

First Principle Calculation of Electronic Structure

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First Principle Calculation of Electronic Structure

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by

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Supervisor's Certificate

This is to certify that the work presented in the thesis entitled *First Principle Calculation of Electronic Structure* submitted by *Mahasweta Pandit*, Roll Number 414PH2049, is a record of reproduction of some existing research work carried out by her using TB-LMTO and Quantum Espresso under my supervision and guidance in partial fulfillment of the requirements of the degree of *Master of Science* in *Department of Physics and Astronomy*.

Biplab Ganguli

Dedication

To my loving family..

Signature

Acknowledgement

I would like to convey my gratitude to my mentor Prof. Biplab Ganguli for supporting me throughout the whole project work, for his motivation and immense knowledge. I also would like to express my special appreciation and sincere thanks to Prof. Sanjoy Datta for his aspiring guidance and advices.

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Abstract

The aim of this project was to study the superconducting properties of crystalline H_2S in extremely high pressure (approximately 150 GPa) using first principle calculation. The first principle calculation is a computational method to study the electronic structure of materials. In this present work, self-consistent calculation was carried out using TB-LMTO code and Quantum Espresso package to generate the band structure and density of states of the materials taken under consideration. Also all the crystal structures were recreated using the softwares XCrySDen and VESTA. Using XCrySDen the crystal structure can be formed directly using the self-consistent input file, the same that has been used for Quantum espresso. Whereas VESTA takes the space group and atomic positions as input. The materials that had been analysed were two semiconductors ,crystalline Silicon(Si), Germanium(Ge); two compounds, Cadmium telluride (CdTe), Mercury telluride (HgTe) and crystalline Hydrogen sulphide (H_2S) (phase III, ambient pressure). A comparison between the energy gaps that had been found using TB-LMTO and Quantum Espresso respectively was done.

Key words : First principle calculation, Density functional Theory, Kohn-Sham equation, TB-LMTO, Quantum Espresso, Pseudopotential.

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Chapter 1

Introduction

This thesis contains a detailed description about the implementation of **First Principle Calculation** in order to understand the electronic structure of few materials. For comprehending the electronic structure of the materials, it is required to study the behaviour of the electrons in it. Where classical mechanics fails, quantum mechanics provides the correct description of materials. For a bulk system one needs to take into account a large number of degrees of freedom to describe a huge number of electrons and atomic cores and has to solve the many-body Schrödinger equation for interacting electrons and nuclei in order to grasp knowledge about the electronic behaviour of materials. But most of the many-body quantum mechanical problems are either impossible or very difficult to solve. To make this difficult task tractable, the **Density Functional Theory** (DFT) comes into picture. For the last few years DFT has been the dominant and most successful method for the quantum mechanical simulation of periodic systems. It is an independent-particle approach which describes any property of a many-body system of interacting particles in terms of the functional of the ground state density $n_0(r)$, considering it to be the “Basic variable”. The existing proofs of these functionals were given by Hohenberg and Kohn and Mermin. The approximations like **local density approximation** (LDA) and **generalized-gradient approximation** (GGA) of functionals within the Kohn-Sham approach have been well utilized to analyse the electronic structures of different materials.

In this thesis, firstly the fundamentals of density functional theory have been studied to build base sufficient to impose DFT intelligently on real electronic structure problems and to expose potential pitfalls and possible avenues for future developments. Then, the detailed analysis of band structure calculation and density of state (DOS) calculation has been discussed for Silicon(*Si*), Germanium(*Ge*), Nickel(*Ni*), Cadmium Telluride (*CdTe*) and Mercury Telluride (*HgTe*). Finally, in order to study the superconducting behaviour of H_2S , the band structure has been analysed for crystallised Hydrogen sulfide (H_2S) in ambient pressure. The calculations have been done using ab initio method, **Tight binding linear muffin tin orbital method** (TB-LMTO) (Stuttgart code) and **Quantum Espresso** (QE). These softwares use self-consistent calculation to solve the Schrödinger equation for

many body systems.

Many Body Problem : A Quantum Description

Density functional theory deals with the many-body problem of bulk sample consisting of huge sea of electrons with ion cores. In this method, a functional of ground state particle density $n_0(r)$ is used to solve the Schrodinger equation.

Born- Oppenheimer Approximation

This brilliant approximation , proposed by J. R. Oppenheimer and Max Born (1927), was the first attempt of simplification of many-body problem by decoupling the electronic and ionic system. Depending upon the fact that the electrons, for being much smaller, move quite faster than the ions, the system consisting the ions can be assumed to be frozen at their current positions with respect to the electrons. And also the motion of the electrons is adiabatic. Such a system can be visualised by the Hamiltonian,

$$\begin{aligned}
 H &= K_e + K_i + V_{ii} + V_{ee} + V_{ie} \\
 &= -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2m_i} \sum_I \nabla_I^2 + \frac{1}{2} \sum_{I,I'}' \frac{e^2}{4\pi\epsilon_0} \frac{Z_I Z_{I'}}{|\mathbf{R}_I - \mathbf{R}_{I'}|} \\
 &\quad + \frac{1}{2} \sum_{j,k}' \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|} - \sum_{j,I} \frac{e^2}{4\pi\epsilon_0} \frac{Z_I}{|\mathbf{r}_j - \mathbf{R}_I|}
 \end{aligned} \tag{1.1}$$

To solve this Hamiltonian Born-Oppenheimer approximation is been taken into account and it is assumed that the position of ion varies very slightly with respect to the electrons and hence the wave function can be assumed to be,

$$\Phi_n = \chi_I(\mathbf{R}) \psi_i(\mathbf{r}, \mathbf{R}) \tag{1.2}$$

And the Schrödinger equation for the electron with a background of frozen atom core will be,

$$(K_e + V_{ee} + V_{ie}) \psi_i(\mathbf{r}, \mathbf{R}) = \epsilon_i \psi_i(\mathbf{r}, \mathbf{R}) \tag{1.3}$$

The Schrödinger equation for the whole system will be,

$$H \Phi_n = E \Phi_n \tag{1.4}$$

By substituting the suitable values and simplifying, one can get,

$$\begin{aligned} \psi_i(\mathbf{r}, \mathbf{R}) \left(-\frac{\hbar}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar}{2m_i} \sum_I \nabla_I^2 + V_{ii} + \varepsilon_i \right) \chi_I(\mathbf{R}) \\ - \frac{\hbar}{2m_i} \sum_I \left(2 \cdot \frac{\partial \psi_i(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_I} \cdot \frac{\partial \chi_I(\mathbf{R})}{\partial \mathbf{R}_I} + \frac{\partial^2 \psi_i(\mathbf{r}, \mathbf{R})}{\partial \mathbf{R}_I^2} \chi_I(\mathbf{R}) \right) = E\Phi \end{aligned} \quad (1.5)$$

And by further simplification and by neglecting the second term which doesn't contribute significantly in the energy eigenvalue one can derive a Schrödinger like equation for the ion core only. But in case of metallic systems where there is no energy gap between the valance band and conduction band, the ionic motion

$$\left(-\frac{\hbar}{2m_i} \sum_I \nabla_I^2 + V_{ii} + \varepsilon_i \right) \chi_I(\mathbf{R}) = E\chi_I(\mathbf{R}) \quad (1.6)$$

Therefore, one can now solve two independent equations for the electrons and ion cores respectively. Hence generalizing the wave function for n sites of a bulk system,

$$\Phi = \sum_n \Phi_n = \sum_n \chi_I^n(\mathbf{R}) \psi_i^n(\mathbf{r}, \mathbf{R}) \quad (1.7)$$

The Born-Oppenheimer approximation [1] was proven to be a successful approach for semiconductors and insulators and their experimentally found energy gaps fits well onto this approximation. But in case of metallic systems which has no gap between the valance and conduction band, the ionic motion sometimes causes transitions of vanishing energy causing the Born-Oppenheimer approximation to break down.

Hartree - Fock Method

Hartree-Fock method [2] is a standard approximation to solve the many-body Hamiltonian. It takes into account of the Pauli's exclusion principle by considering electrons as fermions and makes the wave function to be antisymmetric. It also takes an average of the electrostatic interactions to make it more simple. The method was first proposed by Fock in 1930.

The anti-symmetric wave function was provided by the famous “**Slater determinant**”

proposed by Slater in 1929. The wave function is given by for total N number of electrons,

$$\psi(\mathbf{r}_1, \dots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \cdots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix} \quad (1.8)$$

$$= \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \psi_1(x_1) \dots \psi_N(x_N) \quad (1.9)$$

Each element of the Slater determinant is linearly independent single particle spin orbitals and P is the permutation operator where p is the number of exchange corresponding to the permutation. This is called the “**Spin restricted Hartree-Fock Approximation**”.

Therefore, the total energy will be,

$$\begin{aligned} E &= \langle \psi | H | \psi \rangle \\ &= \frac{1}{\sqrt{N!}} \sum_P \int \psi^* H (-1)^P P \psi_1(x_1) \dots \psi_N(x_N) d\tau \\ &= \frac{1}{\sqrt{N!}} \sum_P P \int \psi^* H (-1)^P \psi_1(x_1) \dots \psi_N(x_N) d\tau \end{aligned} \quad (1.10)$$

After integrating, the term on which the permutation operator will operate is independent of any x_i and hence the result will be nothing but $N!$ times the integral. Therefore,

$$\begin{aligned} E &= \sqrt{N!} \int (P^{-1} \psi^*) H \psi_1(x_1) \dots \psi_N(x_N) d\tau \\ &= \sqrt{N!} \frac{1}{\sqrt{N!}} \sum_P \int (-1)^{P-1} P \psi_1^*(x_1) \dots \psi_N^*(x_N) \left(-\frac{\hbar}{2m_e} \sum_I \nabla_i^2 \right. \\ &\quad \left. + \frac{1}{2} \sum_{i,j}' \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{1}{4\pi\epsilon_0} \frac{e^2 \mathcal{Z}_I}{|\mathbf{r}_i - \mathbf{R}_I|} \right) \psi_1(x_1) \dots \psi_N(x_N) d\tau \end{aligned} \quad (1.11)$$

Now if one considers the method of lagrange multiplier,

$$\mathcal{E}_i \psi(\mathbf{r}) = \left[\left(-\frac{\hbar}{2m_e} \sum_I \nabla_i^2 + V_I(\mathbf{r}) + V_H(\mathbf{r}) \right) \psi_i(\mathbf{r}) - \int \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \psi_j^*(\mathbf{r}') d^3 r' \right] \quad (1.12)$$

And finally the total energy will be,

$$\begin{aligned} E &= \sum_i \mathcal{E}_i - \frac{1}{2} \sum_{i,j} \int \int \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\psi_j|^2 |\psi_i|^2 d^3 r d^3 r' \\ &\quad + \frac{1}{2} \sum_{i,j} \int \int \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r} - \mathbf{r}'|} |\psi_j|^2 |\psi_i|^2 d^3 r d^3 r' \end{aligned} \quad (1.13)$$

Where, $\psi_i = \psi_i(\mathbf{r}_i)a(\sigma_i)$ if $\sigma_i = 1$ and,

$$\psi_i = \psi_i(\mathbf{r}_i)b(\sigma_i) \quad \text{if } \sigma_i = -1$$

and $a(1) = 1, a(-1) = 0; b(1) = 0, b(-1) = 1$.

$a(\sigma)$ and $b(\sigma)$ are the orthonormal functions corresponding to up spin and down spin. And the wavefunction has been reproduced as a product of two parts, namely spatial ((\mathbf{r}) part) and spin (σ).

By introducing Hartree-Fock method, improvement was introduced over the conventional energy value by including the exchange correlation energy which involves the energy caused by the antisymmetric wave function. H-F method is basically a mean-field theory where the many-body system is converted to one electron system assuming that they move in an average field generated by other elements in the system. It determines the mean field in such a way so that the Coulomb correlation can be ignored and portrays the problem in such a manner as if the electrons are ignoring each other. It also includes the parallel spin exchange correlation which is actually reduced by the Coulomb correlations. However, the H-F theory overestimates the importance of the exchange correlation causing a totally incorrect behaviour for the electrons in solids where it is successful enough in case of compact systems.

Chapter 2

Density Functional Theory

Density functional theory (DFT) is the key step towards the development of independent-particle methods for solving many-body problems. It includes tools like the local density approximation (LDA) and followed by an approximation providing improved structural and magnetic properties, the generalized-gradient approximations (GGAs) which turned out to be very successful for studying the electronic structures of materials. The theoretical foundation for this promising approach was originated by P.Hohenberg and W. Kohn in 1964 by assigning density as a ‘basic variable’ and deriving all other features of the material as *functionals* of its ground state electron density.

Thomas-Fermi-Dirac Approximation

Thomas-Fermi-Dirac approximation [1] is one of the earliest schemes for solving many-body problems, proposed by Thomas and Fermi in 1927 and further extended by Dirac in 1930 by including the exchange and inter-electron correlation and local approximation for exchange. The basic idea of describing electronic structures in terms of density where the kinetic energy of a many-body system is assumed to be an explicit functional of density. The approximation is not accurate enough for present day illustration.

The approximation is initially implemented for electron gas with uniform density. The energy functional for electrons travelling in an externally applied potential $V_0(\mathbf{r})$ is given by,

$$E_{TF}[n] = K + V_{Ii} + V_{ii} \quad (2.1)$$

$$\begin{aligned} &= C_1 \int n(\mathbf{r})^{\frac{5}{3}} d^3r + \int V_0(\mathbf{r}) n(\mathbf{r}) d^3r \\ &\quad + C_2 \int n(\mathbf{r}) d^3r + \frac{1}{2} \int \int \frac{e^2}{4\pi\epsilon_0} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' \end{aligned} \quad (2.2)$$

where, total number of electrons in volume Ω is given by,

$$N = 2 \frac{4}{3} \frac{k_F^3 \Omega}{8\pi^2} \quad (2.3)$$

and,

$$C_1 = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} = 2.871 a.u. \quad (2.4)$$

$$C_2 = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}} \quad (2.5)$$

The last term is the electrostatic Hartree energy. By minimizing the the functional $E[n]$ one can find the ground state energy for all possible $n(\mathbf{r})$ and the constrain will be,

$$N = \int d^3r n(\mathbf{r}) \quad (2.6)$$

And using the Lagrange-multiplier method, one can derive an unconstrained minimization of the functional,

$$\mathcal{E}_{TF}[n] = \mathcal{E}_{TF}[n] - \lambda \left(\int d^3r n(\mathbf{r}) - N \right) \quad (2.7)$$

where, λ , the Lagrange multiplier, is nothing but the Fermi energy or chemical potential. Due to a very small variation of the density $\delta n(\mathbf{r})$,

$$\begin{aligned} \int d^3r \left(\mathcal{E}_{TF}[n(\mathbf{r}) + \delta n(\mathbf{r})] - \mathcal{E}_{TF}[n(\mathbf{r})] \right) &= 0 \\ \rightarrow \int d^3r \left(\frac{5}{3} C_1 n(\mathbf{r})^{\frac{2}{3}} + V(r) - \lambda \right) \delta n(\mathbf{r}) &= 0 \end{aligned} \quad (2.8)$$

where, $V(r) = V_0(\mathbf{r}) + V_H(r) + V(r)$ is the total effective potential. And, then,

$$\frac{1}{2}(3\pi^2)^{\frac{2}{3}} n(\mathbf{r})^{\frac{2}{3}} + V(\mathbf{r}) - \lambda = 0 \quad (2.9)$$

This is a desired correspondence between electron density and externally applied potential. The main attraction to this relation is that it is much simpler to solve this equation than a full many-body Schrödinger equation and hence highly useful description in matter.

Hohenberg-Kohn Theorems

The theorems of Hohenberg-Kohn played an important role to formulate the density functional theory of many-body systems.

An interacting system in an external potential can be visualized using DFT with the help of the two famous theorems provided by Hohenberg and Kohn in 1964. These theorems are the keys to replace the interacting many-body system with a relatively easy to solve supplementary system. The ansatz was based upon the fact that the ground state density of the many-body problem is equal to the ground state density of the chosen non-interacting system. Hence equations independent of individual particles can be constructed for an system which

is exactly solvable as well as non-interacting. And hence by solving those equations with an exchange-correlation density functional, the ground state density and energy of the actual system can be calculated.

Theorem I:

For an interacting system in an external potential $V_0(\mathbf{r})$, it is possible to determine it uniquely, other than a constant, with the help of the ground state particle density $n_0(\mathbf{r})$.

• **Corollary:** The Hamiltonian for the system can be fully determined, except for a constant shift in the energy energy. Hence it can be concluded that the many-body wave functions for every states are determined as well and hence the properties of the system can be predicted from the calculated ground state density $n_0(\mathbf{r})$.

Proof:

Assuming that there are two dissimilar potentials $v_a(\mathbf{r})$ and $v_b(\mathbf{r})$ with the ground states ψ and ψ' respectively which produce same particle density $n(\mathbf{r})$. Now, the ground state is non-degenerate because,

$$v_a(\mathbf{r}) \neq v_b(\mathbf{r})$$

Therefore,

$$\psi \neq \psi'$$

If the Hamiltonian and the ground state energies corresponding to ψ and ψ' are H and H' and E and E' respectively then, from the variational principle, it can be written,

$$E = \langle \psi | H | \psi \rangle \leq \langle \psi' | H | \psi' \rangle \quad (2.10)$$

and similarly,

$$E' = \langle \psi' | H' | \psi' \rangle \leq \langle \psi | H' | \psi \rangle \quad (2.11)$$

$$\begin{aligned} \langle \psi' | H | \psi' \rangle &= \langle \psi' | (H - H') + H' | \psi' \rangle \\ &= \langle \psi' | H' | \psi' \rangle + \langle \psi' | V_a - V_b | \psi' \rangle \\ &= E' + \int \left(v_a(\mathbf{r}) - v_b(\mathbf{r}) \right) n_0(\mathbf{r}) d^3r \\ &\geq E \end{aligned}$$

Similarly, for the term $\langle \psi | H' | \psi \rangle$, one can get,

$$E' \leq E + \int \left(v_b(\mathbf{r}) - v_a(\mathbf{r}) \right) n_0(\mathbf{r}) d^3r$$

And, by merging one can get,

$$E + E' \leq E + E'$$

Which is a contradictory conclusion. Hence, the electron density $n(\mathbf{r})$ corresponding to the ground state of the system with respect to an external potential $v(\mathbf{r})$ cannot be reproduced by the $n_0(\mathbf{r})$ with respect to a dissimilar potential $v'(\mathbf{r})$ and hence a corollary can be drawn that for a uniquely determined $n_0(\mathbf{r})$ is produced from a uniquely determines the non-degenerate ground-state wave function.

Theorem II:

The universal functional for the total energy of an interacting system in an external potential $V_0(\mathbf{r})$, $E[n]$ can be defined in terms of the particle density $n(\mathbf{r})$ and its ground state energy which is the global minimum value for the functional and also for the particle density $n(\mathbf{r})$ which will minimize the functional up to its ground state which is nothing but the ground state particle density $n_0(\mathbf{r})$.

• **Corollary:** $E[n]$ itself is adequate for determining the ground state energy exactly as well as the density for the system. And the excited states of can be determined by other means and thermal equilibrium properties, e.g., specific heat, can be directly determined by the free energy functional.

Proof:

Let the ground state energy of the system be $E_0[n(\mathbf{r})]$. Then,

$$\begin{aligned} E_0[n(\mathbf{r})] &= \langle \psi | V | \psi \rangle + \langle \psi | K + V_{EE} | \psi \rangle \\ &= \int v(\mathbf{r})n(\mathbf{r})d^3r + \mathcal{F}[n(\mathbf{r})] \end{aligned} \quad (2.12)$$

where, $\mathcal{F}[n(\mathbf{r})]$ is a functional of $n(\mathbf{r})$.

Considering a many-electron system with N electron in a constant external potential. Hence, the energy functional for the density $n_1(\mathbf{r})$,

$$E_0[n'(\mathbf{r})] = \int v(\mathbf{r})n_1(\mathbf{r})d^3r + \mathcal{F}[n_1(\mathbf{r})] \quad (2.13)$$

The energy functional must satisfy the inequality given by,

$$E_0[n(\mathbf{r})] > E_0[n_1(\mathbf{r})] \quad (2.14)$$

$n(\mathbf{r})$ is the ground state electron density and hence the functional $E[n]$ for the total energy will be equal to the zero point energy of the system.

$\mathcal{F}[n(\mathbf{r})]$ is independent of the external potential and can be divided into three parts, given by,

$$\mathcal{F}[n(\mathbf{r})] = \mathcal{T}[n(\mathbf{r})] + \frac{e^2}{2} \iint \frac{1}{4\pi\epsilon_0} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \mathcal{E}_{xc}[n(\mathbf{r})] \quad (2.15)$$

$\mathcal{T}[n(\mathbf{r})]$ is the ground state kinetic energy functional of the non-interacting electron gas of density $n(\mathbf{r})$.

$\mathcal{E}_{xc}[n(\mathbf{r})]$ is the exchange-correlation energy which contains a part of the total kinetic energy.

Importances of Hohenberg and Kohn theorems

Hohenberg and Kohn theorems claimed that there is a one-to-one matching between $n(\mathbf{r})$ and $V_0(\mathbf{r})$ and also applied few constraints under certain circumstances which is quite successful for our points in practice.

The theorems are proven to be very useful for first-principles or “ab initio” calculations to study the properties of matter. Approximations like LDA or GGAs are widely used to study IV and II-V semiconductors and *sp*-bonded metals and also insulators and cases where electrons have stronger effects of correlations (transition metals).

Kohn-Sham Equations

The Kohn-Sham supplementary system [2] for the ground state corresponding to a many-body system of interacting particles is assumed to be a minimization problem regarding either particle density $n(\mathbf{r}, \sigma)$ or the external potential $V_0(\mathbf{r})$. Now ,

$$E[n(\mathbf{r})] = \int v(\mathbf{r})n(\mathbf{r})d^3r + \mathcal{T}[n(\mathbf{r})] + \frac{e^2}{2} \iint \frac{1}{4\pi\epsilon_0} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \mathcal{E}_{xc}[n(\mathbf{r})]$$

minimizing under the constrain,

$$\int n(\mathbf{r})d^3r = N$$

using the Lagrange multiplier method,

$$\begin{aligned} & \frac{\delta E[n]}{\delta n(\mathbf{r})} - \lambda = 0 \\ \rightarrow & \frac{\delta \mathcal{T}[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + \frac{e^2}{2} \int \frac{1}{4\pi\epsilon_0} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \frac{\delta \mathcal{E}_{xc}[n]}{\delta n(\mathbf{r})} - \lambda = 0 \\ \rightarrow & \frac{\delta \mathcal{T}[n]}{\delta n(\mathbf{r})} + v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) - \lambda = 0 \end{aligned} \quad (2.16)$$

Where,

$$v_H(\mathbf{r}) = \frac{e^2}{2} \int \frac{1}{4\pi\epsilon_0} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r'$$

and

$$v_{xc}(\mathbf{r}) = \frac{\delta \mathcal{E}_{xc}[n]}{\delta n(\mathbf{r})}$$

The major problem behind the complexity of solving this problem is that $T[n]$ and $v_{xc}(\mathbf{r})$ are unknown quantities. To resolve this problem one needs to take the Thomas-Fermi equation into account and neglect $v_{xc}(\mathbf{r})$. According to Thomas-Fermi theory,

$$\mathcal{T}[n] = C_1 \int n(\mathbf{r})^{\frac{5}{3}} d^3r \quad (2.17)$$

And by nullifying $E_{xc}[n]$, the final equation becomes identical with the Hartree's expression. Therefore, the equation can be solved by using the trial solution,

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2 \quad (2.18)$$

Therefore,

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + v(\mathbf{r}) + v_H(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \mathcal{E}_i \psi_i(\mathbf{r}) \quad (2.19)$$

And if, $v_{xc}(\mathbf{r})$ is not negligible then,

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + v_H(\mathbf{r}) + v_{xc}(\mathbf{r}) \quad (2.20)$$

and the Hamiltonian will be,

$$H = -\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \quad (2.21)$$

and corresponding Schroedinger equation will be,

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \mathcal{E}_i \psi_i(\mathbf{r}) \quad (2.22)$$

This Hamiltonian is famously known as the “**Kohn-Sham Hamiltonian**” and the equation is known as the “**Kohn-Sham Equation**”.

The Kohn-Sham Equation is required to be solved in a self-consistent way. One trial

solution is required to be taken into account which is referred to be an orbital which is nothing but mapping the interacting many-body problem onto an supplementary system of independent particles. It is also assumed that the ground state energy is same for both the interacting and non-interacting system but in case of the supplementary system, the particles are moving in an effective potential. Unlike, the Hartree-Fock method, this equation includes the exchange correlation term which is an unknown quantity and several approximations can be done to determine this quantity.

Hence, the energy of the i^{th} particle is given by,

$$\mathcal{E}_i = \int \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \right) \psi_i(\mathbf{r}) d^3r \quad (2.23)$$

and ,

$$\begin{aligned} \sum_i \mathcal{E}_i &= \sum_i \int \psi_i^*(\mathbf{r}) \left(-\frac{\hbar^2}{2m_e} \nabla^2 \right) \psi_i(\mathbf{r}) d^3r + \sum_i \int \psi_i^*(\mathbf{r}) v(\mathbf{r}) \psi_i(\mathbf{r}) d^3r \\ &\quad + \int \frac{e^2}{4\pi\epsilon_0} \frac{\psi_i^* \psi_i n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \int v_{xc}(\mathbf{r}) \psi_i^* \psi_i d^3r \end{aligned} \quad (2.24)$$

Therefore, the total energy of the system is,

$$E = \sum_i \mathcal{E}_i - + \frac{e^2}{2} \int \int \frac{1}{4\pi\epsilon_0} \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r d^3r' + \mathcal{E}_{xc}[n(\mathbf{r})] - \int v_{xc}(\mathbf{r}) n(\mathbf{r}) d^3r \quad (2.25)$$

The Kohn-Sham approach readily separates the kinetic energy which is independent of particles as well as the long-range Hartree terms and exchange-correlation functional $\mathcal{E}_{xc}[n]$ which is predicted to be a local or closely local functional of the density.

Local Density Approximation

To predict the exact form of the exchange-correlation term, a lots of approximations have been adopted. Initially an approximation, carried out by Kohn and Sham in 1965, is taken into account, namely **Local Density Approximation** (LDA). LDA was successful enough in case of electronic structures of atoms, molecules and solids.

LDA assumes that the electron density is uniform locally and varies very slowly in space. Hence, in an elementary volume, the electron gas can be considered to be of uniform density. Considering $\varepsilon_{xc}(n)$ to be the exchange-correlation energy per particle, therefore the total

exchange-correlation energy for the whole system is given by,

$$E_{xc}[n] = \int \varepsilon_{xc}[n(\mathbf{r})]n(\mathbf{r})d^3r \quad (2.26)$$

Now,

$$v_{xc}(\mathbf{r}) = \frac{\delta \mathcal{E}_{xc}[n]}{\delta n(\mathbf{r})} = \frac{d}{dn(\mathbf{r})}(\varepsilon_{xc}[n(\mathbf{r})]n(\mathbf{r})) = \lambda_{xc}(n(\mathbf{r})) \quad (2.27)$$

One proposed value (in atomic units) for the exchange-correlation energy per particle (Gunnarsson and Lundqvist (1976)) is given by,

$$\varepsilon_{xc}[n(\mathbf{r})] = -\frac{0.458}{r_s} - 0.0666 \left[\frac{1}{2} \left((1+x^3) \ln(1+x^{-1}) - x^2 + \frac{x}{2} - \frac{1}{3} \right) \right] \left(\frac{r_s}{11.4} \right) \quad (2.28)$$

where, r_s is the radius of the spherical volume that is associated with the point under consideration. This value fits well for most of the materials' electronic structure that have been taken into consideration.

• Conclusion

Hence it can be concluded that LDA is a good approximation if the electron density is varying slowly in space. For metals LDA is not a good approximation as electron density varies very rapidly. Regarding to the single-particle exchange correlation energy, the physical meaning is that for infinite systems, the highest occupied level is proven to be the chemical potential and hence it can be concluded that the chemical potential itself is the Fermi energy level. And the dissimilarity between the ground state energies of the interacting systems consisting of N and $(N+m)$ number of particles where, $m \ll N$,

$$\begin{aligned} \delta N &= \sum_{i=N+1}^{N+m} |\psi_i(\mathbf{r})|^2 \\ \rightarrow \delta E &= \mathcal{J}[n(\mathbf{r}) + \delta n(\mathbf{r})] - \mathcal{J}[n(\mathbf{r})] + \int \delta n(\mathbf{r}) \left(v(\mathbf{r}) \right. \\ &\quad \left. + \int \frac{e^2}{4\pi\epsilon_0} \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3r' + \frac{\delta \mathcal{E}_{ec}}{\delta n(\mathbf{r}')} \right) d^3r \\ &= \sum_{i=N+1}^{N+m} \varepsilon_i = m\varepsilon_F \end{aligned}$$

Also, $\int \delta n(\mathbf{r}) d^3r = m$, therefore,

$$\begin{aligned}\delta E[n(\mathbf{r})] &= \varepsilon_F \int \delta n(\mathbf{r}) \\ \frac{\delta E[n(\mathbf{r})]}{\delta n(\mathbf{r})} &= \varepsilon_F = \nu\end{aligned}$$

Generalized Gradient Approximations (GGAs)

As the electron density in the system that has been considered while formulating LDA is varying very slowly in space, then it can be further generalized in terms of its gradient in Taylor series. This is called “Gradient expansion approximation” (GEA), proposed by Herman et al at 1969. But this approximation broke down heavily as well as failed to satisfy certain rules, because of the large value of the gradients in case of real systems. But later on, it had been realized that that kind of expansion is not required. Rather the exchange-correlation can be written in terms of many functions,

$$\mathcal{E}_{xc} = \int f(n(\mathbf{r}, \uparrow), n(\mathbf{r}, \downarrow), \nabla n(\mathbf{r}, \uparrow), \nabla n(\mathbf{r}, \downarrow)) d^3r \quad (2.29)$$

This is called “Generalized Gradient Approximation” which often deals with structural and magnetic properties of materials with great accuracy. Many function have been implemented so far and worked successfully. But it fails to produce correct results for ferroelectric materials and gives incorrect band gap for semiconductors.

Chapter 3

Methods for First Principle Calculation

Several methods have been approached so far in order to solve the Kohn-Sham equation and study the band structure of various materials, e.g., plane wave expansion (PW) method, tight-binding method, orthogonalized plane wave (OPW) method and pseudopotential method.

Plane Wave Expansion Method

Plane wave expansion method [1] is a computational technique in which is a generalization of **nearly free electron (NFE) model**. In this method it is assumed that the effective potential, $v_{eff}(\mathbf{r})$ is very weak. Hence perturbation theory can be implemented to find the solution of the Kohn-Sham equation.

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + v_{eff}(\mathbf{r}) = H_0 + v_{eff}(\mathbf{r}) \quad (3.1)$$

The eigenvectors for the unperturbed Hamiltonian is given by,

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{\Omega}} \exp(i\mathbf{k}\cdot\mathbf{r}) \quad (3.2)$$

and the corresponding energy eigenvalue,

$$\varepsilon_{\mathbf{k},\mathbf{r}}^0 = \frac{\hbar^2 k^2}{2m_e} \quad (3.3)$$

where, Ω is the volume of the material. And according to the perturbation theory, the energy eigen value is corrected to,

$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}}^0 + \langle \mathbf{k} | v_{eff} | \mathbf{k} \rangle + \sum' \frac{|\langle \mathbf{k} | v_{eff} | \mathbf{k}' \rangle|^2}{\varepsilon_{\mathbf{k}}^0 - \varepsilon_{\mathbf{k}'}^0} \quad (3.4)$$

and

$$\Psi_{\mathbf{k}}(\mathbf{r}) = |\mathbf{k}\rangle + \sum' \frac{\langle \mathbf{k} | v_{eff} | \mathbf{k}' \rangle}{\varepsilon_{\mathbf{k}}^0 - \varepsilon_{\mathbf{k}'}^0} |\mathbf{k}'\rangle \quad (3.5)$$

where, H_0 is the unperturbed Hamiltonian which is exactly solvable and the rest is the perturbation. v_{eff} is periodic in \mathbf{r} and is assumed to be,

$$v_{eff}(\mathbf{r}) = \sum_{\mathcal{G}} v(\mathcal{G}) \exp(i\mathcal{G} \cdot \mathbf{r}) \quad (3.6)$$

\mathbf{G} is the reciprocal lattice vector. Since the effective potential is real,

$$v(\mathcal{G})^* = v(-\mathcal{G})$$

In plane wave expansion method, many plane waves are summed up in a linear combination to produce the final expression of the wave function which follows the Bloch's theorem,

$$\Psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathcal{G}} C_{\mathbf{k}-\mathcal{G}} |\mathbf{k} - \mathcal{G}\rangle \quad (3.7)$$

Kohn-Sham equation,

$$\begin{aligned} & \left(-\frac{\hbar^2}{2m_e} \nabla^2 + v_{eff}(\mathbf{r}) \right) \Psi_{\mathbf{k}}(\mathbf{r}) = \varepsilon_{\mathbf{k}} \Psi_{\mathbf{k}}(\mathbf{r}) \\ \rightarrow & (\varepsilon_{\mathbf{k}-\mathcal{G}} - \varepsilon_{\mathbf{k}}) C_{\mathbf{k}-\mathcal{G}} + \sum_{\mathcal{G}'}' v(\mathcal{G}' - \mathcal{G}) C_{\mathbf{k}-\mathcal{G}'} = 0 \end{aligned} \quad (3.8)$$

There will one equation corresponding to each reciprocal lattice vector and these equations will be solvable non-trivially if and only if,

$$\det (\varepsilon_{\mathbf{k}-\mathcal{G}} - \varepsilon_{\mathbf{k}}) \delta_{\mathcal{G},\mathcal{G}'} + v(\mathcal{G} - \mathcal{G}') = 0 \quad (3.9)$$

One can compute the energy $\varepsilon_{\mathbf{k}}$ corresponding to each \mathbf{k} -point and find out the band structure for any material.

Tight-Binding Method

It is known to us that in a crystal lattice, the electrons travel in the vicinity of a periodic potential caused by the ions or nucleus core in the background and hence energy bands are formed. Hence the wavefunction, describing the space-time character of the electron gas must satisfy Bloch's theorem,

$$\Phi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{r}} \Phi_{\mathbf{k}}(\mathbf{r}) \quad (3.10)$$

and the wave function can be written in the form,

$$\Phi_{\mathbf{k}}(\mathbf{r}) = \sum_j A_{\mathbf{k},j} \phi(\mathbf{r} - \mathbf{R}_j) = \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \phi(\mathbf{r} - \mathbf{R}_j) \quad (3.11)$$

This is called the “Wernier function”.

The purpose served by the tight binding model, also known as linear combination of atomic orbitals (LCAO) method is to calculate band structure and single-particle Bloch states of materials. It is a semi-empirical method and computationally very fast providing great accuracy for large systems. It is based on the fact that the electrons are tightly bound to the atoms located at the lattice sites. And hence the wave function defining the electrons will be similar to that of the atoms or ions.

Tight binding model works well for tightly bound electrons like core electrons or d-electrons in transition metals where the system can be described in terms of the superposition of wave functions for isolated atoms.

Orthogonalized Plane Wave Method (OPW)

In solids, there are two kinds of atoms - the core electrons which are tightly bound with the nucleus and the valence electrons which comparatively loosely bound to the nucleus. The wave function for core electrons are localized whereas the wave function for the valence electrons are expected to be plane wave-like in the interstitial region and oscillatory in the core region. Due to the oscillations, the convergence of plane wave is poor which can be recovered by choosing the basis set. Herring in 1949, proposed that one can find the wave function for the core electrons using tight binding model and as all solutions of the KS equation are orthogonal to each other, the wave function for the valence electrons are orthogonal to that of the core electrons. An orthogonalized plane wave is hence defined using Gram-Schmidt orthogonalization process,

$$\zeta_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\Omega} e^{i\mathbf{k} \cdot \mathbf{r}} - \sum_i \zeta_{\mathbf{k}i} \varphi_{\mathbf{k}i}(\mathbf{r}) \quad (3.12)$$

where, $\zeta_{\mathbf{k}i}$ is a coefficient determining that the wave function is orthogonal to the core-electron wave function ($\varphi_{\mathbf{k}i}(\mathbf{r})$). The OPW satisfies the Bloch's theorem and has been proven to be very successful in case of valence electrons.

Pseudopotential Method

The “Pseudopotential Method” [1] is nothing but an extension of OPW method which states that the many-body wave function can be written in a linear combination of two wave functions, oscillatory and smooth. The smooth part of the wave function are pictured to be under the influence of a strong potential, generally called as pseudo potential, which is caused by the ion core in the background. Philips and Kleinman, in 1959, constructed this smooth wave function or pseudo wave function in terms of orthogonal core states along with the orthogonalization coefficients,

$$|\psi\rangle = |\psi\rangle + \sum_i \beta_i |\psi_i\rangle \quad (3.13)$$

And the potential associated with this wave function, the pseudopotential is given by,

$$\mathcal{V} = V + \sum_i (\epsilon - \epsilon_i) |\psi_i\rangle \langle \psi_i| \quad (3.14)$$

Chapter 4

TB-LMTO and Quantum Espresso

TB-LMTO Method

Muffin Tin Approximation

One of the very successful methodology to shape the potential in which the electrons travel in a material, i.e., the external potential due to the ions or nucleus core in the background is the “Muffin Tin Approximation” [2] which is a linear version of Korringa-Kohn Rostoker (KKR) method. It simulates the band structure of solids on the basis of the fact that the wave functions determining the state of the electrons in space-time as an expansion of certain number of fixed basis functions quite similar to the linear combination of atomic orbitals (LCAO) and plane wave expansion method.

The muffin-tin orbital (MTO) method was proposed by Andersen in 1975 for a single muffin-tin potential in background and hence the result was expanded around a reference energy ε_{ref} using Taylor series expansion method,

$$\psi_{lmt}(\varepsilon, \mathbf{r}) = \psi_{lmt}(\varepsilon_{ref}, \mathbf{r}) + (\varepsilon - \varepsilon_{ref}) \frac{d\psi_{lmt}(\varepsilon_{ref}, \mathbf{r})}{d\varepsilon} \quad (4.1)$$

And then the wave function can be expressed in terms of these orbitals which satisfying Bloch's theorem,

$$\Phi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{R}, l} \alpha_l^{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{R}} \psi_{lmt}(\varepsilon, \mathbf{r}) \quad (4.2)$$

In this method, the potential is presumed to be distributed spherically around the atomic cores, namely muffin tin sphere and the potential in between is approximated to possess a interstitial constant value. The advantage of this method is that this method is easy to handle.

Tight Binding LMTO

This is the tight-binding version of LMTO which is nothing but the same methodology specified into a screened or short ranged basis. In this method, the muffin tin orbitals are effectively screened and short ranged by multipoles that are situated at the neighbouring sites.

It can reproduce the result that are obtained by LMTO method with high accuracy using fast convergence method. Every orbital constructed using this method satisfies Schrodinger's equation.

Quantum Espresso

Quantum Espresso is an integrated software suite used for "ab initio" calculations to analyze the electronic structure simulation and materials modelling. This suite is free for public under GNU general public license. Quantum Espresso includes independent and interoperable codes to serve the purpose. The codes have been developed on the basis of Density Functional Theory, Plane wave expansion method, Pseudopotential Method. It uses different types of pseudopotentials such as coulomb potential, PAW, norm-conserving and ultrasoft kinds.

The plane wave density functional which is required to solve the KS equation is produced by running a plane wave self-consistent field (PWscf) program in presence of suitable pseudopotentials file. Then the wave function is utilized for analysing various electronic properties.

Quantum Espresso has different distributions for different purposes. It contains some basic packages and some additional packages for self-consistent calculation, generation of pseudopotential, analysing X-Ray spectrum etc.

The TB-LMTO method predicts that the electrons are tightly bound with the nucleus. But in reality the valence electrons are loosely bound to the core. Hence TB-LMTO does not fit well for most of the solids. Whereas Quantum Espresso distribution adopts mostly pseudopotential method which is an extension of OPW method and predicts the electrons behaviour correctly. It also has a wide range of choices for the potential and one can choose a pseudopotential according to the requirement and nature of the sample.

Chapter 5

Lattice Structure of The Materials

Benchmarking

Firstly, for understanding the features and tricks that are used to perform first principle calculation using TB-LMTO and Quantum Espresso, some simple known examples are taken into account (Si and Ge). Thereafter self-consistent calculations are done for two compounds Cadmium telluride (CdTe) and Mercury telluride (HgTe). And finally an attempt has been taken to perform first principle calculation for crystalline Hydrogen sulphide (H_2S) in ambient pressure.

Crystal Structure of Silicon (Si)

Silicon(Si) is an intrinsic semiconductor,i.e., it has a small indirect energy gap between its valance and conduction band. Crystalline Silicon has a diamond like crystal structure where two face centred cubic lattices are partially interpenetrating into each other. The space group of Silicon is **Fd-3m** (group no. 227) and is a cubic close-packed (ccp) structure. The lattice constant for Silicon is 543.09 pm. Silicon is a widely used semiconductor in the field of electronics due to its versatility of applications' as well as its excellent performance at higher temperature.

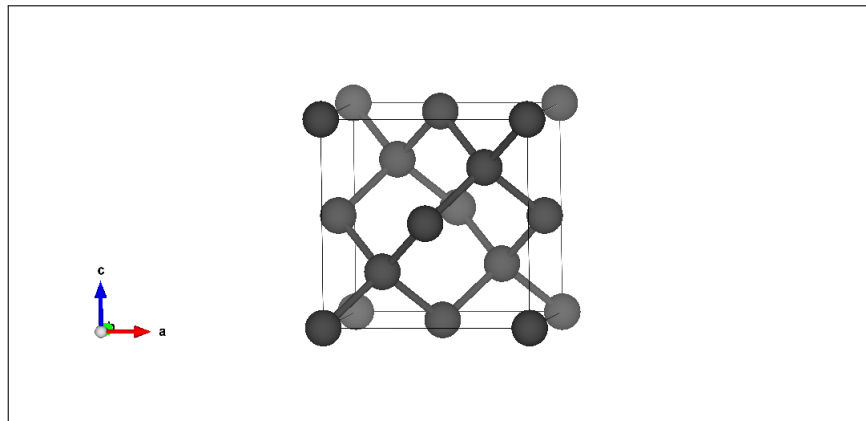


Figure 5.1: Crystal structure of Silicon (reproduced using VESTA)

Crystal Structure of Germanium (Ge)

Similar to Silicon, Germanium is also an intrinsic semiconductor having an indirect energy gap between valence and conduction band. The space group of germanium is **Fm-3m**(group no. 225) and it is a close-packed (ccp) structure. The lattice constant of crystalline germanium is 565.75 pm. It also has a diamond-like crystal structure and it is one of the semiconductors that have been found initially. But due to less efficient performance in high temperature it has been highly replaced by silicon. Presently germanium is used mostly in the field of fibre-optics, infra-red optics and solar cell applications.

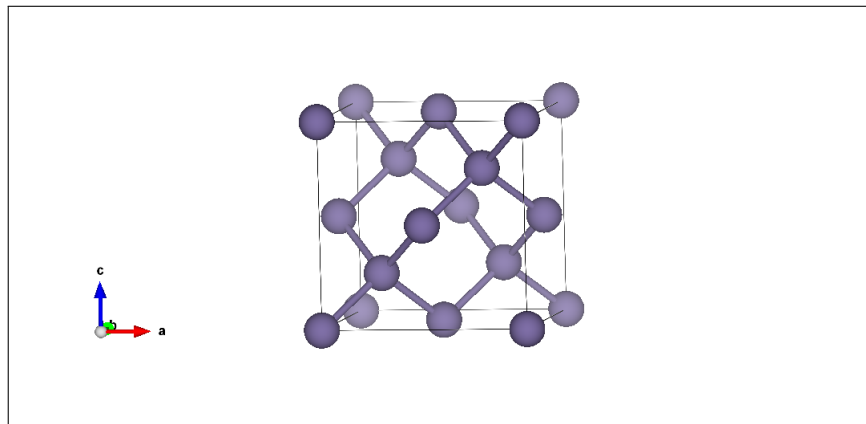


Figure 5.2: Crystal structure of Germanium (reproduced using VESTA)

Crystal Structure of Mercury telluride (HgTe)

Mercury telluride is a face-centred cubic crystal and lies under the space group $T_d^2(F4\bar{3}m)(216)$. It is a binary compound of mercury and tellurium and it is a semi-metal. It can be found naturally as coloradoite. It can also act as a p-type semiconductor and can be doped (n-type) by the entities like boron, gallium, aluminium, indium etc. Its lattice constant is 646 pm. Currently HgTe has been categorized as a topological insulator which has a unique property of carrying current through the edges and acts as an insulator in the rest of the bulk.

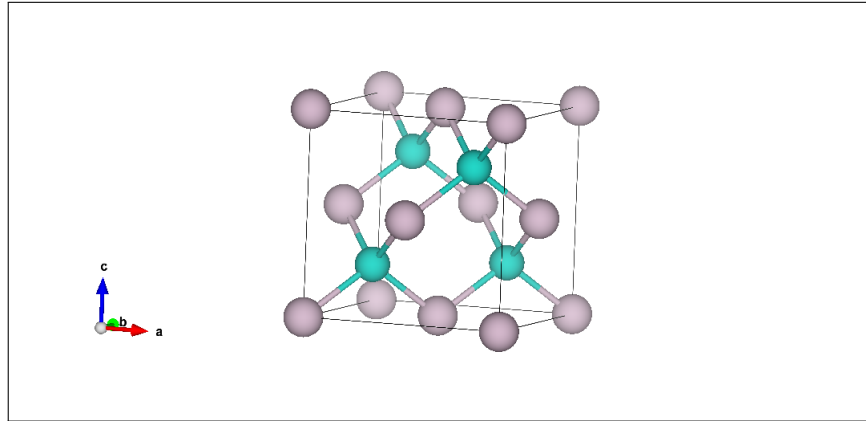


Figure 5.3: Crystal structure of Mercury telluride (reproduced using XCrySDen)

Crystal Structure of Cadmium telluride (CdTe)

Cadmium telluride [3] is a face-centred lattice having lattice constant is 648 pm and comes under the space group $T_d^2(F4\bar{3}m)(216)$. Cadmium telluride is a very good γ and X ray detector and also large band gap and high electron mobility. However the transport properties of the hole is poor. CdTe has its application as semiconducting material in the field of cadmium telluride photovoltaics and an infrared optical window.

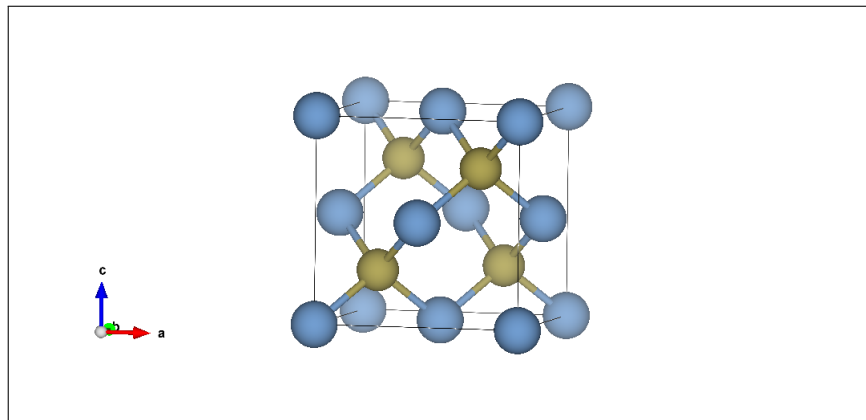


Figure 5.4: Crystal structure of Cadmium telluride (reproduced using VESTA)

Crystal Structure of Hydrogen sulphide (H_2S)

Now a days crystalline Hydrogen sulphide [4, 5] [6] has become centre of interest due to the evidences of having a high transition temperature superconductor. H_2S is a gas in room temperature and standard pressure. It requires a very high pressure to get crystallized and hence from standard to deformed structures in different phases. Previously the phase diagram of crystalline H_2S in high pressure was unavailable due to complexity of having loosely bound sulphur and hydrogen atom and larger atomic core difference between the atoms. Interestingly it has different structure in different phase. The metallization was achieved for

H_2S at a pressure 96 GPa. Phase IV and V of H_2S is non metallic. And at pressure 160 GPa and temperature 80 K, H_2S acts as a metal with superconductive potential. The crystal that has been reproduced in the diagram provided bellow is a phase III H_2S in ambient pressure and the lowest temperature possible. It is a stable orthorhombic structure under the space group $Pbcm$ (group no. 57) and has lattice constants 407.60 pm , 1338.01pm and 672.15 at 1.5 K respectively. It has 8 molecules in each unit cell. It is a prototype molecular system and can have enormous application in future due to its extraordinary features.

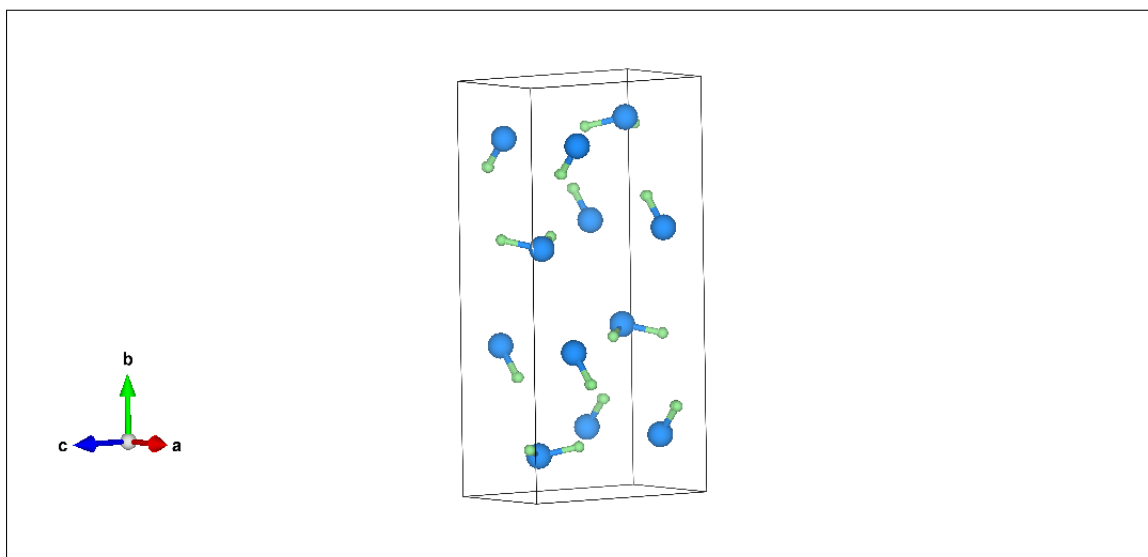


Figure 5.5: Crystal structure of Hydrogen sulphide (reproduced using VESTA)

Chapter 6

Band Structure of Materials

Benchmarking

Band Structure of Silicon (Si)

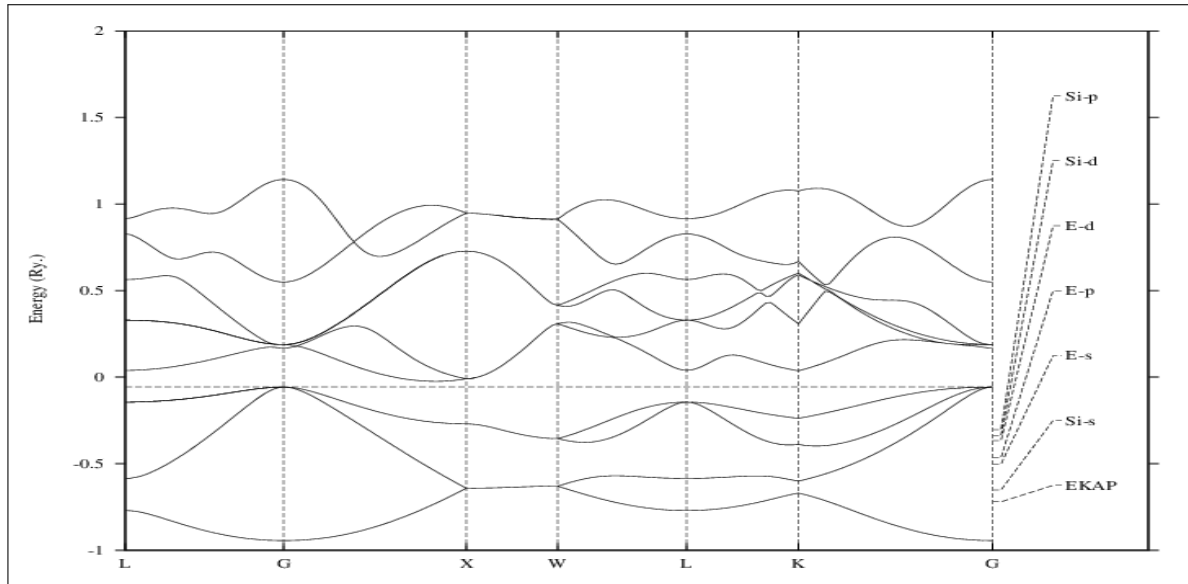


Figure 6.1: Band Structure of Silicon (Using TB-LMTO)

The band structure of Silicon has been plotted using TB-LMTO in the above figure. From the figure it can be concluded that Silicon has indirect band gap.

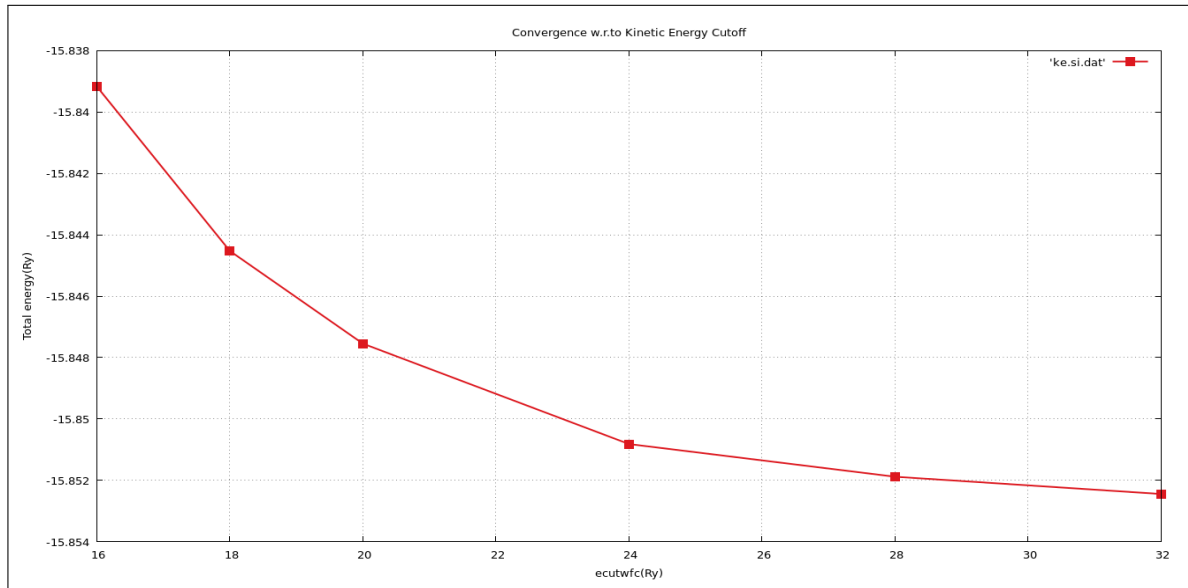


Figure 6.2: Total energy convergence with respect to cut-off kinetic energy ('ecutwfc')(Using Quantum Espresso)

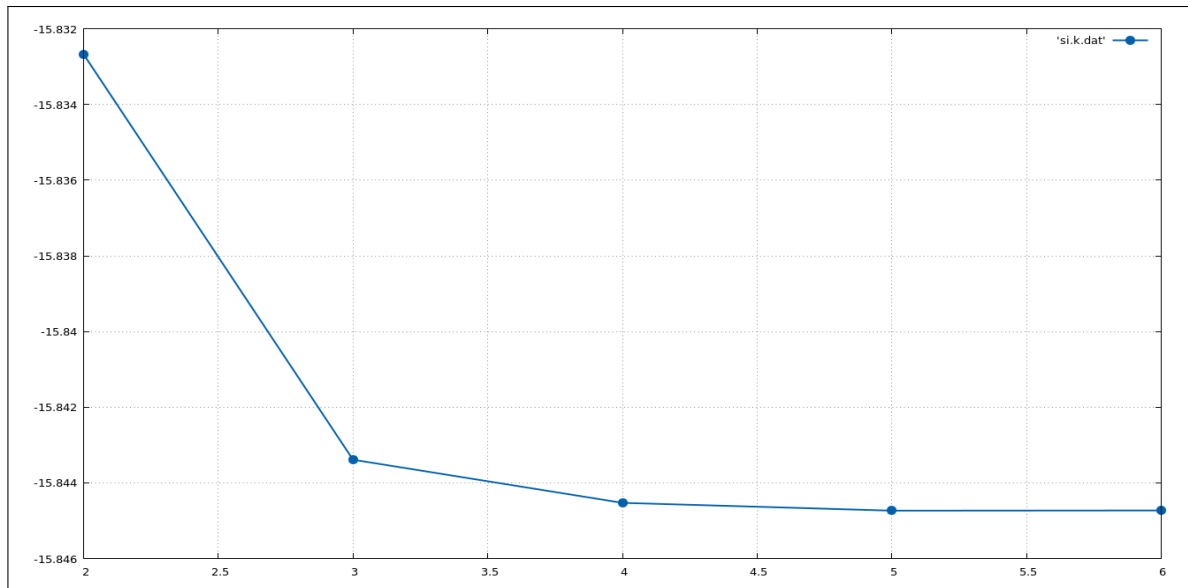


Figure 6.3: Total energy convergence with respect to choice of k-points (Using Quantum Espresso)

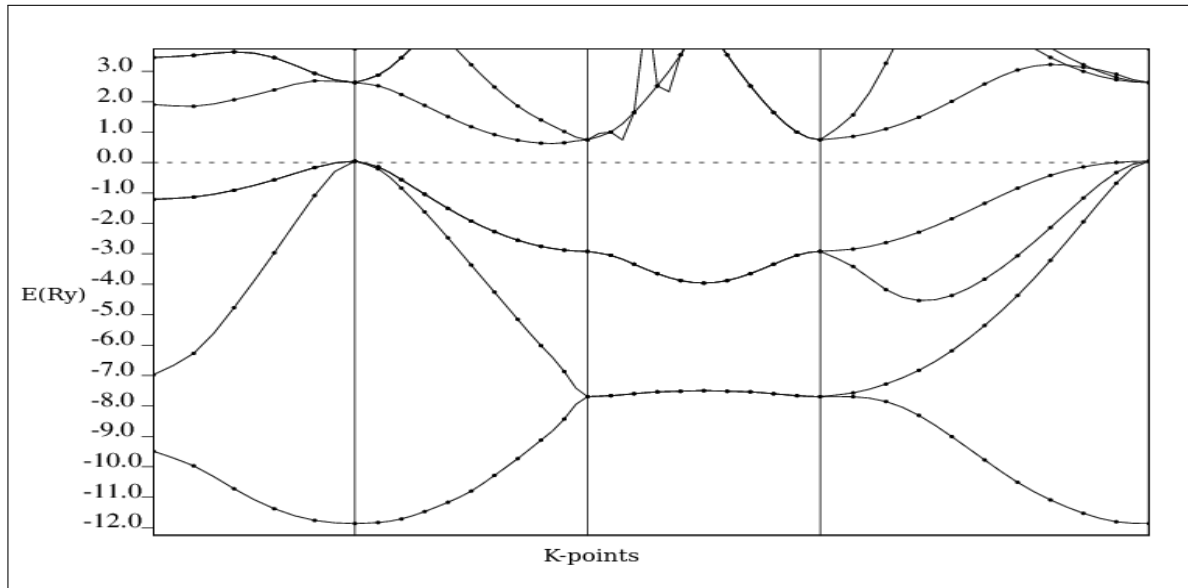


Figure 6.4: Band Structure of Silicon (Using Quantum Espresso)

The band structure of Silicon has been plotted using Quantum Espresso in the above figure. From the figure it can be concluded that Silicon has indirect band gap.

Band Structure of Germanium (Ge)

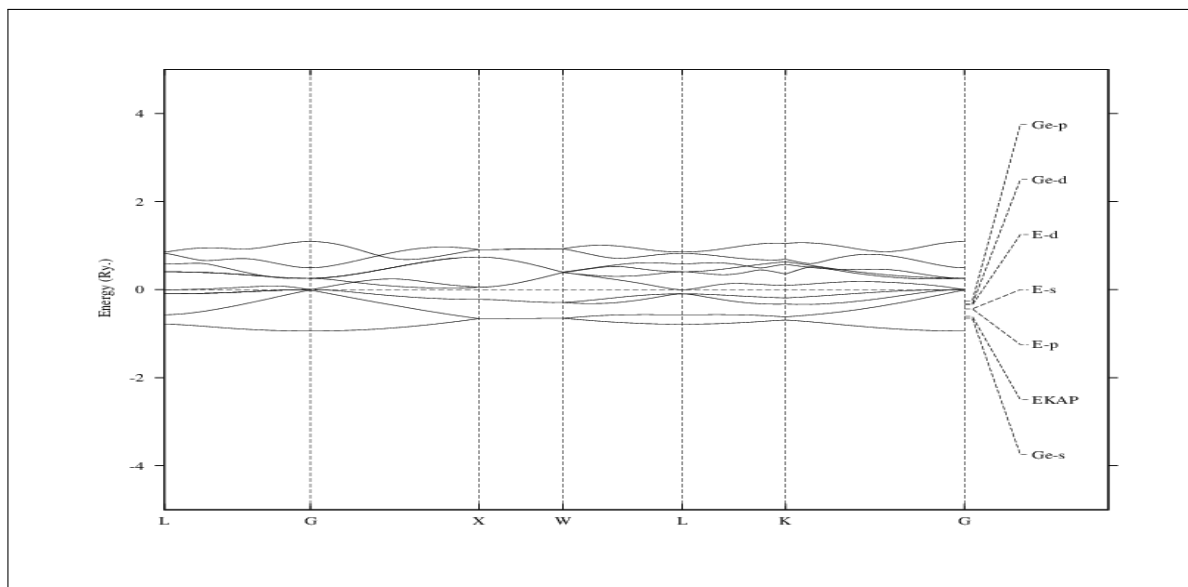


Figure 6.5: Band Structure of Germanium (Using TB-LMTO)

The band structure of Germanium has been plotted using TB-LMTO in the above figure. From the figure it can be concluded that Germanium has indirect band gap.

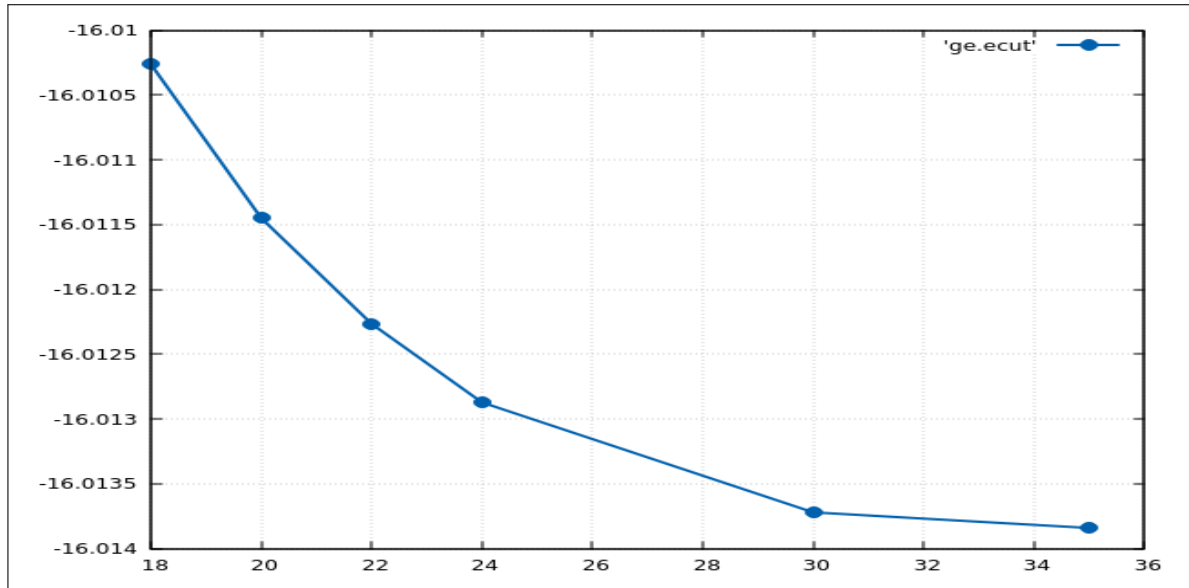


Figure 6.6: Total energy convergence with respect to cut-off kinetic energy (ecutwfc) (Using Quantum Espresso)

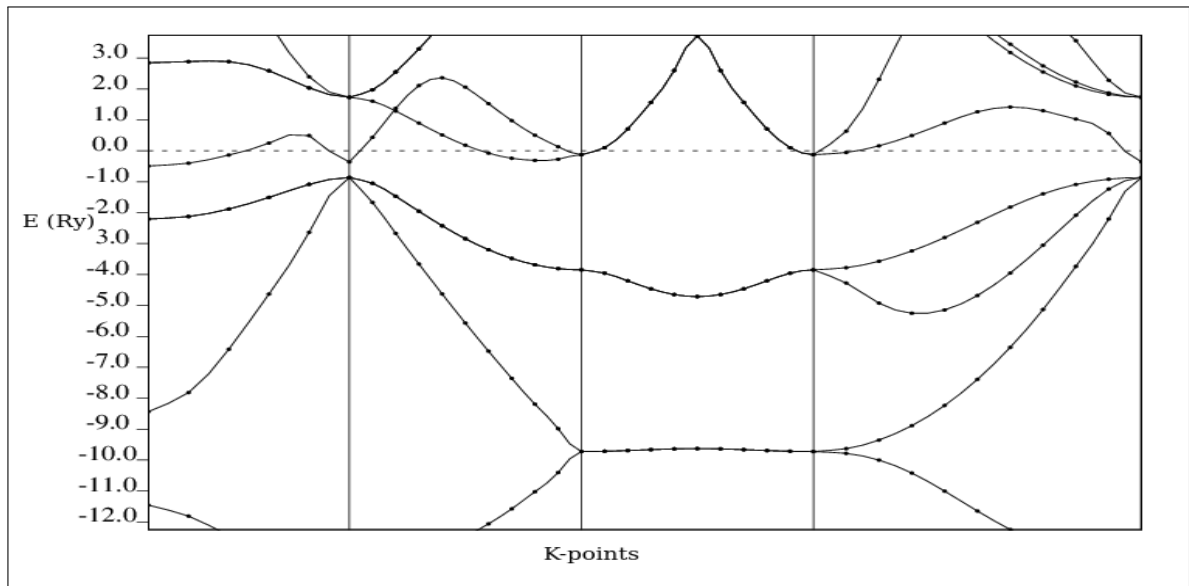


Figure 6.7: Band Structure of Germanium (Using Quantum Espresso)

The band structure of Germanium has been plotted using Quantum Espresso in the above

figure. From the figure it can be concluded that Germanium has indirect band gap.

Band Structure of Cadmium telluride (CdTe)

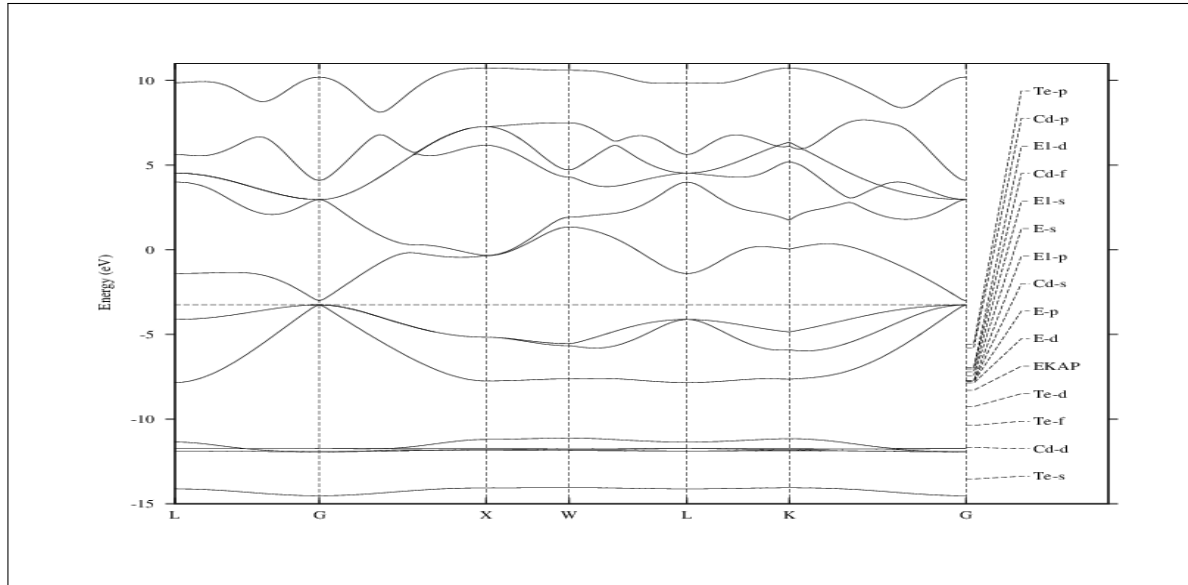


Figure 6.8: Band Structure of Cadmium telluride (Using TB-LMTO)

The band structure of Cadmium telluride [3] has been plotted using TB-LMTO in the above figure. From the figure it can be concluded that Cadmium telluride has a direct band gap.

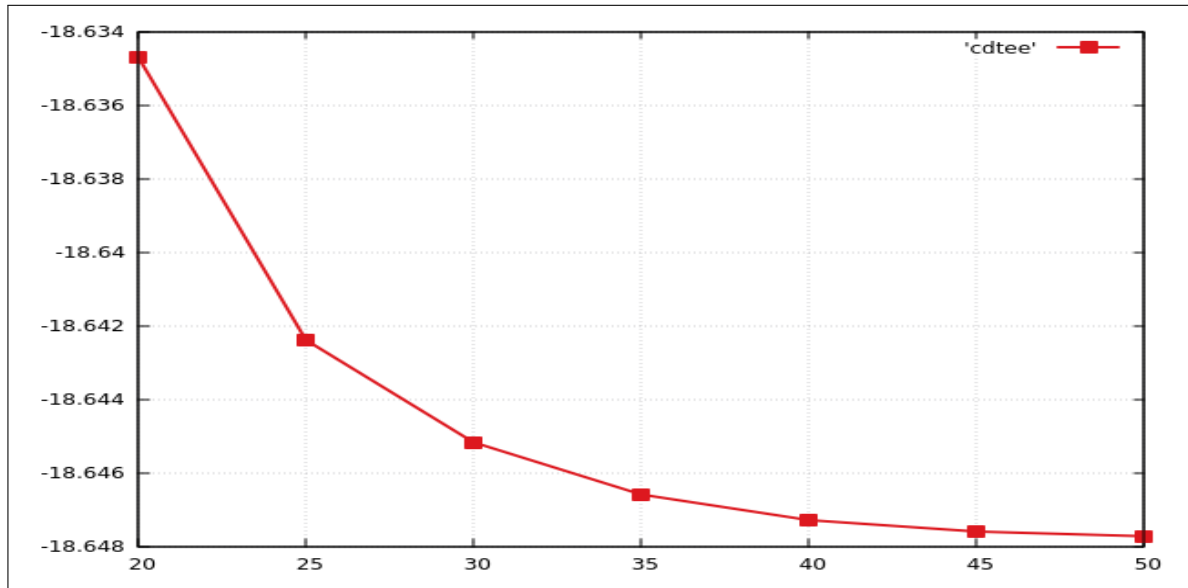


Figure 6.9: Total energy convergence with respect to cut-off kinetic energy (ecutwfc) (Using Quantum Espresso)

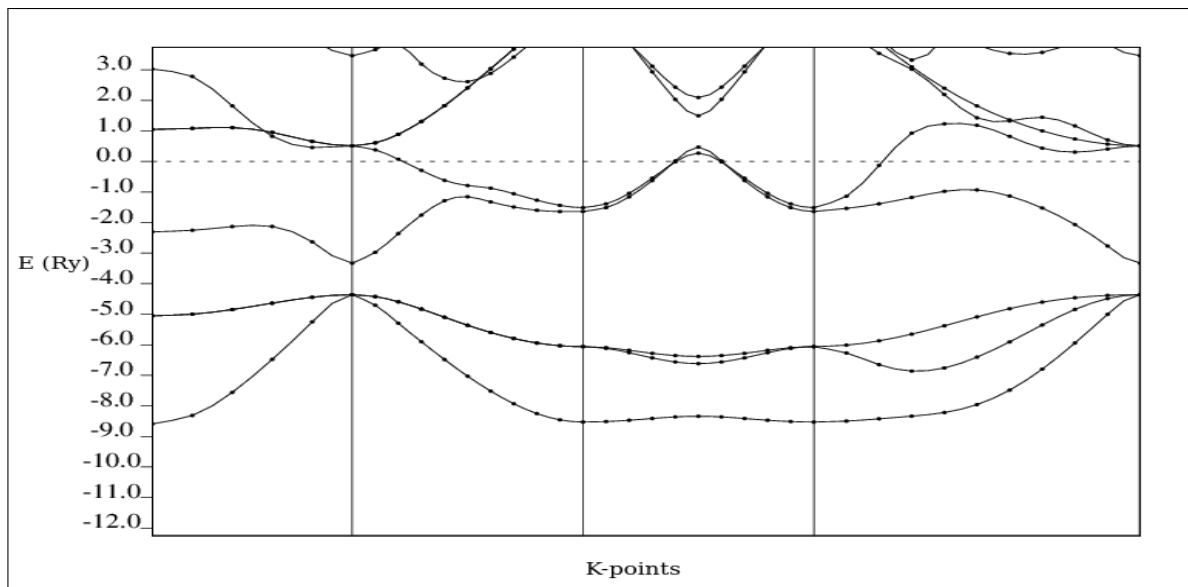


Figure 6.10: Band Structure of Cadmium telluride (Using Quantum Espresso)

The band structure of Cadmium telluride has been plotted using Quantum Espresso in the above figure. From the figure it can be concluded that Cadmium telluride has a direct band gap.

Band Structure of Mercury telluride (HgTe)

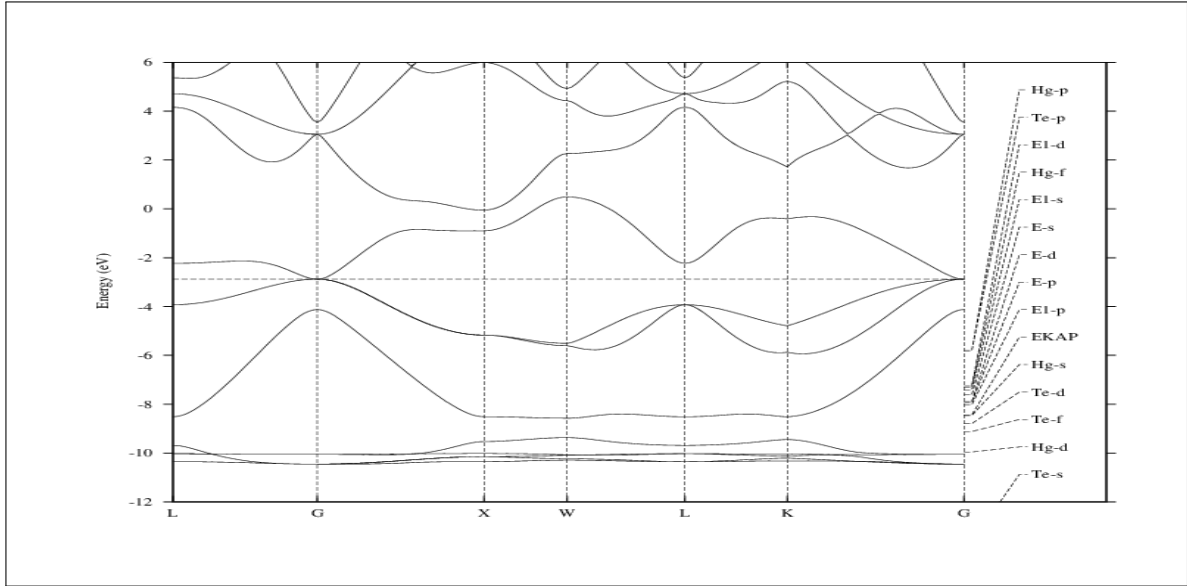


Figure 6.11: Band Structure of Mercury telluride (Using TB-LMTO)

The band structure of Mercury telluride has been plotted using TB-LMTO in the above figure. From the figure it can be concluded that Mercury telluride has a direct band gap.

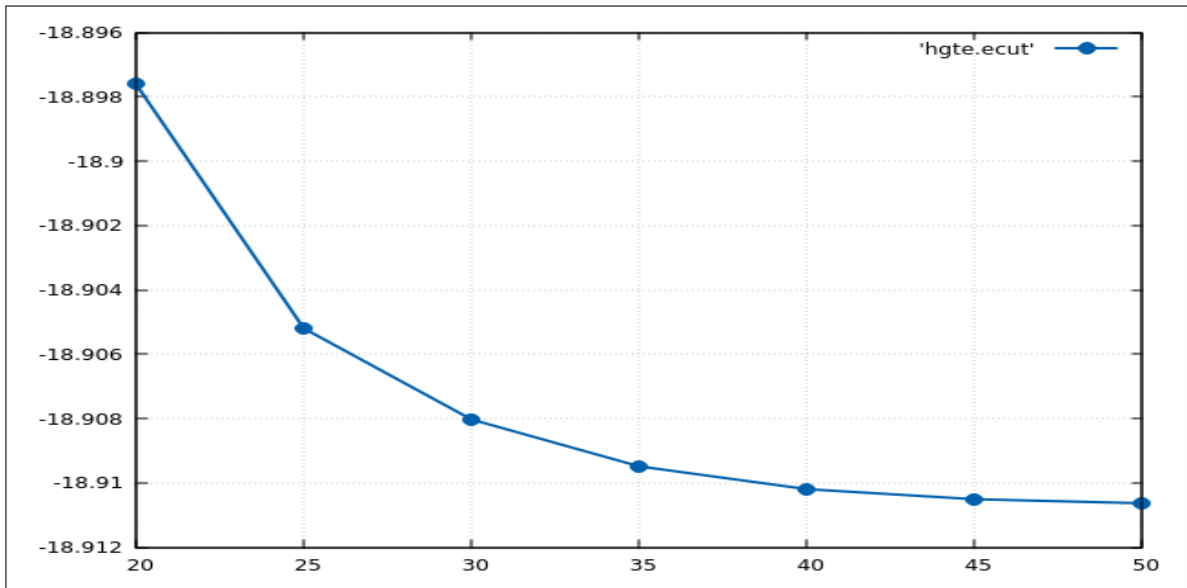


Figure 6.12: Total energy convergence with respect to cut-off kinetic energy (ecutwfc) (Using Quantum Espresso)

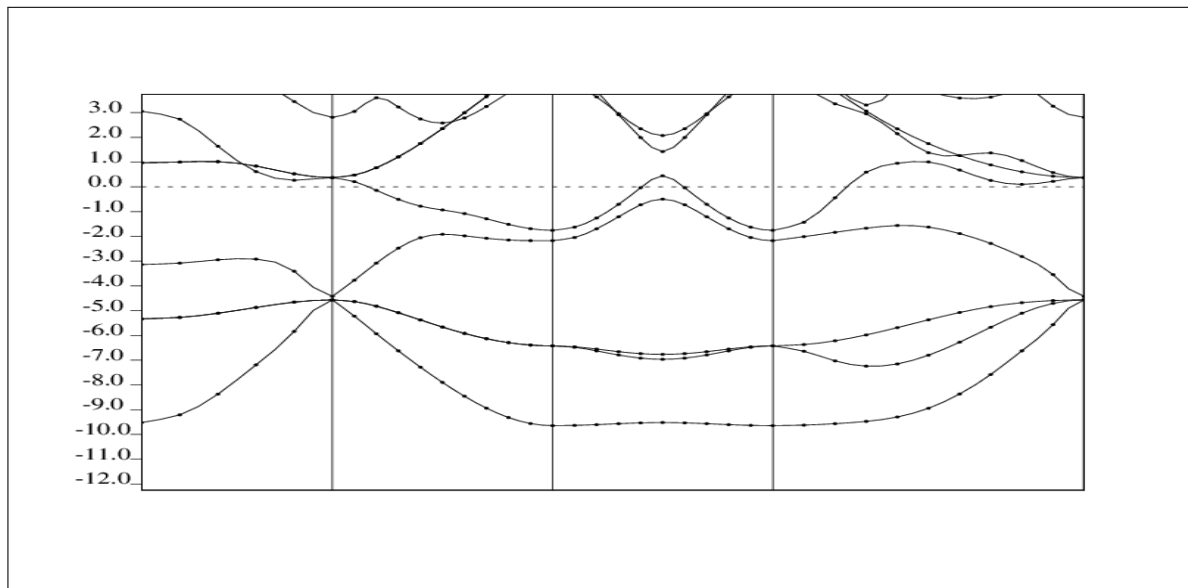


Figure 6.13: Band Structure of Mercury telluride (Using Quantum Espresso)

The band structure of Mercury telluride has been plotted using Quantum Espresso in the above figure. From the figure it can be concluded that Mercury telluride has a direct band gap.

Total Energy Convergence of Hydrogen sulfide (H_2S) with respect to kinetic-energy cut-off

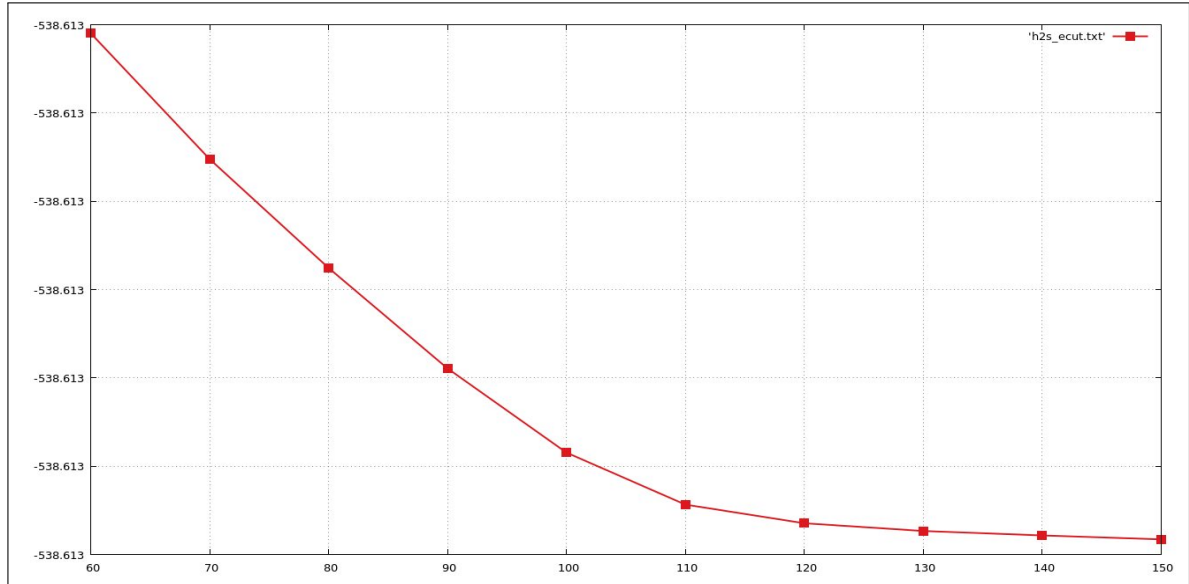


Figure 6.14: Total energy convergence with respect to cut-off kinetic energy (ecutwfc) (Using Quantum Espresso)

Chapter 7

Density of States (DOS) of The Materials

Benchmarking

DOS of Silicon (Si)

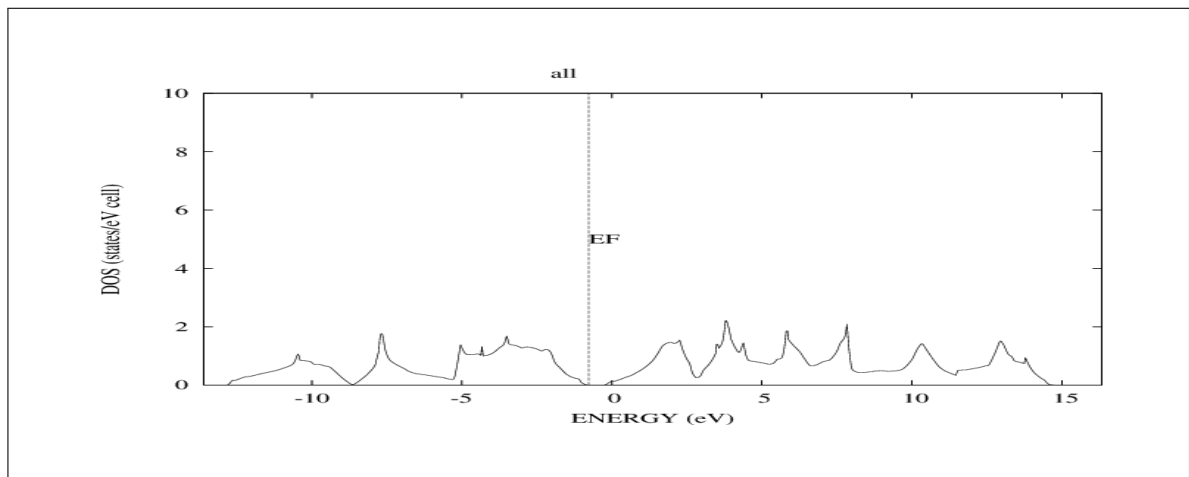


Figure 7.1: Density of States of Silicon (Using TB-LMTO)

DOS of Germanium (Ge)

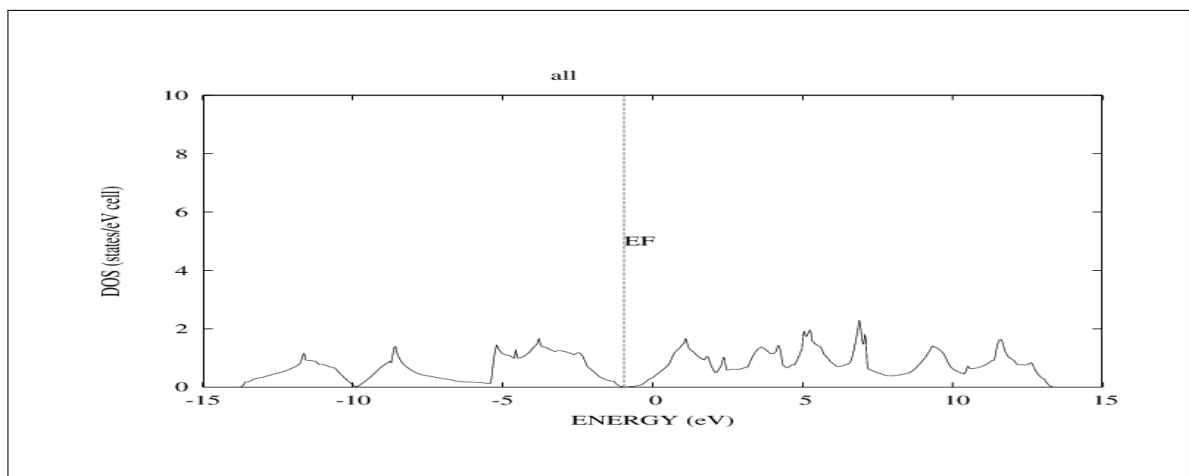


Figure 7.2: Density of States of Germanium (Using TB-LMTO)

DOS of Cadmium telluride (CdTe)

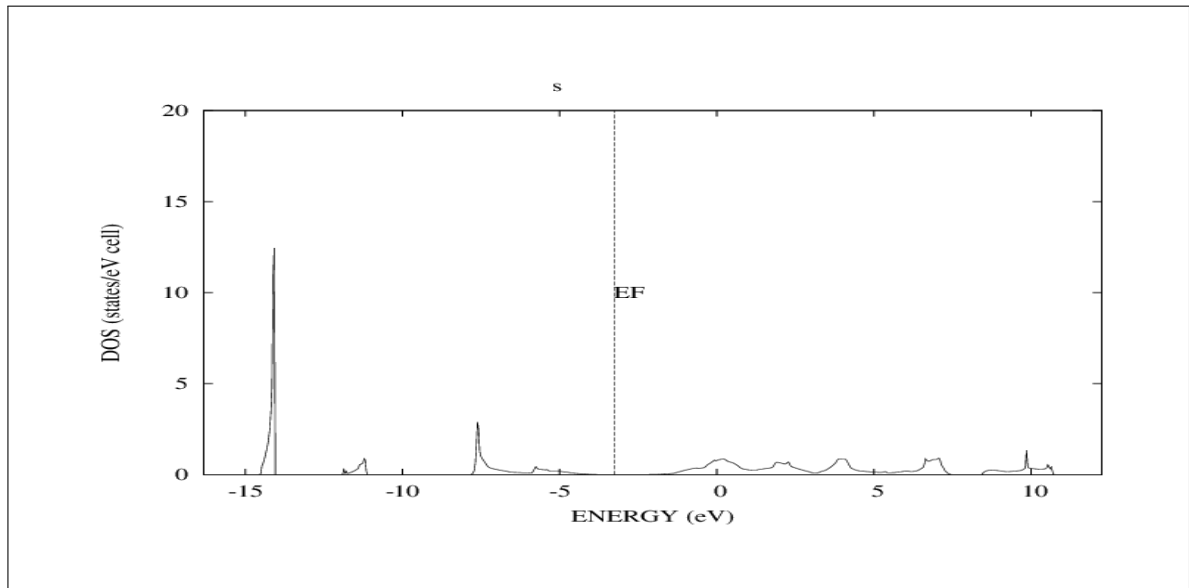


Figure 7.3: Density of States of Cadmium telluride (Using TB-LMTO)

DOS of Mercury telluride (HgTe)

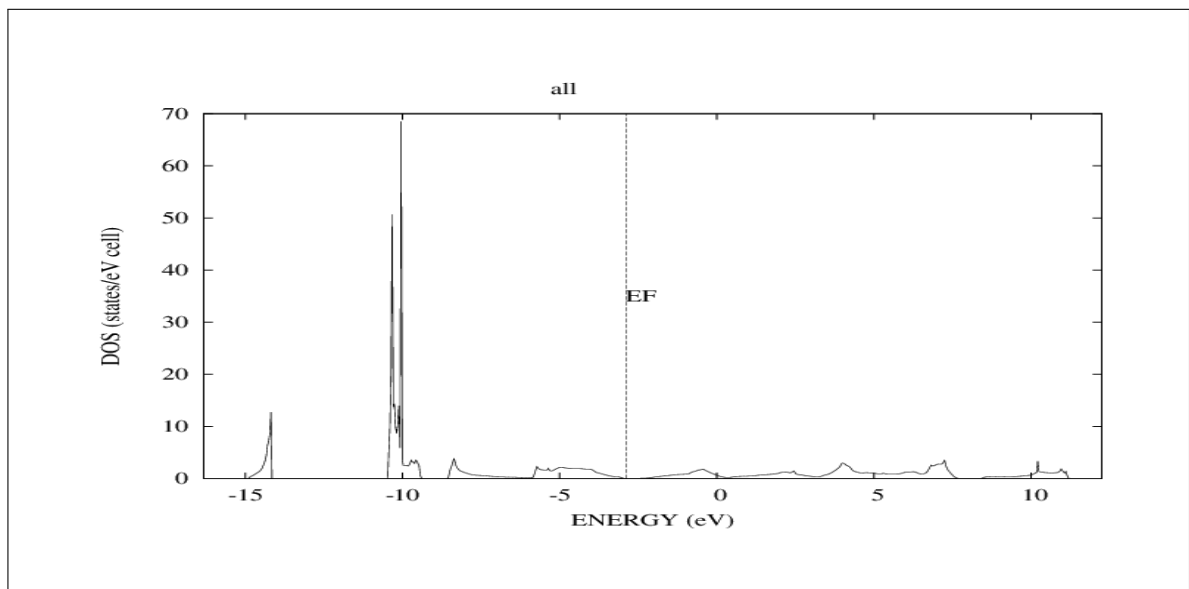


Figure 7.4: Density of States of Mercury telluride (Using TB-LMTO)

Chapter 8

Conclusion

The aim of the project was to study the superconducting state of crystalline H_2S using first principle calculation. First principle calculation plays a vital role in the field of theoretical study of different materials. Many useful information about the structure and geometry of materials which are not obtainable directly from the experiments can be predicted by this kind of calculation. Also using this method, the experimentally obtained informations can be cross-checked and verified. TB-LMTO is one of the very widely used methods for first principle calculation. But it gives accurate results mostly for tightly bound electron systems. Whereas, Quantum espresso uses pseudopotential method for determining the electronic structure.

Firstly to understand and learn the basic features and tricks of the method and distribution, some simple semiconducting materials were taken into account, namely Silicon and Germanium. Then in the next step some compounds had been studied. The reason behind choosing Cadmium telluride (CdTe) and Mercury telluride (HgTe) was that they have interesting properties. For example, CdTe has exceptionally high electron mobility and HgTe behaves as a topological insulator. Band structure calculation was carried out for all four materials in both TB-LMTO and Quantum Espresso. Also Density of states had been calculated for these materials using TB-LMTO. As TB-LMTO is a good approximation only for the electrons in a closely bound state with the nucleus, Quantum Espresso which uses pseudopotential method estimates the band structure better. However, in both the cases the band gap was underestimated in case of both the intrinsic semiconductors.

The density of states calculation could not be done in Quantum Espresso because the calculation required a huge number of k-points [7] and the technique of generating appropriate set of k-points could not be resolved. As the program highly dependent upon the convergence of total energy with respect to the choice of k-points to generate a stable structure, it could not be carried out further.

Finally the Phase III orthorhombic ($Pbcm$) Hydrogen Sulphide was considered. This material has gained a lot of interest recently because of its superconducting behaviour in reasonably high temperature. The $Pbcm$ structure had been observed experimentally in ambient pressure and extremely low temperature.

A band structure calculation could not be carried out for H_2S in TBLMTO due to the fact that there exists a more compatible and stable structure (H_4S_4) for the same input and hence generation of H_2S was denied. However, an appropriate self-consistent input file (.scf) was generated by providing the lattice parameters and atomic positions for the $Pbcm$ crystal structure in VESTA. But the again the band structure calculation remains undone because of insufficient information about the k-point generation.

As a future work, one can continue with resolving the problem of generating the appropriate set of k-points and calculate the band structure and DOS for Hydrogen Sulphide and more evidences and reasons can be explored behind the exceptional behaviour of this material.

References

- [1] R. Prasad, *Electronic Structure of Materials*, ser. Chapman & Hall book. Taylor & Francis, 2013. [Online]. Available: <https://books.google.co.in/books?id=UpEAAAAAQBAJ>
- [2] R. Martin, *Electronic Structure: Basic Theory and Practical Methods*. Cambridge University Press, 2004. [Online]. Available: <https://books.google.co.in/books?id=dmRTFLpSGNsC>
- [3] V. L. Bekenev and S. M. Zubkova, “Electronic structure of the cdte(111)a-(2 × 2) surface,” *Physics of the Solid State*, vol. 57, no. 9, pp. 1878–1887, 2015. [Online]. Available: <http://dx.doi.org/10.1134/S1063783415090048>
- [4] A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov, and S. I. Shylin, “Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system,” *Nature*, vol. 525, no. 7567, pp. 73–76, Sep 2015, letter. [Online]. Available: <http://dx.doi.org/10.1038/nature14964>
- [5] A. N. F. Jeremy K. Cockcroft, “The solid phases of deuterium sulphide by powder neutron diffraction,” *Zeitschrift für Kristallographie*, vol. 193, no. 2, pp. 1 – 19, November 1989.
- [6] Y. Li, J. Hao, H. Liu, Y. Li, and Y. Ma, “The metallization and superconductivity of dense hydrogen sulfide,” *The Journal of Chemical Physics*, vol. 140, no. 17, 2014. [Online]. Available: <http://scitation.aip.org/content/aip/journal/jcp/140/17/10.1063/1.4874158>
- [7] H. J. Monkhorst and J. D. Pack, “Special points for brillouin-zone integrations,” *Phys. Rev. B*, vol. 13, pp. 5188–5192, Jun 1976. [Online]. Available: <http://link.aps.org/doi/10.1103/PhysRevB.13.5188>