state, then E is a unique functional of Electron density. The consequence of this statement is that, in order to calculate the total energy E in the ground state, electron density is the only required quantity[33].

$$E[\Psi] = \langle \Psi \mid \hat{H} \mid \Psi \rangle \tag{2.13}$$

Using $\Psi_0[\rho_0]$ one can determine all properties by calculating;

$$\langle \hat{O} \rangle [\rho_0] = \langle \Psi_0[\rho_0] \mid \hat{O} \mid \Psi_0[\rho_0] \rangle \tag{2.14}$$

Where $\hat{O}$ is an arbitrary operator.

The proof of the statement is based on three premises,

- The external potential of the nuclei V_n is uniquely determined by the electron density in the ground state.

- This external potential determines uniquely the many electron wavefunction Ψ, in any quantum state.

- In any quantum state the total energy E, is a functional of many body wavefunction Ψ

By combining three premises we can say that, in ground state, the density uniquely determines the total energy: $n \rightarrow V_n \rightarrow \Psi \rightarrow$ E. The third premise simply reinstate equation 2.12 and the second premise means that if we change the positions of nuclei, we will obtain different many body wave function. In order to prove first premise, we assume that the same ground state electron density can be obtained from two different external potentials. If we can show our assumption leads to contradiction, then we can say the first premise is valid. To do that the kinetic energy and potential energy terms are introduced [36].

$$\hat{T} = -\sum_i \frac{1}{2} \nabla_i^2 \;, \qquad \hat{W} = \frac{1}{2} \sum_{i \neq j} \left(\frac{1}{\mid r_i - r_j \mid} \right) \tag{2.15}$$

Using this we can write the total energy notation as follows:

$$E = \int dr n(r) V_n(r) + \langle \Psi \mid \hat{T} + \hat{W} \mid \Psi \rangle \tag{2.16}$$

Now, let us assume that Ψ is the ground state wavefunction for the potential V_n. If there exist another external potential $V_n' \neq V_n$, which generates the same Energy, density n, $\hat{H}, \hat{\Psi}$ and $\hat{E}$ are the Hamiltonian ,ground state wavefunction and the ground state energy corresponding to the new potential. Since, Ψ is not the ground state of the V_n' we can write:

$$E' < \int drn(r)V_n'(r) + \langle \Psi \mid \hat{T} + \hat{W} \mid \Psi \rangle \qquad (2.17)$$

Combining equations 2.16 and 2.17:

$E - E' > \int drn(r)[V_n'(r) - V_n(r)]$ or

$E' - E > \int drn(r)[V_n(r) - V_n'(r)]$

Since we did not make any assumptions for external potentials. As a result, adding up the last two equations obtain, $0 > 0$. This is a contradiction and our assumption that the two different potentials give same ground state density is false. This proves that the first premise stated above is valid for the ground state energy. In general, this theorem states that there exists a one-to-one mapping between the ground-state wave function and the ground-state electron density.

2.10.2 Second Theorem of Hohenberg-Kohn

A universal functional for the energy $E[n]$ interms of the density $n(r)$ can be defined, valid for any particular $V_{ext}(r)$, the exact ground state energy of the system is the global minimum value of this functional, and the density that minimize the functional is the exact ground state density $n_0(r)$[37].

$E[n] = T[n] + V_{Ne}[n] + V_{ee}[n]$

$$= F_{HK}[n] + V_{Ne}[n] \qquad (2.18)$$

where $F_{HK}[n] = T[n] + V_{ee}[n]$ which is universal functional. The second theorem answers the question how to identify the ground state density.

2.11   The Kohn-Sham Approach/ theory

In 1965 Kohn and Sham took the total energy in the independent electron approximation as the combination of kinetic and Coulomb energy of independent electrons and the exchange and correlation energy that accounts for all the difference. The Hohenberg and Kohn theorems facilitate the treatment of quantum systems by stating, that

the electron density of the ground state completely describes a system. Kohn and Sham (KS) proposed to put wave mechanics in to the kinetic energy functional, but retain the density variable $n(r)$ elsewhere. Their theory was tightly linked to Hartree-Fock slater approximation of many body fermions theory [38, 37]. The weakest part of Thomas Fermi theory was the treatment of kinetic energy functional in this theory. Kohn-Sham considered the exchange and correlation energies and supposed to calculate the exact kinetic energy of a noninteracting reference system with the same density as the real interacting system.

$$E_{KS}[\phi_1, \ldots, \phi_n] = \sum_a^N \frac{\hbar^2}{2m} \int d^3r \, \nabla \phi_a^* \cdot \nabla \phi_a + \frac{1}{2} \int d^3r \frac{e^2}{|r-r'|} n(r)n(r') +$$

$$E_{xc}[n] + \sum_a d^3r V_{ext}(r)|\phi|^2 \tag{2.19}$$

Actual one-particle wave-functions are constructed as combinations of position dependent parts and spin functions. The ground state wave-function of the many-independent particle system is a Slater determinant $\Psi = 1/\sqrt{N!} \det_{ij} \psi_j(r_i, \sigma_i) \; \psi_r(r, \sigma) = \phi_i(r)\chi(\sigma)$. The many-particle wave function is inserted in the usual expression for the electron density Eq.2.9 to give the particle density,

Which is used together with the definition,

$n(r) = \sum_a^N \mid \phi_a(r) \mid^2$

where the sum is taken over all occupied spin-states a (i.e, two per fully occupied orbital). Accurate values of the exchange and correlation energies obtained for chemically interacting systems are crucial for analysis of the impact of electron correlation with in Kohn-Sham (KS) idea. The accuracy of the results of a good calculation (i.e, use of a software with an accurate implementation of the KS equations) relies only on the chosen exchange-correlation functional. In the theory of Kohn and Sham, the problem of calculating the ground state properties of the system of interacting electrons is reduced to the problem of calculating these properties via a hypothetical system of non-interacting electrons in an effective potential with the respective single electron wave functions.

$$\Psi_i(r) = \begin{pmatrix} \Psi_i^\uparrow(r) \\ \Psi_i^\downarrow(r) \end{pmatrix}$$

the spin-density matrix ρ is;

$$\rho_{\alpha,\alpha'} = \sum_{i=1}^{N} \Psi_i^{\alpha}(r)(\Psi_i^{\alpha'}(r))^* \tag{2.20}$$

with $\alpha = \uparrow, \downarrow$ can be defined. It is useful to introduce the particle density as well.

$$n(r) = \sum_{i=1}^{N} (|\Psi_i^{\uparrow}(r)|^2 + |\Psi_i^{\downarrow}(r)|^2) \tag{2.21}$$

The Kohn-Sham solutions have been obtained from ab-initio wave function.

2.12 The exchange- correlation energy

The exchange-correlation energy E_{xc} of many electron system is the quantity of DFT. In the context of Kohn-Sham theory, E_{xc} is defined as a functional of the electron density ρ. In K-S expression the total electronic energy $E[\rho]$ is given by;

$$E[\rho] = T_s[\rho] + V[\rho] + W_H[\rho] + E_{xc} \tag{2.22}$$

Where T_s- is the kinetic energy of a non-interacting particle system with density ρ, V is the energy of electron-nuclear interaction, W_H is the coulomb or Hartree energy and E_{xc} is the exchange-correlation energy. $E_{xc}[\rho]$ is the sum of distinct exchange and correlation terms:

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \tag{2.23}$$

where,

$$E_x[n] = <\Psi_n^{min}|\hat{V}_{ee}|\Psi_n^{min}> -U[n] \tag{2.24}$$

Where Ψ_n^{min} is a single Slater determinant, equation 2.24 is just the usual Fock integral applied to the Kohn-Sham orbitals, i.e, it differs from the Hartree-Fock exchange energy only to the extent that the Kohn-Sham orbitals differ from the Hartree-Fock orbitals for a given system or density (in the same way that $T_s[n]$ differs from the Hartree-Fock kinetic energy).
We note that

$$<\Psi_n^{min}|\hat{T} + \hat{V}_{ee}|\Psi_n^{min}> = T_s[n] + U[n] + E_x[n] \tag{2.25}$$

and that, in the one-electron ($\hat{V}_{ee} = 0$) limit [29],

$$E_x[n] = -U[n] \quad (N = 1) \tag{2.26}$$

The correlation energy is

$$E_c[n] = < \Psi_n^{min}|\hat{T} + \hat{V}_{ee}|\Psi_n^{min} > - < \Psi_n^{min}|\hat{T} + \hat{V}_{ee}|\Psi_n^{min} > \quad (2.27)$$

$$E_c[n] \leq 0 \quad (2.28)$$

Since Ψ_n^{min} is that wave function which yields density n and minimizes $\hat{T} + \hat{V}_{ee}$ equation 2.27 shows that $E_c[n]$ is the sum of a positive kinetic energy piece and a negative potential energy piece. These pieces of E_c Clearly for any one-electron system [27].

$$E_c[n] = 0 \quad (N = 1) \quad (2.29)$$

Equations 2.26 and 2.29 show that the exchange-correlation energy of a one electron system simply cancels the spurious self-interaction $U[n]$. An accurate values of the exchange and correlation energies obtained for chemically interacting systems are essential for analysis of the electron correlation within Kohn-Sham theory and in order to test and calibrate various DFT approximations (Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA)) [39].

2.12.1 The Local Density Approximation (LDA)

The local density approximation (LDA) is the most straightforward approximation of the exchange-correlation energy. It was proposed already in the first works on a uniform electron gas system has a constant V_{eff}. The symmetry of this system requires the electron density to be constant $n(r) = n^{unif}$. It also follows that the exchange-correlation energy per particle is constant in space and thus can be expressed as a function (not a functional) of the uniform density. The idea of this functional is the first look at the case of a homogenous electron gas [40, 41]. In such a system, one considers the electron moving in uniform external potential. LDA has been a great success e.g. for applications in the solid state. However, there are cases where its accuracy is not sufficient. For example in the description of certain molecular system and for systems where explicit surfaces are present. In particular, LDA has a tendency to make chemical bindings much too strong, i.e, LDA overbinds. In DFT, the electron density rather than the wave function is the basic variable [41].

$$E_{xc}^{LDA}[n] = \int n(r)\varepsilon_{xc}[n(r)]d\vec{r} \quad (2.30)$$

In LDA, there is no known formula to calculate the total energy of many electrons moving in an external potential using the density. Hohnberg and Kohn proved that there exist a universal functional of the density called, G[ρ] such that:

$$E[\rho_r] = \int V(r)\rho d^3r + \frac{1}{2} \int \frac{\rho_r \rho_{\acute{r}}}{\mid r - \acute{r} \mid} d^3r d^3\acute{r} + G[\rho] \qquad (2.31)$$

Where the first term on the right hand side is the energy due to external potential while the second term is the classical coulomb energy of the electron system. The main deficiency of LDA was the strong over binding with bond energies in error by about 1 eV. Due to this LDA is useless for most applications in condensed matter physics. On other hand, the problem was hardly visible in solid state physics where bonds are rarely broken, rearranged so that the errors canceled [39, 40]. Because of this, it is not applied for computational purpose in this work.

2.12.2 The Generalized Gradient Approximation (GGA)

A generalized-gradient approximation (GGA) is abstractly defined as any generic function of the local value of the density and its squared gradient that is constructed to approximate the exchange-correlation energy per particle [39, 40]. This functional (GGA) depends on the local electron density as the spatial variation of the electron density that is represented by density gradient. The idea behind this functional was to improve the approximation of LDA by considering not only the electron density, but also the local gradient of that density [39]. The GGA functional can be written as;

$$E_{xc}^{GGA}[n] = \int n(r)\varepsilon_{xc}[n(r)] \bigtriangledown_n d\vec{r} \qquad (2.32)$$

The $E_{xc}^{GGA}[n]$ is the exchange correlation energy per particle of an electron gas. The GGA gives better total energies. When a bond between two atoms is broken, the surface is increased. In GGA, this bond-breaking process is more favorable than in LDA and hence bond is weakened. Thus the GGA therapies the over binding error of the LDA. These gradient corrections greatly improved the bond energies and made density functional theory useful also for chemists. The most widely distributed GGA functional is the Perdew Burke-Ernzerhof (PBE) functional [39] and which is used in DFT to calculate electronic and structural properties in this study.

2.13   Plane wave basis sets and Pseudo-potentials

2.13.1   Plane wave basis set

In calculations of solid states or condensed matter, the DFT will be applied with plane wave basis sets. When dealing with a crystal which has atoms periodically arranged, the electrons are in a periodic potential $U(r)$, where $U(r + R) = U(r)$ and R is the Bravais lattice. As the Bloch theorem states that, a discrete plane-wave basis sets are used to expand the electronic wave function at each K-points. In principle, an infinite plane wave basis sets required to expand the electronic wave function. However, the coefficients C_i, $K + G$ for the plane waves with small kinetic energy, $\frac{\hbar}{2m}|K + G|^2$ are typically more important than those with large kinetic energy. Thus, plane wave basis sets can be truncated to include only plane wave that have kinetic energy less than some particular cut-off energy [42].

2.13.2   The Pseudo-potential

Pseudo-potential is a smooth effective potential that reproduces the nucleus plus core electrons on valence electrons [42, 43]. We want our pseudopotential and pseudo-orbitals to be as smooth as possible so that expansion into plane waves is convenient (i.e, the required kinetic energy cutoff is small). Pseudo-potentials have been introduced to avoid describing the core elements explicitly and to avoid the rapid oscillation of the wave function near the nucleus, which normally require either complicated or large base sets. Due to this, the fundamental idea of pseudo-potential is the replacement of one problem with another, that means its primary application in electronic structure is to replace the strong coulomb potential of the nucleus and the effects of tightly bound core electrons by an effective ionic potential acting on the valence electron [42]. The pseudo-potential approximation is motivated by the fact that the behavior of valence electrons in the bonding region primarily determines the electronic structure and the structural properties of many materials. In a pseudo-potential formulation, the effect of the core electrons and that of nuclear potential are combined to form an effective ionic pseudo-potential. The pseudo-potentials are commonly constructed, so that outside of a core region the valence pseudo wave functions match the corresponding states derived from all electron calculation, inside the region they are smooth functional. This formulation makes pseudo-potential calculations quite effi-

cient, since the core orbital do not need to be recomputed. The relaxation correction takes in to account the relaxation of the electron system up on the excitation of an electron. The orthogonalized plane waves(OPW) ϕ_k is defined $\phi_k = e^{ik.\vec{r}} + \sum_c bc\Psi_k^c \check{r}$ where $\Psi_k(r)$ is the core wave function the sum is over all core levels with Bloch wave vector $\vec{k}$ and we require that ϕ_k are orthogonal to every core level.

$\int d\vec{r}\phi_k^c(\vec{r})\phi_k = 0$

The starting point for pseudo potential calculations and analysis is the application of nearly free electron (NFE) theory to find the valence levels (ϕ_k^v). The pseudo-potential is the sum of the actual periodic potential and V_R.

where $V_R = \sum_c^{max}(E_k^v - E_c)(\int dr\Psi_k^{c^*}\Psi)\Psi_k^c$

$$H + V_R = -\frac{\hbar^2}{2m} + U + V_R \tag{2.33}$$

Where, $U + V_R = V$

U- is negative near ion cores while V_R - is always positive.

Hamann, Schluter and Chiang showed in 1979 how pseudo-potentials can be constructed in such a way that their scattering properties are identical to that of an atom to first order in energy. There is a vast amount of principles by which the pseudopotentials are constructed, but the main two requirements always have to be fulfilled:softness and transferability. Softness implies that the small amount of plane waves should be used for the core atomic region wave function. Transferability is the ability of the pseudopotential to be used in any environment: molecules, solids, in compounds with different elements, without any corrections in connection to the changes of environment. These first principles pseudo-potentials relieved the calculation from the restrictions of empirical parameters. Highly accurate calculations have become possible especially for semiconductors and simple metals. An approach by Zunger and Cohen towards first principles pseudo-potentials precedes other approaches.

Generally the D.Vanderbilt self-consistent ultra-soft pseudo-potentials have not only reduced the cut-off energy we need, they have also let us concentrate on the valence electron, reducing the number of states we need from Schr$\ddot{o}$dinger equation [43].

2.14 Periodic super cells

We would define the shape of the cell that is repeated periodically in space, the super cell, by lattice vector $\vec{a}_1, \vec{a}_2$ and $\vec{a}_3$. If we solve the Schrödinger equation for this periodic system, the solution must satisfy a fundamental property known as Bloch's theorem.

2.14.1 Bloch theorem

A Bloch function is the generalization of a plane wave for an electron in periodic potential. Bloch theorem states that in a periodic solid each electronic wave function can be written as the product of cell periodic and wave like part.

$$\Psi_k(\vec{r}) = e^{i.G\vec{r}} U_k(r) \tag{2.34}$$

Where $U_k(r)$ is the periodic potential in space with the same periodicity as the supper cell [19]. That is;

$$U_k(\vec{r} + n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3) = U_k(\vec{r}) \tag{2.35}$$

for any integers n_1, n_2 and n_3. This theorem is means that it is possible to try and solve the Schrödinger equation for each value of k independently. The cell-periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$v_k(r) = \sum_G C_{i,G e^{i\vec{G}.\vec{r}}} \tag{2.36}$$

where $C_{i,G}$ are expansion coefficients, the reciprocal lattice vectors G are defined by;

$$\vec{G}\vec{a} = 2\pi n \tag{2.37}$$

for all $\vec{a}$, where $\vec{a}$ is a lattice vector of the crystal and n is an integer. Therefore each electronic wave function can be written as a sum of plane waves,

$$\Psi_k(r) = \sum_G C_{i,k+G e^{i(\vec{k}+\vec{G}).\vec{r}}} \tag{2.38}$$

The electronic wave functions at each k-point can be expressed in terms of a discrete plane wave basis set. In principle the Fourier series is infinite. However, in practice we can not work with an infinite basis set, it has to be truncated or limited. The number of plane waves can be restricted by placing an upper boundary to the kinetic energy of the plane waves. This boundary is called energy cut-off (E_{cut})

2.14.2 Cut-off energy

The Cut-off energy limits the number of plane wave components. The minimum length scale depends on the elements in the system. Energy monotonically decreases to the ground state energy as E_{cut} increases [43, 44]. Our discussion of k-space would begin with Bloch's theorem, which tells us the solutions of the Schrödinger equations for a super cell that have the form;

$$\Psi_k(r) = e^{i\vec{k}.\vec{r}} \upsilon_k(r) \tag{2.39}$$

where $\upsilon_k(r)$ is periodic in space with the same periodicity as the super cell. It is now time to look at this part of the problem more carefully. The periodicity of $\upsilon_k(r)$ means that it can be expanded in terms of a special set of plane waves:

$$\Psi_k(r) = \sum_G C_{i,G} e^{[i(\vec{k}+\vec{G}).\vec{r}]} \tag{2.40}$$

where the summation is over all vectors defined by;

$$\vec{G} = n_1 \vec{b_1} + n_2 \vec{b_2} + n_3 \vec{b_3} \tag{2.41}$$

with integer values n_i. The set of vectors defined by $\vec{G}$ in reciprocal space are defined. So that for any real space lattice vector, combining equation 2.40 and 2.41 gives;

$$\Psi_k(r) = \sum_G C_{i,k+G} e^{[i(\vec{k}+\vec{G}).\vec{r}]} \tag{2.42}$$

According to this expression, evaluating the solution at even a single point in k-space involves a summation over an infinite number of possible values of G. This does not use for practical calculations. they are solutions with kinetic energy:

$$E = \frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2 \tag{2.43}$$

It is reasonable to expect that the solutions with lower energies are more physically important than solutions with very high energies. As a result, it is usual to truncate the infinite sum above to include only solutions with kinetic energies less than some value:

$$E_{cut} = \frac{\hbar^2}{2m} \vec{G}_{cut}^2 \tag{2.44}$$

The infinite sum then reduces to;

$$\Psi_k(r) = \sum_{|G+k|<G_{cut}} C_{G+k} e^{[i(\vec{k}+\vec{G}).\vec{r}]} \tag{2.45}$$

This expression includes slightly different numbers of terms for different values of k. The discussion above has introduced one more parameter that must be defined whenever a DFT calculation is performed, the cutoff energy (E_{cut}). In many ways, this parameter is easier to define than the k-points, as most packages will apply sensible default settings if no other information is supplied by the user. One very important thing is we always have to ensure the cut-off energy to give accurate results. This can be done by repeating the calculation with higher cut-off energies until the properties we are interested in have converged [43, 44].

2.14.3 K-points sampling

The solution that is used most widely was developed by Monk-horst pack in 1976 a regular grid in k-space. The symmetry of the cell may be used to reduce the number of k-points which are needed. Using these methods, one can obtain an accurate approximation for the electronic potential and the total energy of an insulators or semiconductor by calculating the electronic states at a very small number of k-points. The electronic potential and total energy are more difficult to calculate if the system is metallic because a dense set of k-points is required to define the Fermi surface precisely. The magnitude of any error in the total energy due to inadequacy of the k-points sampling can always be reduced by using a denser set of k-points. This means we need to make sure that we use enough k-points to get accurate results. The computational cost of performing a very dense sampling of k-space can be significantly reduced by using the k-point total energy. For smaller numbers of k points, however, the energy varies considerably as the number of k points is changed a clear indication that the number of k points is insufficient to give a well-converged result [43, 44].

3

Methodology

3.1 Methodology

In this thesis Density Functional Theory calculations were performed with the generalized gradient approximations of Perdew-Burke-Ernzerhof (GGA-PBE) exchange correlation functional, Vanderbilt ultra soft pseudo-potential and the plane wave basis sets are implemented in the Quantum ESPRESSO program package. Quantum ESPRESSO is an integrated module of computer codes for electronic structural calculations and materials modeling depending on the frame work of DFT, plane wave basis sets (PW) and pseudo-potentials to represent the electron-ion interaction. It is free, open-source package distributed under the terms of the GNU General Public Licence (GPL).

The most important input parameters in Quantum Espresso are number of atoms in unit cell,types of atoms in the periodic cell, bravais-lattice index, lattice parameters, the kinetic energy cut-off, k-points, atomic species and atomic position. The structure of the normal phase of CdTe was optimized until the total energy has been converged. Also several sets of Monk-Horst-Pack k-point grid samplings were tested. Plane waves are easy lattice-periodic basis functions but in general not possible to expand the crystal wave function in plane waves because of the strong oscillation near the cores (almost infinitely many plane waves) would be required. The pseudo-potential method avoids the problem. A very famous one is the ultrasoft pseudo-potential. The ultrasoft pseudopotential is constructed to be smoother, which has the advantage that an even smaller amount of plane waves are needed for the expansion, so that it predicts the exact ground state energy than the other. A popular implementation of the ultrasoft pseudopotential method is the open source plane-wave self-consistent-field (PWscf). The PWscf or the iterative approach to self consistency using different techniques in the frame work of the plane wave pseudopotential method with regards to the ultrasoft pseudopotentials are implemented. In this work, PWscf with GGA exchange correlation

functionals were used.

To solve the Kohn-Sham equations, we first specify the nuclear coordinates in order to obtain the nuclear potential $V_{ion}(r)$. Now an assumed value for electron density is used to determine approximate hartree and exchange and correlation potentials. By solving the Koh-Sham equations, we obtain the new wavefunctions Ψ_i, which can be used to construct a better estimate of density and the total potential. These iterations continue till the new density matches the old density within an acceptable tolerance. Once, we calculate the electron density in ground state, $n(r)$, it is possible to calculate the total energy E of the system, as it is functional of ground state electron density. The flow chart, in figure 3.1 illustrates a clear computational procedure for calculation.
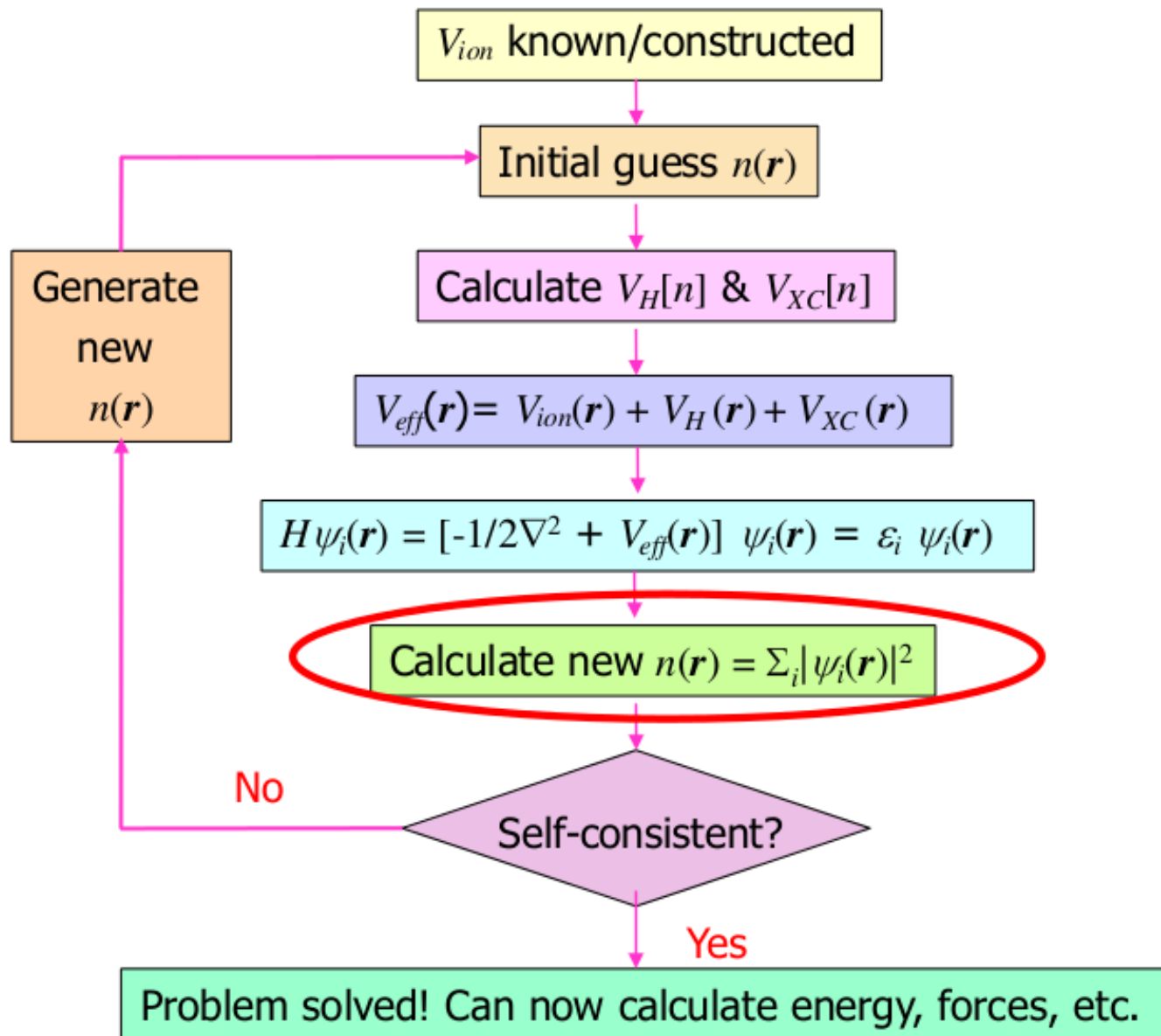
V_{ion} known/constructed

Initial guess $n(r)$

Calculate $V_H[n]$ & $V_{XC}[n]$

$V_{eff}(r) = V_{ion}(r) + V_H(r) + V_{XC}(r)$

$H\psi_i(r) = [-1/2\nabla^2 + V_{eff}(r)]\ \psi_i(r) = \varepsilon_i\ \psi_i(r)$

Calculate new $n(r) = \Sigma_i|\psi_i(r)|^2$

Generate new $n(r)$

Self-consistent?

No

Yes

Problem solved! Can now calculate energy, forces, etc.

Figure 3.1: Schematic flow diagram for finding the self consistent solutions for Kohn-Sham equations

4

Results and Discussion

Introduction

In this thesis first principle calculation was employed to calculate the electronic and structural properties of CdTe using Quantum espresso package. The plane wave self-consistent field (PWscf) code is implemented as our first principle energy code which uses ultra-soft pseudopotentials (US-PP) within density functional theory. The main features of pseudising process is to eliminate the effects of rapid oscillations of the core electrons near the nuclei or to replace the strong coulomb potential with the weaker one. Thus the ultra-soft pseudopotentials with Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange correlation functional were employed to calculate the electronic and structural properties of wurtzite and zincblende CdTe. The convergence issue was checked in two ways for both structure (wurtzite and zincblende). Firstly by varying cutoff energy from 50 Ry to 140 Ry for fixed Monk-Pack mesh grid (K-points) and lattice constants. Secondly, by varying K-point samplings (2 to 12) keeping cutoff energy and lattice parameters constant for wurtzite and zincblende structure.

The equilibrium lattice constant was calculated by fixing cutoff energy at 110 Ry and K-point at 7×7×7 for wurtzite CdTe and 110 Ry and 4×4×4 for zincblende CdTe. Finally the band structure and density of states of CdTe have been investigated based on DFT.

4.1   Total minimum energy of CdTe per atom with respect to energy cutoff

The total minimum energy of CdTe per atom with respect to cutoff energy was calculated for fixed values of K-Points and lattice constant. The calculation was done using different energy cutoff values from 50 Ry to 140 Ry.

Table 4.1: The computed results of total minimum energy with respect to energy cutoff for wurtzite and zincblende CdTe

Energy cutoffs (Ry)	Total minimum energy (Ry)	
	wurtzite CdTe	zincblende CdTe
50	-282.56440686	-141.28383555
60	-282.57268164	-141.28797450
70	-282.57659668	-141.28991597
80	-282.57691969	-141.28991597
90	-282.57843382	-141.29083741
100	-282.57992962	-141.29158398
110	-282.58023647	-141.29173426
120	-282.58033525	-141.29178420
130	-282.58074079	-141.29198791
140	-282.58113269	-141.29218312

4.1.1   Convergence test of total minimum energy of CdTe per atom with respect to cutoff energy

The convergence test of the total minimum energy of CdTe with respect to the plane wave cutoff energy was investigated. An increment of energy cutoff for wave function is made until the convergence is achieved. The total minimum energy was converged for wurtzite and zincblende at 110 Ry plane wave cutoff energy and the total ground state energy had its minimum at -282.58023647 Ry and -141.29173426 Ry respectively. The calculated results show that the total minimum energy for wurtzite and zincblende, is monotonically decreasing with increasing energy cutoffs for wave function as shown in Fig 4.1. The accuracy of the ground state energy depends on the number of basis functions. We can realize that when the number of basis functions approaches infinity, energy is close to the ground state energy.
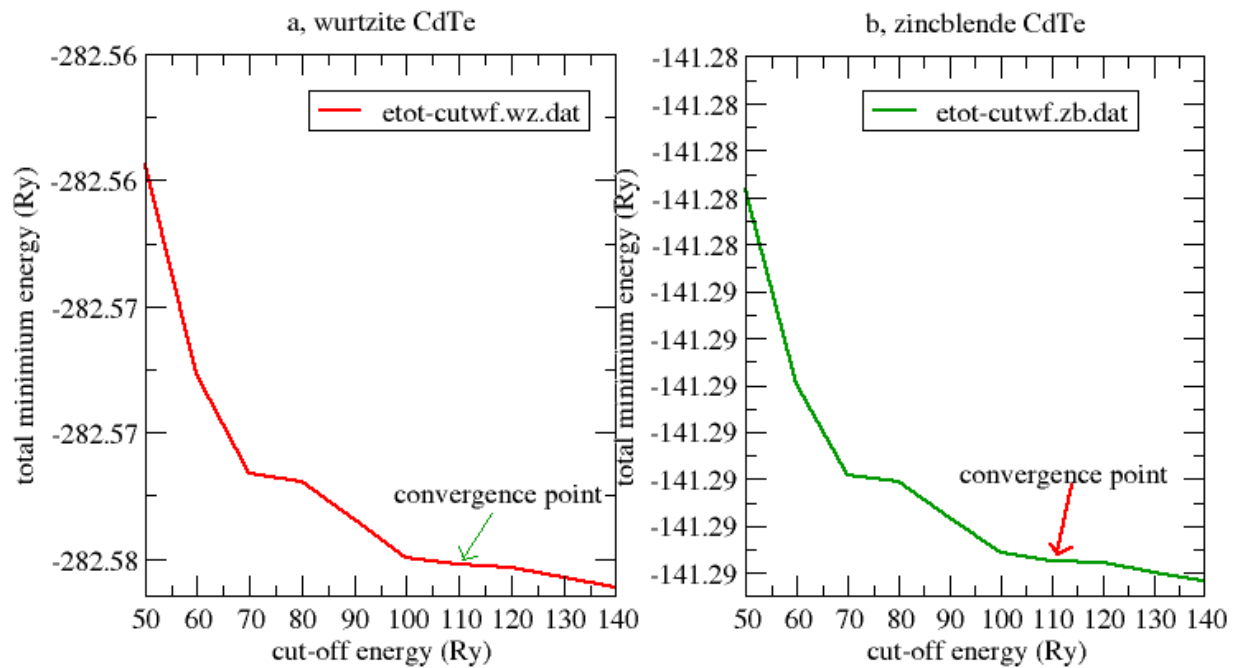
Figure 4.1: Total minimum energy of CdTe per atom with respect to cutoff energy

4.2   Total minimum energy of CdTe per atom with respect to K-point grids

In this case, the calculation was done using different k-point grids from 2×2×2 to 12×12×12 mesh grids. Here the other variables such as lattice constant and energy cut-off were kept fixed. The computed result is described in Table 4.2.

Table 4.2: The computed results of total minimum energy with respect to K-point grids for wurtzite and zincblende CdTe

k-points grid	Total minimum energy (Ry)	
	wurtzite CdTe	zincblende CdTe
2x2x2	-282.50364423	-141.27964292
3x3x3	-282.57268164	-141.28394088
4x4x4	-282.58552855	-141.28383555
5x5x5	-282.58848056	-141.28376582
6x6x6	-282.58928270	-141.28375938
7x7x7	-282.58954203	-141.28376020
8x8x8	-282.58962377	-141.28375706
9x9x9	-282.58965573	-141.28376067
10x10x10	-282.58966995	-141.28376036
11x11x11	-282.58967666	-141.28375866
12x12x12	-282.58968077	-141.28375906

4.2.1 Convergence test of total minimum energy of CdTe per atom with respect to K-points sampling

A convergence test of total minimum energy for k-point sampling was performed on CdTe. The total minimum energy of CdTe atom was calculated using various sets of k-points ranging from 2×2×2 to 12×12×12 for both wurtzite and zincblende structure. In each of these cases the plane wave kinetic energy cutoff 50 Ry was used. The total minimum energy of CdTe is calculated as a function of k-points grid size using PWscf code. For this calculations, the other variables (lattice constant, energy cutoff) are kept constant. Convergence of the total energy with respect to the discrete Brillouin zone sampling for wurtzite CdTe was achieved at 7×7×7 Monkhorst-Pack mesh grid. The total ground state energy has its minimum at -282.58954203 Ry. Convergence of the total energy with respect to the discrete Brillouin zone sampling for zincblende CdTe was achieved at 4×4×4 Monkhorst-Pack mesh grid. The total ground state energy has its minimum at -141.28383555Ry as shown in fig 4.2
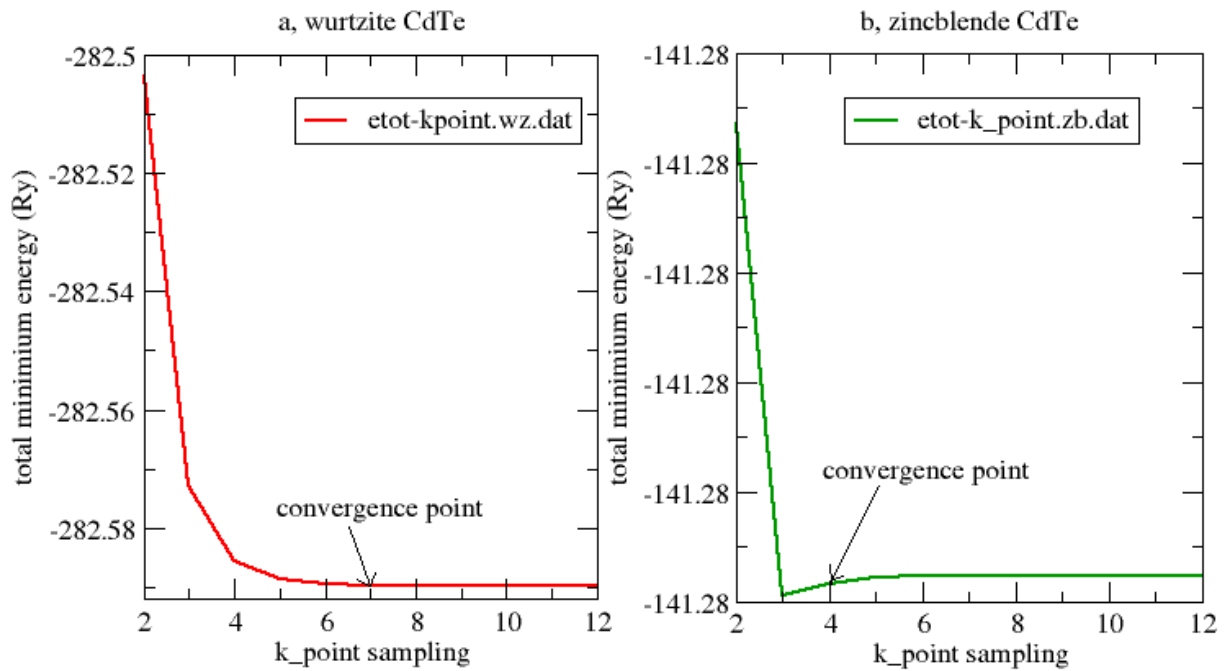
Figure 4.2: Total minimum energy of CdTe per atom with respect to K-point grids

4.3 The equilibrium lattice constant of CdTe

4.3.1 Structural optimization

To optimize the structural parameter of CdTe in wurtzite structure, 110 Ry cutoff energy and 7×7×7 k-point grid size were used. Similarly to optimize the structural parameter of CdTe in zincblende structure, 110 Ry cutoff energy and 4×4×4 k-point grid size were used from the above convergence test for both structure. To perform this calculation we varied the value of lattice constant of 'a' around experimental value fixing the other parameters constant. The lattice constant versus the total minimum energy of CdTe is shown in fig 4.3.

4.3.2 Convergence test of total minimum energy of CdTe versus lattice constant

To find the equilibrium lattice constant of wurtzite and zincblende CdTe we perform total energy calculation for a series of plausible parameters. In this calculation the energy cutoff and the k-point sampling for wurtzite structures are made fixed (110 Ry, 7×7×7 k-point) using the cutoff and k-point grid criteria for energy convergence. The numerical calculation shows that the equilibrium lattice constant for wurtzite CdTe, is a= 8.8515 bohrs, c=14.502bohrs (a=4.684 Å, c=7.684 Å). Similarly for zincblende struc-
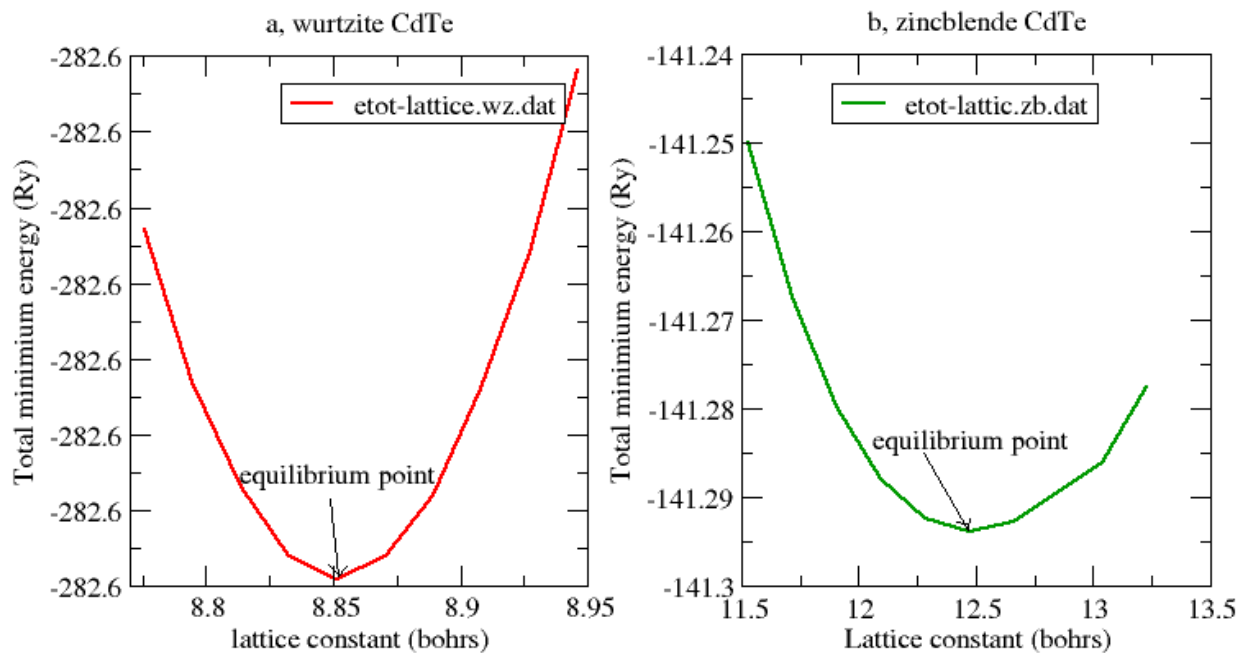
Figure 4.3: Total minimum energy of CdTe versus lattice constant

ture the energy cutoff and the k-point sampling are made fixed (110 Ry, 4×4×4 k-point) using the cutoff and k-point grid criteria for energy convergence. The numerical calculation shows that the equilibrium lattice constant for zincblende CdTe, is 12.4722 bohrs (6.60 Å). The calculated error for wurtzite structure is 2.49% and for zincblende structure is 1.82%. For both structure the result is in a good agreement with experimental value and the published results [16, 47].

4.4   Band structure of Cadmium Telluride

To determine the band structure the k-points are generated along high symmetry points using k-point path with the help of xcrysden software. The energy band structure of CdTe is presented in fig 4.4. Energy gap between occupied and unoccupied energy levels is among the ways that we can determine the difference between electrical properties of metals, semiconductors and insulators. The band gap has been calculated as the difference between the energies for the minimum of the conduction band and the maximum of the valence band. From the band structure of CdTe, we calculated the band gap energy, for wurtzite and zincblende CdTe the values are 0.595 eV and 0.605 eV respectively. For both structure the calculated results are in a good agreement with the published results [45, 46, 47]. The band gap obtained in this work is much smaller than the experimental value of 1.5 eV [45]. The calculated error for wurtzite structure is
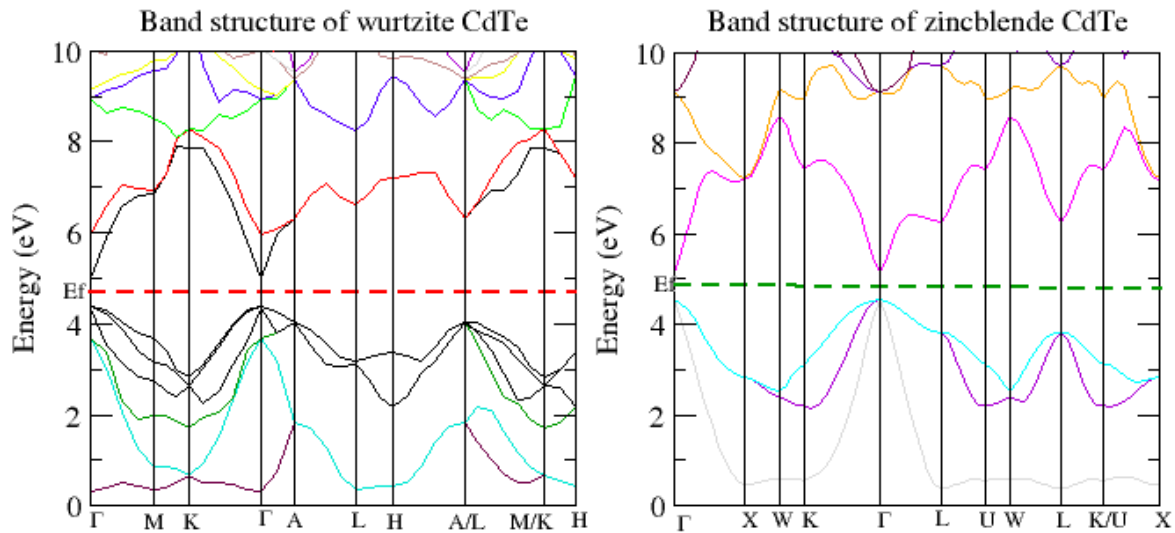
58.68% and for zincblende structure is 58 %.

Figure 4.4: Band structure of Cadmium Telluride

Table 4.3: Comparison of calculated structural and electronic properties of CdTe in this study to others

Results from	GGA Calculation			
	wz(LP in Å)	zb(LP in Å)	wz(BG in eV)	zb(BG in eV)
our work	A=4.684, C=7.684	6.60	0.595	0.605
Applying quantum ATK [36]		6.614		0.89
A validation of the ACBN0 functional. [45]	A=4.55, C= 7.451.	6.621	0.64	0.58
Relative stability of zb and wz in CdX(X=S,Se,Te) [16]			0.65	0.69
LDA/GGA calculations dependence on U [46]		6.630		0.58
Experiment [46]	A=4.57, C=7.674	6.482	1.5	1.5

4.5 Density of state of Cadmium Telluride

The main issue we can see from calculating the density of states (DOS) of Cadmium Telluride is the investigation of its electronic transport properties. The Fermi level was referenced at 4.699 eV and 4.722 eV for wurtzite and zincblende respectively In the fig 4.5. The calculated energy gap of CdTe between unoccupied (conduction) energy level and

occupied (valence) energy level is 0.58 eV for wurtzite and 0.79 eV for zincblende CdTe. So the calculated value shows us, the system (CdTe) is a semiconductor.
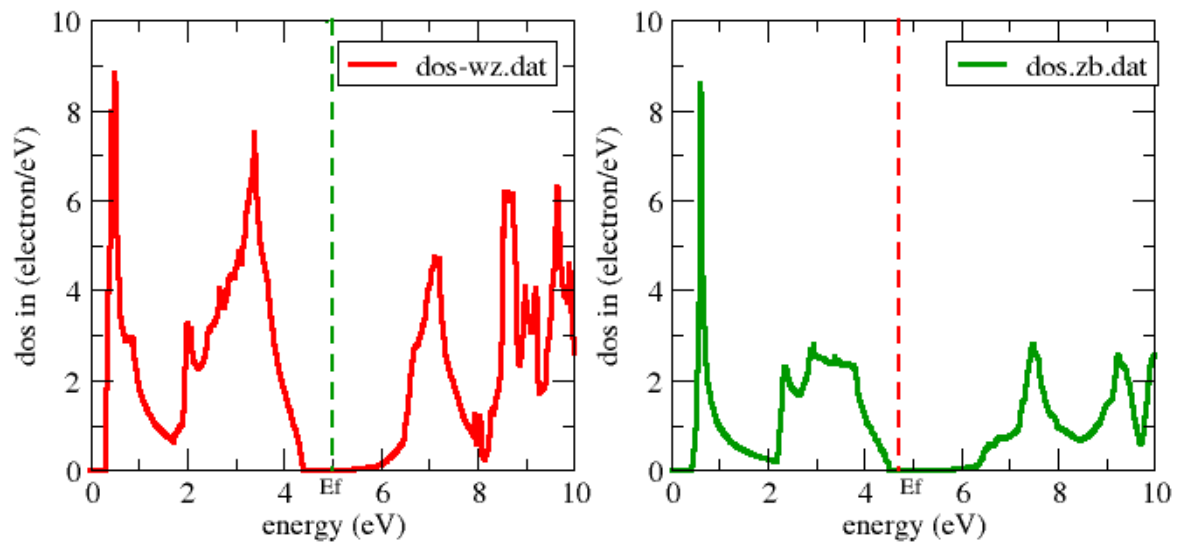

Figure 4.5: Density of states (DOS) of Cadmium Telluride.

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Conclusion

In this thesis first principle calculation (DFT) was used to investigate the electronic and structural properties of CdTe. The plane wave self consistent field (PWscf) and ultra-soft pseudopotentials with generalized gradient approximation (GGA) were implemented in Quantum Espresso package. All calculations have been carried out using Quantum Espresso package. The total minimum energy calculation was performed as a function of cutoff energy and k-point samplings. The total minimum energy of wurtzite CdTe per atom is -282.58023647 Ry with respect to energy cutoff and -282.58954203 Ry with respect to k-point grid size. The total minimum energy of zincblende CdTe per atom is -141.29173426 Ry with respect to energy cutoff and -141.28383555 Ry with respect to k-point grid size. The computational results show that the total minimum energy per atom is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-point sampling. The optimal lattice constant of CdTe was calculated using the above total energy convergence test by varying lattice parameter of 'a'. Our numerical calculation shows that the equilibrium lattice constant is (a = 4.684 Å and c = 7.684 Å, for wurtzite and a=6.60 Å for zincblende). The obtained result is overestimated as compared to the experimental result (a = 4.57 Å, c = 7.674 Å for wurtzite and a=6.482 Å for zincblende) due to the approximate nature of the applied DFT. The band structure was determined by generating k-points along high symmetry points using K-point path with the help of xcrysden software. The computed values of band structure and density of states of wurtzite Cadmium Telluride was 0.595 eV and 0.58 eV respectively. The computed values of band structure and density of states of zincblende Cadmium Telluride was 0.605 eV and 0.79 eV respectively.

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