



# FIRST PRINCIPLE CALCULATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF CARBON

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A Thesis Submitted to

The Department of Physics

PRESENTED IN FULFILMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE  
JIMMA UNIVERSITY  
JIMMA, ETHIOPIA  
SEPTEMBER 2017

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JIMMA UNIVERSITY  
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JIMMA UNIVERSITY

Date: **September 2017**

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Title: **First principle calculation of structural and  
electronic properties of carbon**

Department: **Physics**

Degree: **M.Sc.** Convocation: **October** Year: **2017**

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*TO MY FAMILY.*

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Title of the Thesis:

**First principle calculation of structural and electronic properties of carbon**

# Acknowledgement

First of all I would like to take this opportunity to thank my God, just for giving me this chance. And next to that my advisor Dr.Menberu Mengesha an Associate professor of physics in Jimma University, deserves a great thanks for his valuable comments and advise that he gave me, for the accomplishment of this thesis. As for my family, I don't have any words just to express the good things that you did for me, in my education. God bless you all.



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# Abstract

In this study the electronic and structural properties of carbon are determined with respect to density functional theory employing QUANTUM ESPRESSO package. The exchange-correlation energies are computed using local density approximation (LDA) and generalized gradient approximation (GGA). The total minimum energy of carbon is calculated as a function of cutoff energy and Monk Horst Pack mesh. The result reveals that the total minimum energy is monotonically decreasing with an increment of cutoff energy. Moreover, the total minimum energy as a function of  $\vec{k}$ -point sampling has such a determined systematic trend. The total minimum force of carbon is computed by displaying carbon atom as a function of cutoff energy and  $\vec{k}$ -point sampling, by 0.05 bohr. Moreover, the theoretical equilibrium lattice constant is calculated and compared with experimental values of equilibrium lattice constant. Interestingly the calculated theoretical equilibrium lattice constant is in good agreement with experimental data.

# Chapter 1

## Introduction

The element carbon has an atomic number 6, as a member of group-14 on the periodic table and it is nonmetallic and tetravalent with the ground state electronic configuration of  $2s^2 2p^2$ . This element is widely distributed in nature. Its occurrence ranges from earth to the universe. In the earth's crust it exists in the ratio of 180ppm, mostly in the form of compounds. It is also detected in abundance in the universe, in the sun, stars, comets, and in the atmosphere of the planets. It is the fourth most abundant element in the solar system, after hydrogen, helium, and oxygen. It is found most widely in the form of hydrocarbons and other compounds. Carbon is different from other elements in one important respect, that is its diversity. It has several material forms in which it exists, known as allotropes [1]. Carbon has 8 different allotropes among those graphite and diamond are the very important ones. In its crystal structure for the graphite it has a simple hexagonal crystal structure, and it has face centered cubic (FCC) crystal structure for diamond which is more stable structure. The wide-variety of carbon allotropes and their associated physical properties are largely due to the flexibility of carbons valence electrons and resulting dimensionality of its bonding structures [2].

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The extraordinary variety of carbon allotropes, as well as their present and potential applications in such diverse fields as nano-electronics or bioengineering, gives them a special place among all the elements [3]. Graphite is widely used as a solid lubricant for preventing wear and abrasion and can also be dispersed in water and organic fluids to make a liquid lubricant. Graphite is soft, smooth, inflammable, nontoxic, is inert in ambient air, does not emit fumes, and has a low coefficient of friction. It is cheaper and environmentally safer to produce and use than many other tribological coatings and lubricants such as polymers, diamond, DLC, and the various borides, nitrides and carbides [4-6]. As for diamond, it is a wide band gap material with band gap energy of  $E_g = 5.5eV$ , electronic excitations do not account for thermal properties up to high temperatures [3]. Diamond films are potential materials for commercial applications such as machine tools, optical coatings, and high temperature electronics, due to its properties which includes extreme hardness, high thermal conductivity, high dispersion of light, and chemical inertness [7]. For both structures different first principle structural and electronic calculations has been made on different circumstances [2-4,7].

In this study, we are more interested to study the diamond structure of carbon, as it is a stable structure and more valuable in both basic science and technological perspective. In this paper, we report first principle or ab initio studies of the electronic and structural properties of carbon (diamond) structure. First principle or ab initio approaches is based on the density functional theory methodology [8, 9]. It is a well established and a very powerful tools for studying properties of semiconductors, metals, surfaces, or interfaces [10-14]. The convergence issues of total energy per atom, total force per atom, and theoretical lattice constant is investigated with respect

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to the cutoff energy and  $\vec{k}$ -point sampling.

## 1.1 Statement of the Problem

In electronic structure theory we describe the motion of electrons in atoms or molecules. Generally this is done in the context of the Born-Oppenheimer approximation, an approximation where the nuclei of an atom is held fixed. Since the electrons are so small, one needs to use quantum mechanics to solve for their motion. Quantum mechanics tells us that the electrons will not be localized at particular points in space. But they are best thought of as matter waves which is described by the wave function, at the point  $x$ . The non relativistic Schrödinger's theory of quantum mechanics provides us with such a procedure, and it is the foundation of the theory of electronic structure of matter. So our goal tends to solve for time independent Schrödinger equation. In this study we are interested to calculate the electronic and structural properties of carbon with respect to density functional theory.

## 1.2 Objective of the Study

### 1.2.1 General objective

The main aim of this study is to calculate the electronic and structural properties of carbon.

### 1.2.2 Specific objectives

- To calculate the total minimum energy of carbon with respect to cutoff energy
- To calculate the total minimum energy of carbon with respect to  $\vec{k}$ -point sampling

- 
- To calculate the minimum force of carbon with respect to cutoff energy
  - To calculate the minimum force of carbon with respect to  $\vec{k}$ -point sampling
  - To determine the theoretical equilibrium lattice constant

### 1.3 Basic Research Questions

- What is the total minimum energy of carbon with respect to cutoff energy?
- What is the total minimum energy of carbon with respect to  $\vec{k}$ -point sampling?
- What is the minimum force of carbon with respect to cutoff energy?
- What is the minimum force of carbon with respect to  $\vec{k}$ -point sampling?
- What is the theoretical equilibrium lattice constant of carbon?

### 1.4 Significance of the Study

Understanding the electronic, and structural property of carbon helps to know the system in depth. Moreover it helps to develop computational skills for solving many body problems.

# Chapter 2

## Literature Review

This chapter focuses starting from the basic quantum mechanical description of many electron system, up to the theoretical background of the electronic and structural calculation methodologies used in this thesis. For approximately solving the many electron problem, Hartree-Fock, Thomas-Fermi theory, and at last the modern density functional theory are discussed in some detail. Also some of the practicalities necessary to consider in performing such calculation (concerning to my system) such as plane wave basis set and pseudo-potential are discussed.

### 2.1 Elementary Quantum Mechanics

In this chapter we will review the basic descriptions of many electron system given in quantum mechanics, which are used as a fundamental aspects of electronic structure theory. In order to lay the foundations for the theoretical discussion on density functional theory (DFT) presented in later parts of this chapter.

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### 2.1.1 The Shrödinger equations

In quantum mechanics experimental evidence have presented, which shows conclusively that, unlike the macroscopic particles which obeyed the Newtonian's laws of motion, the microscopic particles move according to the laws of some form of wave motion. Thus a microscopic particle acts as if certain aspects of its behavior are governed by the behavior of an associated de Broglie wave, or wave function [15]. The experiments considered dealt only with simple cases (such as free particles, or simple harmonic oscillators, etc) that can be analyzed with simple procedures (involving direct applications of the de Broglie postulate, Planck's postulate, etc) [16]. But we certainly want to be able to treat the more complicated cases that occur in nature. To be able to do this we must have a more general procedure that can be used to treat the behavior of the particles of any microscopic system. Shrödinger's equation of quantum mechanics provides us with such a procedure [15]. The theory specifies the laws of wave motion that the particles of any microscopic system obey. This is done by specifying, for each system, the equation that controls the behavior of the wave function, and also by specifying the connection between the behavior of the wave function and the behavior of the particle. This theory will enable us to obtain a detailed understanding of the properties of atoms. These properties form basis of much of chemistry and solid state physics [15].

The time independent Shrödinger equation for a system consisting of 'M' nuclei and 'N' electrons is written as,

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M) = E_i\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M), \quad (2.1.1)$$



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where  $\hat{H}$  is differential Hamiltonian operator presenting the total energy

$$\hat{H} = \frac{-1}{2} \sum_{i=1}^N \nabla_i^2 - \frac{1}{2} \sum_{A=1}^M \frac{1}{M_A} \nabla_A^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (2.1.2)$$

Here, 'A' and 'B' run over the 'M' nuclei, while 'i' and 'j' denote the 'N' electrons in the system. The first two terms describe the kinetic energy of the electrons and the nuclei respectively, where the Laplacian operator  $\nabla_q^2$  is defined as a sum of differential operators (in cartesian coordinates),

$$\nabla_q^2 = \frac{\partial^2}{\partial x_q^2} + \frac{\partial^2}{\partial y_q^2} + \frac{\partial^2}{\partial z_q^2}, \quad (2.1.3)$$

and  $M_A$  is the mass of the nucleus 'A' in multiples of the mass of the electron. The remaining three terms define, the potential part of the Hamiltonian and represents the attractive electrostatic interaction between the electrons and the nuclei, and the repulsive potential due to the electron-electron and nucleus-nucleus interactions respectively.

$r_{ij}$  (and similarly  $R_{AB}$ ) is the distance between the particles 'i' and 'j', which is,  $r_{ij} = |\vec{r}_i - \vec{r}_j|$ , where as  $r_{iA} = |r_i - R_A|$  represent the distance between the  $i^{th}$  electron and  $A^{th}$  nucleus.  $\Psi_i(\vec{x}_1, \vec{x}_2, \dots, \vec{x}_N, \vec{R}_1, \vec{R}_2, \dots, \vec{R}_M)$  stands for the wave function of the  $i^{th}$  state of the system, which depends on the  $3N$  spatial coordinates  $[\vec{r}_i]$ , and the  $N$  spin coordinates  $[S_i]$  of the electrons, which are collectively termed  $[\vec{x}_i]$  and the  $3M$  spatial coordinates of the nuclei,  $[\vec{R}_M]$ . This wave function contains all information that can possibly be known about the quantum system at hand. Finally,  $E_i$  is the numerical value of the energy of the state described by  $\Psi_i$  [16].

The compact form of Eq. (2.1.2) is as a result of using system of atomic units, which is particularly adapted for working with quantum system. In this system, physical quantities are expressed as multiples of fundamental constants. The definition of

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atomic units used through out this chapter and there relations to the corresponding SI units are summarized in Table 2.1.1, where, a quantity  $Q$  in SI units is related to its value in atomic unit  $Q'$  by

$$Q = XQ'. \quad (2.1.4)$$

**Table 2.1.1: Conversion of atomic units to SI units.**

Quantity	Atomic unit	Value in SI unit (X)	Symbol(name)
mass	rest mass of electron	$9.1094 * 10^{-31} Kg$	$m_e$
charge	elementary charge	$1.6022 * 10^{-19} C$	$e$
angular momentum	$\frac{Planck's\ constant}{2\pi}$	$1.0546 * 10^{-34} Js$	$\hbar$
length	$\frac{4\pi\epsilon_0\hbar}{m_e e^2}$	$5.2918 * 10^{-11} m$	$a_o(\text{bohr})$
energy	$\frac{\hbar^2}{m_e a_o^2}$	$4.3597 * 10^{-18} J$	$E_h(\text{hartree})$

### 2.1.2 Multi-electron atom (Defining the system)

A multi-electron atom of atomic number  $Z$  contains a nucleus of charge  $+Ze$  surrounded by  $Z$  electrons each of charge  $-e$ . Every electron in this system moves under the influence of an attractive Coulomb interactions exerted by the nucleus, and the repulsive Coulomb interactions exerted by all the other  $Z-1$  electrons as mentioned in Eq. (2.1.2), as well as certain weaker interactions involving the angular momenta [15]. Our system that we have considered in this thesis, i.e., carbon is a multi electron atom with atomic number  $Z=6$ , and contains a nucleus of charge  $+Ze$  surrounded by  $Z=6$  electrons each of charge  $-e$ . The electrons in this multi electron atom is best expressed by the following two quantum mechanical properties.

---

### *Identical particles*

The question of "How to give an accurate quantum mechanical description of a system containing two or more identical particles, such as electrons?", is the very powerful question since it contains all the information we need for the description that we are going to give. But the question itself was born from the fact that our quantum mechanical systems contain identical particles like electrons, protons, or  $\alpha$ -particles.

Electrons are identical particles, meaning that any electron is exactly the same as any other electron. The wave functions associated with each electron, as described by the Schrödinger equation of quantum mechanics may lead to an overlapping of these wave functions. That makes it difficult to tell which wave function was associated correctly with which electron. From this difficulty one quantum mechanical aspect is born which describes identical particles. That is, identical particles are indistinguishable. So that eigenfunctions that carry the burden of describing a quantum mechanical system must be designed, in a way that they contain a mathematical expression of the above qualitative idea (indistinguishability property of identical particles) [15].

### *The exclusion principle*

Based on the analysis of data concerning the energy levels of atoms, in 1925 a famous exclusion principle that represents the property of electrons in any system was established.

The principle states that: ***In a multielectron atom there can never be more than one electron in the same quantum state.*** Equivalently the principle can be stated as, a system containing several electrons (identical-particles) must be

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described by an antisymmetric total eigenfunction [15]. We shall see later the meaning of antisymmetric eigenfunction.

## 2.2 Electronic Structure of the Problem

The foundation of the theory of electronic structure of matter is the non relativistic Shrödinger equation for the multi-electron wave function  $\Psi$  [17]. So our major goal in this electronic and structural calculation of carbon is to solve the non-relativistic time independent Shrödinger equation,

$$\hat{H}\Psi = E\Psi.$$

### 2.2.1 Born Oppenheimer Approximation

The Born-Oppenheimer approximation plays a vital role in electronic structure calculations. The main contribution of this approximation in electronic structure problem is that, it provides a method of separating the total eigen function of the quantum system as a sum of electronic and nuclear eigen functions (the qualitative rationalization to separate the movement of electrons and nuclei). The Shrödinger equation may be written more compactly as;

$$\hat{H} = \hat{T}_N(R) + \hat{T}_e(r) + \hat{V}_{eN}(r, R) + \hat{V}_{NN}(R) + \hat{V}_{ee}(r) \quad (2.2.1)$$

unfortunately, the  $\hat{V}_{ee}(r)$  term prevents us from separating  $\hat{H}$  in to nuclear and electronic parts, which would allow us to write the molecular wave function as a product of nuclear and electronic terms

$$\Psi_{total}(r, R) = \psi_{electronic}(r) * \psi_{nuclear}(R). \quad (2.2.2)$$

---

We thus introduce the Born-Oppenheimer approximation by which we conclude that this nuclear and electronic separation is approximately correct. The Born-Oppenheimer (BO) approximation rests on the fact that the nuclei are much more massive than the electrons. This allows us to say that the nuclei are nearly fixed with respect to electron motion.

So we can consider the electrons as moving in the field of fixed nuclei. This first step of the BO approximation is therefore often referred to as the clamped nuclei approximation. The nuclear kinetic energy is zero and their potential is merely a constant. Thus the Hamiltonian in Eq. (2.2.1) reduces to,

$$\hat{H}_{ele} = \hat{T}_e(r) + \hat{V}_{eN}(r, R) + \hat{V}_{ee}(r) \quad (2.2.3)$$

and the solution of the Schrödinger equation with  $\hat{H}_{ele}$ , is the electronic wave function  $\Psi_{ele}(r, R)$ , which describes the motion of the electrons and explicitly depends on the electronic coordinates ( $r$ ) but parametrically on the nuclear coordinates ( $R$ )

$$\hat{H}_{ele}\Psi_{ele}(r, R) = E_{ele}\Psi_{ele}(r, R). \quad (2.2.4)$$

This is the clamped nuclei Schrödinger equation.  $\hat{V}_{NN}(R)$  which is justified, since in this case  $R$  is just a parameter so that  $\hat{V}_{NN}(R)$  is just a constant and shifts the eigenvalues only by some constant amount.

The total energy is then the sum of  $E_{ele}$  and the constant nuclear repulsion term  $E_{nucl}$

$$E_{tot} = E_{ele} + E_{nucl}, \quad (2.2.5)$$

where from Eq. (2.1.2)

$$E_{nucl} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}. \quad (2.2.6)$$

---

In this step the nuclear kinetic energy is neglected, that is the corresponding operator  $\hat{T}_N(R)$  is subtracted from the total Hamiltonian. In the remaining electronic Hamiltonian ( $\hat{H}_{ele}$ ) the nuclear position enter as a parameter. The nucleus-electron interaction are not removed and the electrons still feel the Coulomb potential of the nuclei clamped at certain position in space [18-22]. Solving versions of Eq. (2.2.4) and Eq. (2.2.5) is the main focus of the research reported in this thesis and, indeed electronic structure calculations in general. The difficulties in solving Eq. (2.2.4) lies in the electron-electron interaction, which includes all the quantum effects of the electrons. Despite the intractable nature of these interactions, many approximate methods have been developed to solve Shrödinger-like equations. Among those approximate solutions, the ones made use of in this thesis, will be introduced in the following. However, the Slater determinant will be introduced first due to its fundamental role in many aspects of electronic structure theory.

## 2.2.2 Slater determinant

Before we are going to see the Slater determinant first let us see a way of writing non-interacting electron wave functions known as the Hartree products. To do so consider two electrons in a box where they are moving around and bouncing from the walls but they will not scatter from each other. We assumed that there is no interaction between the two particles, the particles move independently. The time-independent Shrödinger equation for our system of two noninteracting particles in three dimensions can be written,

$$\frac{-\hbar^2}{2m} \left( \frac{\partial^2 \Psi_T}{\partial x_1^2} + \frac{\partial^2 \Psi_T}{\partial y_1^2} + \frac{\partial^2 \Psi_T}{\partial z_1^2} \right) - \frac{\hbar^2}{2m} \left( \frac{\partial^2 \Psi_T}{\partial x_2^2} + \frac{\partial^2 \Psi_T}{\partial y_2^2} + \frac{\partial^2 \Psi_T}{\partial z_2^2} \right) + V_T \Psi_T = E_T \Psi_T, \quad (2.2.7)$$

---

where,

$m =$  the mass of either particle

$x_1, y_1, z_1 =$  the coordinates of particle 1

$x_2, y_2, z_2 =$  the coordinates of particle 2

$\Psi_T =$  the eigenfunction for the total system

$V_T =$  the potential energy for the total system

$E_T =$  the total energy for the total system .

The potential energy of the total system is then simply the sum of the potential energies of each particle in its interaction with the walls of the box, since the two particles move independently. There by, each potential energy will depend only on the coordinates of one particle. The particles are identical, so that the two potential energy functions are the same. Thus

$$V_T(x_1, \dots, z_2) = V(x_1, y_1, z_1) + V(x_2, y_2, z_2). \quad (2.2.8)$$

It is easy to show, by applying the technique of separation of variables, with the above potential there are solutions to Eq. (2.2.7) of the form,

$$\Psi_T(x_1, \dots, z_2) = \psi(x_1, y_1, z_1)\psi(x_2, y_2, z_2). \quad (2.2.9)$$

In addition, each requires one more quantum number to specify the orientation of the spin of the particle. We shall shorten the notation by using a single symbol, such as  $\alpha$ ,  $\beta$ , or  $\gamma$  etc., to designate a particular set of the four quantum numbers required to specify the space and spin quantum state of one of the particles. Thus  $\alpha$  for example,

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stands for a certain set of values of the four quantum numbers. Then a particular eigenfunction for particle 1 would be written,

$$\psi_\alpha(x_1, y_1, z_1), \tag{2.2.10}$$

we further shorten the notation by writing this as

$$\psi_\alpha(1).$$

This eigenfunction contains the information that particle 1 is in the space and spin quantum state described by  $\alpha$ . By the same method for particle 2 we have,

$$\psi_\beta(2).$$

The total eigenfunction  $\Psi_T(x_1, \dots, z_2)$  for the case in which particle 1 is in the state  $\alpha$ , and particle 2 is in the state  $\beta$ , is

$$\Psi_T(x_1, \dots, z_2) = \psi_\alpha(1)\psi_\beta(2). \tag{2.2.11}$$

This way of writing the total eigenfunction for non interacting electrons as a product of eigenfunction of each electron in the total system is known as the Hartree product. The next step is writing these non-interacting electron wave functions in a way that do not violate the symmetric property of electrons. According to the Pauli exclusion principle electrons are fermions. This requires that the wave function of electrons should be antisymmetric with respect to the interchange of the coordinates of any two electrons. To understand this in a simple way, let us see whether measurable quantities evaluated from these total eigenfunctions, depend on the assignment of the particle labels. The simplest measurable quantity is the probability density function. For the eigenfunction of Eq. (2.2.11), it is

$$\Psi_T^* \Psi_T = \psi_\alpha^*(1)\psi_\beta^*(2)\psi_\alpha(1)\psi_\beta(2). \tag{2.2.12}$$



---

By the indistinguishability property of electrons, the total eigenfunction can also be written as

$$\Psi_T(x_1, \dots, z_2) = \psi_\beta(1)\psi_\alpha(2). \quad (2.2.13)$$

For this eigenfunction we also have,

$$\Psi_T^* \Psi_T = \psi_\beta^*(1)\psi_\alpha^*(2)\psi_\beta(1)\psi_\alpha(2). \quad (2.2.14)$$

Since the two identical particles are indistinguishable, we should be able to exchange their labels without changing a measurable quantity such as the probability density.

When we perform this operation on Eq. (2.2.12) we have,

$$\psi_\alpha^*(1)\psi_\beta^*(2)\psi_\alpha(1)\psi_\beta(2) \longrightarrow \psi_\alpha^*(2)\psi_\beta^*(1)\psi_\alpha(2)\psi_\beta(1), \quad (2.2.15)$$

where, the expression on the left changes in to the expression on the right when 1 changes into 2 and 2 changes into 1. But the relabeled probability density function is not equal to the original probability density function. For instance, the first term in the relabeled function is  $\psi_\alpha^*$  evaluated at the coordinates  $x_2, y_2, z_2$ , while the first term in the original function is  $\psi_\alpha^*$  evaluated at the coordinates  $x_1, y_1, z_1$ . Thus a relabeling of the particles actually does change the probability density function calculated from the eigenfunction of Eq. (2.2.11). The same is true for the eigenfunction of Eq. (2.2.13). Therefore, we must conclude that these are not acceptable eigenfunctions for the accurate description of a system containing two identical particles. Since it violate the Pauli exclusion principle.

However, by using Slater determinant it is possible to write an eigenfunction that has the acceptable electronic symmetry property. Consider the following linear combination of the eigenfunction of Eq. (2.2.11)

$$\Psi_A = \frac{1}{\sqrt{2}}[\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)], \quad (2.2.16)$$

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this is called an antisymmetric total eigenfunction. By performing the evaluation for the probability density on the above antisymmetric total eigenfunction, we have

$$\Psi_A = \frac{1}{\sqrt{2}}[\psi_\alpha(1)\psi_\beta(2) - \psi_\beta(1)\psi_\alpha(2)] \longrightarrow \frac{1}{\sqrt{2}}[\psi_\alpha(2)\psi_\beta(1) - \psi_\beta(2)\psi_\alpha(1)] = -\Psi_A. \quad (2.2.17)$$

We see that the antisymmetric total eigenfunction  $\Psi_A$  is multiplied by minus one by an exchange of the particle labels. We then have for the probability densities,

$$\Psi_A^* \Psi_A \longrightarrow (-1)^2 \Psi_A^* \Psi_A = \Psi_A^* \Psi_A. \quad (2.2.18)$$

Hence, for the antisymmetric total eigenfunctions, the probability density functions are not changed by an exchange of the particle labels. This antisymmetric wave function can be rewritten as a determinant,

$$\Psi_A = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_\alpha(1) & \psi_\beta(1) \\ \psi_\alpha(2) & \psi_\beta(2) \end{vmatrix}, \quad (2.2.19)$$

and this is called a Slater determinant, where the factor  $2^{-\frac{1}{2}}$  is a normalization factor.

For an N-electron system, the Slater determinant becomes,

$$\Psi_A = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \dots & \psi_N(1) \\ \psi_1(2) & \psi_2(2) & \dots & \psi_N(2) \\ \cdot & \cdot & \dots & \cdot \\ \cdot & \cdot & \dots & \cdot \\ \psi_1(N) & \psi_2(N) & \dots & \psi_N(N) \end{vmatrix}. \quad (2.2.20)$$

Note that, the rows of the N-electron Slater determinant are labeled by electrons, and the columns are labeled by spin orbitales [15].

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### 2.2.3 The Hartree-Fock Approximation

In this section we will introduce the Hartree-Fock (HF) approximation. The HF approximation is the corner stone of almost all conventional, i.e., wave function based quantum mechanical methods, it is also of great conceptual importance. An understanding of the physics behind this approximation will thus be of great help in our later analysis of density functional theory. In the Hartree-Fock scheme the simplest, yet physically sound approximation to the complicated many-electron wave function is utilized. In its general formulation the approximation consists of approximating the N-electron wave function by an anti-symmetrized product of N one-electron wave functions  $\psi_i(\vec{x}_i)$  [23]. This product is usually referred to as a Slater determinant, as shown in Eq. (2.2.20).

To discuss the property of an interacting system, such as electrons in a molecule or solid, it is natural to consider the many-electron wave function,  $\Psi(r_1, r_2, \dots, r_N)$ , where the  $r_i$  denotes the particle coordinates and spins. In 1928 Hartree made the most widely used of all approximations for  $\Psi$ . In his contribution, Hartree approximated the many-electron wave function as a product of single-particle functions termed as Hartree product [24], i.e.,

$$\Psi(r_1, r_2, \dots, r_N) = \psi_1(r_1) \dots \psi_N(r_N). \quad (2.2.21)$$

In this Hartree product, each of the function  $\psi_i(r_i)$  satisfies a one-electron Schrödinger equation, with a potential term arising from the average field of the other electrons, i.e.,

$$\left[ \frac{-\hbar^2}{2m} \nabla^2 + V_{ext} + \Phi_i \right] \psi_i(r) = \epsilon_i \psi_i(r), \quad (2.2.22)$$

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where the Coulomb potential  $\Phi_i$  because of all the other N-1 electrons, is given by Poisson's equation,

$$\nabla^2\Phi_i = 4\pi e^2 \sum_{j=1, i \neq j}^N |\psi_j|^2, \quad (2.2.23)$$

and  $V_{ext}$  is the potential due to the nuclei. After expressing the electronic wave function as a single Slater determinant, the HF procedure will solve for those orbital which minimize the electronic energy based on variational method.

Generally this HF (self consistent field calculation) approximation, assumes that each electron interacts only with the average charge cloud (charge density) of the other electrons.

## 2.3 Density Functional Theory of Electronic Structure

The previous part of this chapter discussed about a basic quantum mechanical description and approach. For understanding a microscopic system, where the identical particles (electrons) moves under the influence of an external potential  $\nu(\vec{r})$ , and also the basics of electronic structure problem. We will see a detailed description about density functional theory (DFT) which is the corner stone of modern electronic and structural calculations, in solid state physics.

### 2.3.1 Thomas-Fermi theory

Unlike the conventional approach which uses the wave function  $\Psi$  as a central quantity, a different approach is taken by Thomas (1927) and Fermi (1927) [25], who proposed a scheme based on the density of electrons in the system,  $\rho(r)$ . This theory is

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regarded as ancestors of modern DFT. In the present context this approach is of only historical interest. So we refrain from an in-depth discussion of the Thomas-Fermi (TF) model, and restrict ourselves to a brief summary of the conclusions important to the general discussion of DFT.

The approach taken by TF is a quantum statistical model of electrons, which in its original formulation, takes in to account only the kinetic energy while treating the nuclear-electron and electron-electron contributions in a completely classical way. In this model, Thomas and Fermi arrive at the following very simple expression for the kinetic energy based on the uniform electron gas, a fictitious model system of constant electron density [26],

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r}. \quad (2.3.1)$$

If this is combined with the classical expression for the nuclear-electron attractive potential, and the electron-electron repulsive potential, we have the famous TF expression for the energy of an atom,

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} - Z \int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1d\vec{r}_2. \quad (2.3.2)$$

The importance of this equation is that, the energy is given completely in terms of the electron density  $\rho(\vec{r})$ . So this is the first expression of density functional for the energy. Because the total energy is given completely in terms of density only.

The next step is to find a strategy of how the correct density that we need to insert in to Eq. (2.3.2) can be identified. For this sake, the TF model employe the variational principle. According to variational principle, the ground state of the

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system is connected to the electron density for which the energy according to Eq. (2.3.2) is minimized under the constraint of,

$$\int \rho(\vec{r}_1) d\vec{r}_1 = N. \quad (2.3.3)$$

Generally in the TF model, the energy is given as a functional of density, and the variational principle is expressed in terms of density, which are completely a new expression. But the TF model has a limited use. Because,  $T_{TF}$  is only a very coarse approximation to the true kinetic energy and exchange and correlation effects are completely neglected [27-29].

### 2.3.2 The Hohenberg-Khon theorem

In the previous part we have seen that a way of writing an expression for the total energy of an atom in terms of density as a basic variable. Modern density functional theory was born in 1964 when a paper by Hohenberg and Khon appeared in the physical review [8].

In their paper, they demonstrated that ground state properties, particularly the total energy of a system of interacting particles, could be related in a rigorous fashion to the density distribution [8]. This sub section discusses the two key results of the Hohenberg-Khon (HK) theorem.

### 2.3.3 The first Hohenberg-Khon theorem

The first HK theorem [8] states that; the electron density,  $\rho(r)$ , determines the external potential because of the nuclei,  $V_{ext}(r)$ , and this density  $\rho(r)$ , determines N, the

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total number of electrons, via its normalization

$$\int \rho(r) dr = N, \quad (2.3.4)$$

and the two parameters  $N$  and  $V_{ext}(r)$  (determined from  $\rho(r)$ ) determine the molecular Hamiltonian, which determine the energy of the system via the Schrödinger's equation. Generally  $\rho(r)$  ultimately determines the system energy and all other ground state (GS) electronic properties. The first theorem may be summarized by saying that the energy is a functional of the density  $E[\rho]$ ,

$$E = E_V[\rho]. \quad (2.3.5)$$

The index "V" has been written to make explicit the dependency on  $V$ . Hohenberg and Khon [8] gave a straightforward proof of this theorem, which was generalized to include systems with degenerate states in proof given by Leavy in 1979 [30]. This part of the HK theorem was proved in a simple manner using the principle of reduction and absurdum, and this is derived for a non-degenerate system [8,16,31-32].

Suppose there is a collection of electrons enclosed in to a box influenced by an external potential  $\nu(r)$ . Consider the electron density of this system is known, and it determines  $\nu(r)$  and those all properties. If there is another external potential  $\nu'(r)$  which differs from  $\nu(r)$  by more than a constant that can also give the same electron density  $\rho(r)$  for the ground state, then we will have two different Hamiltonian  $\hat{H}$  and  $\hat{H}'$  whose GS electron density is the same. But the normalized wave function  $\Phi$  and

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$\Phi'$  would be different. Then we will have,

$$\begin{aligned} E_0 < \langle \Phi' | \hat{H} | \Phi' \rangle &= \langle \Phi' | \hat{H}' | \Phi' \rangle + \langle \Phi' | \hat{H} - \hat{H}' | \Phi' \rangle \\ &= E'_0 + \int \rho(r) [v(r) - v(r)'] dr, \end{aligned} \quad (2.3.6)$$

where  $E_0$  and  $E'_0$  are the ground-state energies for  $\hat{H}$  and  $\hat{H}'$  respectively. Similarly we can get,

$$\begin{aligned} E'_0 < \langle \Phi | \hat{H} | \Phi \rangle &= \langle \Phi | \hat{H}' | \Phi \rangle + \langle \Phi | \hat{H} - \hat{H}' | \Phi \rangle \\ &= E_0 + \int \rho(r) [v(r) - v(r)'] dr. \end{aligned} \quad (2.3.7)$$

Adding Eq. (2.3.6) and Eq. (2.3.7) we will obtain,

$$E_0 + E'_0 < E'_0 + E_0. \quad (2.3.8)$$

This is an obvious contradiction, so there are no two different external potentials that can give the same  $\rho(r)$ . Thus  $\rho(r)$  uniquely determines  $v(r)$  and all ground state properties. This statement can be defined pictorially as follows,

$$\rho(r) \rightarrow (v(r), N) \rightarrow H_{op} \rightarrow E.$$

So now we can write the energy  $E$  explicitly as a function of the electron density  $\rho(r)$ ,

$$\begin{aligned} E[\rho] &= T[\rho] + T_{ne}[\rho] + V_{ee}[\rho] \\ &= \int \rho(r) v(r) dr + F_{Hk}[\rho], \end{aligned} \quad (2.3.9)$$

where,

$$F_{Hk}[\rho] = T[\rho] + V_{ee}[\rho]. \quad (2.3.10)$$



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Here  $F_{HK}[\rho]$  is a universal functional and is valid for any number of particles and any external potential. And only dependent on  $\rho$ , and independent of any other external potential  $\nu(r)$ . While if it includes  $\nu$ , then it's not universal because  $\nu$  depends on the system [8].

### 2.3.4 The second Hohenberg-Khon theorem

Following from the first part of the theorem, in their second theorem, Hohenberg and Khon defines an energy functional in terms of the electron density for the system. Further proves that by taking the minimum of the energy functional according to the electron density, ground state energy can be found [33]. This is equivalent with saying that, ground state density can be found by using a variational principle [8]. Here by the variational ansatz we search for the  $\rho(r)$  which minimize the energy  $E$ . This is expressed as,

$$E_V[\rho_0] \leq E_V[\rho], \quad (2.3.11)$$

where  $\rho_0$  is GS density in potential  $\hat{V}$ , and  $\rho$  is some other density. From a calculation of the expectation value of a Hamiltonian with a trial wave function  $\Psi'$ , that is not its GS wave function  $\Psi_0$ , one can never obtain an energy below the true GS energy  $E_v[\rho_0]$ .

### 2.3.5 The Khon-Sham approach

Density functional theory is based on two pivotal theorems due to Hohenberg and Khon [34]. So practical implementation of DFT require an explicit construction of the HK free energy functional,  $F_{HK}[\rho]$  [35]. As discussed in the HK theorem above, and from the Schrödinger equation, we see that the energy functional contains

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three terms. The kinetic energy, the interaction with the external potential, and the electron-electron interaction as written in Eq. (2.3.9). The challenge of DFT lies in the HK universal functional of the density  $F_{HK}[\rho]$ , which is expressed as a sum of kinetic and electron-electron functionals as unknowns. The possibility of finding a good approximation to these functionals is the subject of much of current research to day [36]. Since it makes the minimization of the energy would be possible.

Kohn and Sham proposed the following approach to approximating the kinetic and electron-electron functionals [9]. The approach does not exclusively work in terms of the particle or charge density, but brings a special kind of wave functions (single-particle orbital) back in to the game. Generally mapping of an interacting many electron system ( $V_{ee} \neq 0$ ) in to a system with independent particles moving into an effective potential (non-interacting system,  $V_{ee} = 0$ ) is made. As a consequence, DFT then looks like an effective single-particle theory, although many-body effects are still-included via the so called exchange-correlation functional [9, 32, 37]. We will now see how this is done.

### 2.3.6 The Kohn-Sham equation

In 1964 Kohn and Sham published a paper in the physical review, which deals with the ground state of an interacting electrons gas in an external potential [9]. We shall be considering a collection of an arbitrary number of electrons, enclosed in a large box and moving under the influence of an external potential  $\nu(r)$ , and the mutual Coulomb repulsion. For such system based on DFT the energy functional is expressed as a sum of the external potential and a universal functional  $F[\rho]$ .

If  $F[\rho]$  were a known and sufficiently simple functional of  $\rho$ , the problem of determining the GS energy and density in a given external potential would be rather easy.

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Since it requires merely the minimization of a functional of the three dimensional density function. The major part of the complexities of the many electron problems are associated with the determination of the universal functional  $F[\rho]$ .

The Kohn-Sham (KS) exact energy functional is written as,

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho]. \quad (2.3.12)$$

In this equation,

$$T_s[\rho] = \frac{-1}{2} \sum_i^N \langle \phi_i | \nabla^2 | \phi_i \rangle = \frac{-\hbar^2}{2m} \sum_{i=1}^N \int d^3r \phi_i^*(r) \nabla^2 \phi_i(r), \quad (2.3.13)$$

is the kinetic energy of a system of non-interacting electrons, whose total GS density  $\rho(r)$  is constructed from a set of orbital,  $\phi_i(r)$ , the so called Kohn-Sham orbitals,

$$\rho(r) = \sum_{i=1}^N |\phi_i|^2. \quad (2.3.14)$$

The functional,

$$V_{ext}[\rho] = \int \rho(r) \nu(r) dr, \quad (2.3.15)$$

is the electrostatic energy of the electron density interacting with the external potential  $\nu(r)$ . The functional,

$$V_H[\rho] = \frac{1}{2} \int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2|} dr_1 dr_2, \quad (2.3.16)$$

is the electron-electron interaction considered as a classical Coulomb interaction or Hartree energy. The last term,  $E_{xc}[\rho]$ , incorporates everything else and is called the exchange correlation energy. It is the only term that is unknown. In a way, the

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KS method packs all the complexity of the total energy function in the exchange-correlation functional [34].

Writing the energy functional explicitly in terms of density built from non-interacting orbital's, and applying the variational theorem, we find that the orbital's which minimize the energy satisfy the following set of equations,

$$\left[\frac{-1}{2}\nabla^2 + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + \nu_{xc}(r)\right]\phi_i(r) = \varepsilon_i\phi_i(r), \quad (2.3.17)$$

where,

$$\nu_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta \rho}, \quad (2.3.18)$$

is the local multiplicative potential (local exchange correlation potential), which is the functional derivative of  $E_{xc}$  with respect to density.

## 2.4 Approximation to Density Functional Theory

In the KS approach two main approximations were made. One is made for the complex electron-electron interaction, which is considered as a classical Coulomb interaction, and the other is made for treating the kinetic energy functional of interacting electrons,  $T[\rho]$ . According to KS approach the accurate scheme for treating this kinetic energy functional is, based on decomposing it into one part that represent the kinetic energy of non interacting particles of density  $\rho$ , i.e., the quantity called  $T_s[\rho]$ , and one that represent the remainder (error), denoted by  $T_c[\rho]$ ,

$$T[\rho] = T_s[\rho] + T_c[\rho]. \quad (2.4.1)$$

The subscripts s and c stand for single-particle and correlation respectively [32]. So the exchange-correlation energy functional introduced in the KS equations, by

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definition contains the differences  $T - T_s$  which is equal to  $T_c$  and  $V - V_H$ . This definition shows that a significant part of the correlation energy  $E_c$ , is due to the difference  $T_c$  between the non-interacting and interacting kinetic energy. In simple term,  $E_{xc}$ , is simply the sum of the error made in using a non-interacting kinetic energy and the error made in treating the electron-electron interaction classically. This term divided into two parts,

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho], \quad (2.4.2)$$

where  $E_x$  is due to the pauli principle (exchange energy) and  $E_c$  is due to correlation. But for both parts no general exact expression in terms of the density is known. In this sense KS density functional theory is an empirical methodology, since we do not know the exact functional. However, the functional is universal [38]. In practice, the utility of DFT rests on the approximation used for  $E_{xc}[\rho]$ . The approximations to DFT discussed below are often referred to as ab initio or first principles methods.

### 2.4.1 The local density approximation for $E_{xc}[\rho]$

The generation of approximations for  $E_{xc}$  has led to a large and still rapidly expanding field of research. As a practical approximate expression for  $E_{xc}[\rho]$ , Khon and Sham [9] suggested what is known in the context of DFT as the local density approximation (LDA) [35]. In the LDA the exchange-correlation energy is [23, 39],

$$E_{xc}[\rho] \approx E^{xc-LDA}[\rho] = \int \rho(r) \varepsilon^{xc-LDA}(\rho(r)) d^3r \quad (2.4.3)$$

this formula of LDA is determined by properties of uniform electron gas. It is a system in which the electrons sit in an infinite region of space, with a uniform positive external potential, chosen to preserve overall charge neutrality [40]. The corresponding xc

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potential is simply,

$$V_{xc}^{LDA}[\rho](r) = \left. \frac{\partial \varepsilon_{xc}(\rho)}{\partial \rho} \right|_{\rho \rightarrow \rho(r)}. \quad (2.4.4)$$

In this LDA, the interesting point is that, the understanding of formulas originally derived for the uniform electron gas works so well for such nonuniform systems as atoms and molecules [37]. In the early 1920's Thomas and Fermi studied the homogeneous electron gas [25]. In the Thomas and Fermi study the exchange and correlation effects are neglected and the electron-electron interaction is approximated by the classical Hartree potential [25].

Under this conditions, the dependency of the kinetic and exchange energy on the density of the electron gas can be extracted and expressed in terms of a local functions of the density. This suggests that in the inhomogeneous system we might approximate the functional as an integral over a local function of the charge density. Using the kinetic and exchange energy density of the non-interacting homogeneous electron gas this leads to,

$$T[\rho] = 2.87 \int \rho^{\frac{5}{3}}(r) dr, \quad (2.4.5)$$

and,

$$E_x[\rho] = 0.74 \int \rho^{\frac{4}{3}}(r) dr. \quad (2.4.6)$$

These results are a representation for  $E_{xc}$  in an inhomogeneous system. So as shown in Eq. (2.4.3) the local exchange correlation energy per electron is approximated as a simple function of the local charge density  $\varepsilon^{xc-LDA}(\rho(r))$ , where,

$$\varepsilon^{xc-LDA}(\rho) = \varepsilon^{x-LDA}(\rho) + \varepsilon^{c-LDA}(\rho), \quad (2.4.7)$$

this  $\varepsilon^{xc-LDA}(\rho)$  is the exchange-correlation energy per electron in a uniform electron

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gas of density  $\rho$ , and computed accurately at densities of interest, using Monte Carlo techniques [39]. Its exchange part leads to,

$$\varepsilon^{x-LDA}(\rho) = \frac{-3}{4\pi}(3\pi^2\rho)^{\frac{1}{3}}, \quad (2.4.8)$$

and for the correlation,  $\varepsilon^{c-LDA}$ , the functional form is unknown, and has been simulated for the homogeneous electron gas in numerical quantum Monte Carlo calculations which yields essentially exact result [38, 41].

For many decades the LDA has been applied in, e.g., calculations of band-structure and total energies in solid state physics [32].

#### 2.4.2 The generalized gradient approximations for $E_{xc}[\rho]$

The previous LDA is based on a reference system of homogeneous electron gas, in which the exchange-correlation energy only depends on the local density, and approximation shows that homogeneous system has properties which are also exact for the inhomogeneous system. More importantly it restricts and guides the search for more accurate practical approximations. Since it has its own success and failure [35, 42], a discussion on the success and faller of LDA can be found in Ref. [42] and references therein.

The first logical step to go beyond LDA is the use of not only the information about the density  $\rho(r)$  at a particular point  $\vec{r}$ , but to supplement the density with information about the gradient of the charge density,  $\nabla\rho(\vec{r})$  in order to account for the non-homogeneity of the true electron density. It is based on a description of exchange-correlation energies in reciprocal space. Thus, we write the exchange-correlation energy in the following form termed generalized gradient approximation

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(GGA) [39, 42],

$$E_{xc}[\rho] \simeq E^{xc-GGA}[\rho] = \int \rho(r) \varepsilon^{xc-GGA}(\rho(r), |\nabla\rho(r)|) d^3r. \quad (2.4.9)$$

As shown in Eq. (2.4.9), in a GGA the xc functionals depends on the density and its gradient [39]. This reciprocal-space approach (GGA) is the most successful ab initio DF method, and which have succeeded in reducing the errors of LDA for many properties. For example, for the, binding energy, GS energy, and geometries of molecules, the GGAs can yield better results than the LDAs [31, 35, 42].

Different functionals within this non-local (GGA) approximations family have been developed, for different problems, like, the band-gap problem, the symmetry problem, the long-range problem, the near degeneracy problem, the surface problem, and the core problem. A discussion of the various GGAs family can be found in Ref. [43-45].

## 2.5 Plane-Waves and Pseudo-Potentials

We now turn to the more practical problem of how the strategies developed so far, can be mapped on to computational schemes, for solving the one electron Kohn-Sham equations. In the practical application of DFT basis sets and pseudo-potential need to be considered. In calculations of solids or condensed matter, which will be the main types of systems that DFT is applied to, in this Thesis, plane-wave basis set is a very common choice. In many cases, combined with plane-wave is the pseudo-potential approach for treating the strong interactions between core electron and nuclei. We will now briefly discuss plane-waves and then pseudo-potentials.



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### 2.5.1 Plane wave basis set

A different DFT based computer program have been developed to solve the one electron KS equations,

$$\left[-\frac{\nabla^2}{2} + v_{ks}[\rho](r)\right]\phi_i(r) = \varepsilon_i\phi_i(r). \quad (2.5.1)$$

Among those codes a PWscf (a plane-wave DFT code) code [46], is used in this thesis. To calculate the total energy of solids, a plane wave expansion of the KS wave functions is very useful as it takes advantage of the periodicity of the crystal [27,47-48]. 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 vectors [31]. According to Bloch's theorem [49], the KS wave functions  $\phi_{k,n}(r)$ , can be written as,

$$\phi_{k,n}(r) = e^{ik \cdot r} \mu_{nk}(r), \quad (2.5.2)$$

where  $k$  is the wave vector,  $n$  is the band index, and  $\mu_{nk}(r)$  is a function with the same periodicity as the potential  $U(r)$ , that  $\mu_{nk}(r+R) = \mu_{nk}(r)$ . Furthermore,  $\mu$  can be expanded as,

$$\mu_{ik} = \frac{1}{\Omega_{cell}} \sum_m c_{i,m} e^{iG_m \cdot r}, \quad (2.5.3)$$

where  $G$  is the reciprocal lattice vector and  $\Omega = N_{cell}\Omega_{cell}$ . Here  $\Omega$  is the whole volume.

We aim to solve the following Schrödinger-like equation (one electron KS equation) where each electron move in effective potential  $V_{eff}(r)$ ,

$$\hat{H}_{eff}\phi_i(r) = \left[-\frac{1}{2}\nabla^2 + V_{eff}(r)\right]\phi_i(r) = \varepsilon_i\phi_i(r). \quad (2.5.4)$$

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By the Bloch theorem in Eq. (2.5.2), the eigenfunctions can be written as

$$\phi_i(r) = \sum_q c_{i,q} \frac{1}{\Omega} e^{iq \cdot r} = \sum_q c_{i,q} \times |q\rangle. \quad (2.5.5)$$

Here  $c_{i,q}$  are the expansion coefficients and  $q = K + G$ , in the basis of the orthonormal plane-wave  $|q\rangle$  satisfying

$$\langle q'|q\rangle = \frac{1}{\Omega} \int e^{iq' \cdot r} e^{iq \cdot r} = \delta_{q'.q}. \quad (2.5.6)$$

Inserting Eq. (2.5.5) into Eq. (2.5.4) with the orthogonality of Eq. (2.5.6) and multiplying from the left by  $\langle q'|$ , leads to the Schrödinger-like equation in Fourier space,

$$\langle q'|[\frac{-1}{2}\nabla^2 + V_{eff}(r)]|q\rangle = \varepsilon_i \langle q'|q\rangle c_{i,q} = \varepsilon_i c_{i,q}. \quad (2.5.7)$$

Considering each term in the Hamiltonian. The first term, kinetic energy operator can be written as,

$$\langle q'|[\frac{-1}{2}\nabla^2]|q\rangle = |q|^2 \delta_{q.q'}. \quad (2.5.8)$$

Second, for a crystal, the periodic potential  $V_{eff}(r)$  can be expressed as a sum of Fourier components,

$$V_{eff}(r) = \sum_m V_{eff}(G_m) e^{iG_m \cdot r}. \quad (2.5.9)$$

Together with Eq. (2.5.8) and Eq. (2.5.9), Eq. (2.5.5) can be rewritten as

$$H_{m,m'}(K) c_{i,m'}(K) = \varepsilon_i(K) c_{i,m'}(K), \quad (2.5.10)$$

where

$$H_{m,m'} = \langle K + G_m | \hat{H}_{eff} | K + G'_m \rangle = |K + G_m|^2 + V_{eff}(G_m - G'_m). \quad (2.5.11)$$

Here  $q$  has been expanded as  $K + G$ . Eq. (2.5.10) and Eq. (2.5.11) are the basic Schrödinger-like equations of a periodic crystal with a plane-wave basis set [27, 31].

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## 2.5.2 Pseudo-potential

The many-electron Schrödinger equation can be very much simplified if electrons are divided into two groups: valence electrons and inner core electrons. The electrons in the inner shells are strongly bound and do not play a significant role in the chemical binding of atoms. This suggests the description of an atom based solely on its valence electrons, which feel an effective potential including both the nuclear attraction and the repulsion of the inner electrons. So, in metals and semiconductors, the physical and chemical properties are almost completely due to the valence electrons. This separation is very important in electronic structure calculation. Because, the valence wave-functions of the large  $Z$  atoms oscillate strongly in the vicinity of the atomic core due to the orthogonalization to the inner electronic wave-functions. To describe these oscillations a large number of plane-waves is required, difficulting the calculation of the total energy. This separation suggests that inner electrons can be ignored in a large number of cases, thereby reducing the atom to a ionic core that interacts with the valence electrons. Such an approximation, that approximates the potential felt by the valence electrons is known as a pseudo-potential. It was first proposed by Fermi in 1934 [27, 50].

### **Ab-initio pseudo-potentials**

Pseudo-potential schemes have been used widely in calculations of the electronic properties of semiconductors and their interfaces, in order to eliminate numerical difficulties, arising from the core electrons and the requirement of orthogonality [51]. To describe the valence charge density accurately, a more realistic pseudo-potentials were given by Topp and Hopfield [27,52-53]. Modern pseudo-potentials are obtained

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by forcing the pseudo wave-functions to coincide with the true valence wave-functions beyond a certain distance  $r_l$ . The pseudo wave-functions are also forced to have the same norm as the true valence wave-functions.

In its mathematical form it is expressed as: if  $r > r_l$ ,

$$R_l^{PP}(r) = R_{nl}^{AE}(r), \quad (2.5.12)$$

if  $r < r_l$ ,

$$\int_0^{r_l} dr |R_l^{PP}(r)|^2 r^2 = \int_0^{r_l} dr |R_{nl}^{AE}(r)|^2 r^2, \quad (2.5.13)$$

where,  $R_l(r)$  is the radial part of the wave-function with angular momentum  $l$ , and PP and AE denote, respectively, the pseudo wave-function and the true (all-electron) wave-function. The index  $n$  in the true wave-functions denotes the valence level. In addition to the above two equations, the pseudo-potential must fulfill the following two conditions. First, the pseudo wave-functions should not have nodal surfaces, and second, the pseudo energy-eigenvalues should match the true valence eigenvalues, i.e.,

$$\varepsilon_l^{PP} = \varepsilon_{nl}^{AE}. \quad (2.5.14)$$

The potentials, contracted in such a way are called norm-conserving pseudo-potentials, and are semi-local potentials that depend on the energies of the reference electronic levels,  $\varepsilon_l^{AE}$ . It is the type of pseudo-potential used in this thesis.

In general, to obtain the pseudo-potential, first, the free atom Kohn-Sham radial equations are solved taking into account all the electrons. And then using Eq. (2.5.12) and Eq. (2.5.13) (norm-conservation), the pseudo wave-functions are determined. From this pseudo wave-functions, the pseudo-potential is calculated based on, the inversion of the radial Kohn-Sham equation for the pseudo wave-function and the

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valence electronic density,

$$\omega_{l,scr}(r) = \varepsilon_l^{PP} - \frac{l(l+1)}{2r^2} + \frac{1}{2rR_l^{PP}(r)} \frac{d^2}{dr^2} [rR_l^{PP}(r)]. \quad (2.5.15)$$

The resulting pseudo-potential,  $\omega_{l,scr}(r)$ , still includes screening effects due to the valence electrons that have to be subtracted to yield

$$\omega_l(r) = \omega_{l,scr}(r) - v_H[\rho^{PP}](r) - v_{XC}[\rho^{PP}](r). \quad (2.5.16)$$

The quality or accuracy of the pseudo-potential constructed by such procedure, is measured by the cutoff radii,  $r_l$ , we chose. Because the cutoff radii establishes the region where the pseudo and true wave-functions coincide. We have two way of choosing this cutoff radii. First, the minimum possible value is determined by the location of the outermost nodal surface of the true wave-functions. For cutoff radii close to this minimum, the pseudo-potential is very realistic, but also very strong. Second, very large cutoff radii are chosen, and the pseudo-potentials will be smooth and almost angular momentum independent, but also very unrealistic. For a plane-wave basis calculations this second way of choosing cutoff radii is appropriate. Since smooth potential leads to a fast convergence of plane-wave basis calculations. So our educational guess (choice) of cutoff radii, must meet our need to basis-set size and pseudo-potential accuracy [27, 51, 54].

Generally, as discussed above most physically interesting properties of solids are determined by the valence electrons rather than the core electrons. But in a first principle calculation, the deeply bound core electrons within plane-wave basis sets, require a huge amount of basis functions for their description. This leads to the fact that less important core electrons will consume a lot of computational cost. To alleviate this problem, the pseudo-potential approximation replaces the strong

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ionic potential with a weaker pseudo-potential. So the combination of DFT, plane-wave basis set, and pseudo-potentials has become a well-established methodology in electronic structure calculations of condensed matter [31, 55, 56].

# Chapter 3

## Materials and Methodology

### 3.1 Materials

The study is purely theoretical for understanding the structural and electronic property of carbon, an intensive literature review is carried out. The main sources of literature review are the published articles, books, thesis and dissertations. Latex software and computers are additional instruments used to accomplish this project.

### 3.2 Methodology

#### 3.2.1 Theoretical method

In this Thesis first-principles (ab-initio) calculations are used for performing the structural and electronic properties of carbon. This method of calculation is based on density functional theory, that is the structural and electronic property of carbon is obtained based on the principles of density functional theory.

#### 3.2.2 Computational method

The calculation is performed computationally using QUANTUM ESPRESSO [46], which is an open-source package for research in electronic structure, simulation and

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Optimization. The QUANTUM ESPRESSO distribution [46] contains the core packages PWscf (Plane-Wave Self-Consistent Field) and CP (Car-Parrinello) for the calculation of electronic-structure properties within density-functional theory using a plane-Wave (PW) basis set and pseudo-potentials. In this Thesis the PWscf package is used.



# Chapter 4

## First Principle Calculation of Structural and Electronic Properties of Carbon

### 4.1 Conceptual Framework and Work Package

In this thesis density functional theory with the help of Quantum Espresso [46] was used to calculate the structural and electronic properties of carbon. The plane wave self-consistent field (PWSCF) code is employed as our first principle energy code. PWSCF is a first principle energy code that uses norm conserved pseudo-potential (PP) and ultra-soft pseudo-potentials (US-PP) with in density functional theory. The pseudo-potential theory is based on the ansatz which separate the total wave function in to an oscillatory and smooth part (Pseudo wave function). The strong true potential of the atom is replaced by a weaker potential valid for the valence electrons, the pseudo-potentials which approaches the unscreened Coulomb potential. The main feature of Pseudising process is to eliminate the strong Coulomb potential within the core region. Thus, the norm conserved pseudo-potentials with Perdew Zunger (PZ) version of the local density approximation (LDA) exchange correlation functional

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and the ultra-soft pseudo-potentials with Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange correlation functional are employed respectively. Carbon has a diamond structure with face-centered cubic (FCC). The states  $2s^2 2p^2$  will be treated as a valance electrons.

For choice of plane wave basis set, the cutoff kinetic energy at 20 Ry, and the cutoff charge density at 250 Ry is used as trial cutoff energy and charge density respectively. For  $\vec{k}$ -point sampling of bulk carbon we start with Monk Horst Pack mesh grid (4x4x4). The convergence issue will be checked in two ways. The minimum total energy will be found by varying cutoff energy (ecutwfc) for fixed Monk Horst Pack mesh. Moreover, the minimum total energy will be obtained by varying the Monk Horst Pack mesh grid or the  $\vec{k}$ -point sampling for fixed cutoff energy.

## 4.2 Results and Discussion

### 4.2.1 Total energy of carbon with respect to cutoff energy

In this part of the calculation the total energy of carbon is performed as a function of cutoff energy. An increment of cutoff energy made until the values of total energy comes to a common value or equivalently until convergence is achieved. While changing the cutoff energy, the lattice constant and the  $\vec{k}$ -point are fixed respectively. In this research we have considered the diamond structure of carbon for total energy calculation, the lattice constants  $a = b = c = a_o = 6.6$  and the  $\vec{k}$ -points are  $4 \times 4 \times 4$ . The total energy versus cutoff energy is shown in the Figure 4.1, in this calculation, the converged cutoff energy appears to be approximately at 170 Ryd for the given lattice constant and  $\vec{k}$  - point grid. The trend of the graph in Figure 4.1 shows that

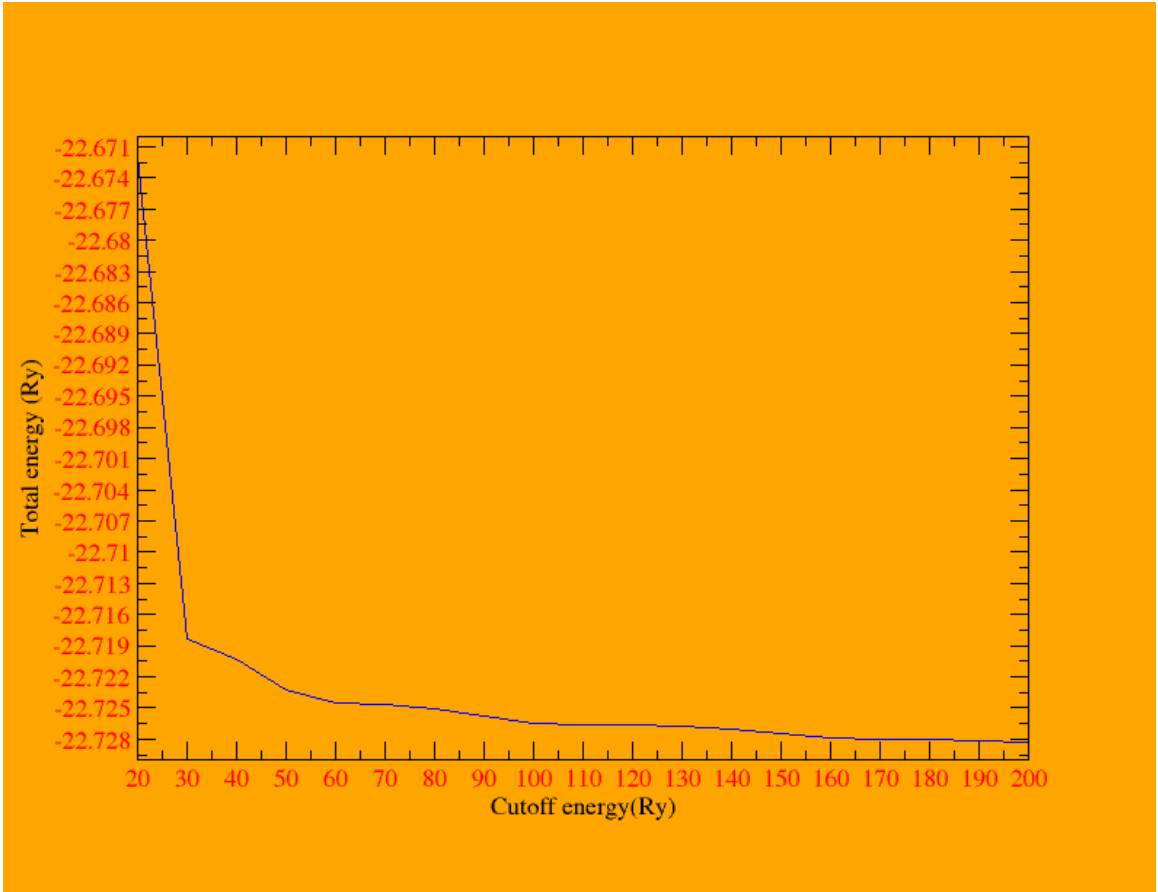


Figure 4.1: Total energy of carbon versus cutoff energy

the total energy is monotonically decreasing with increasing cutoff energy. This behavior is the direct result of variational principle. The accuracy of the ground state energy depends on the number of basic functions or plane waves. As the number of basic functions approach to infinity we can get the energy that close to the ground state energy.

#### 4.2.2 Total energy of carbon with respect to $\vec{k}$ -point sampling

In this part the total energy of carbon is calculated as a function of  $\vec{k}$ -points. The other parameters such as lattice constant, cutoff energy etc. are made fixed. That is

the lattice constant  $a = b = c = a_o = 6.6$  and from the previous convergency test of total energy with respect to cutoff energy, we fix cutoff energy to be 170 Ryd. The total energy of carbon versus  $\vec{k}$ -points grid size is shown in Fig.4.2.

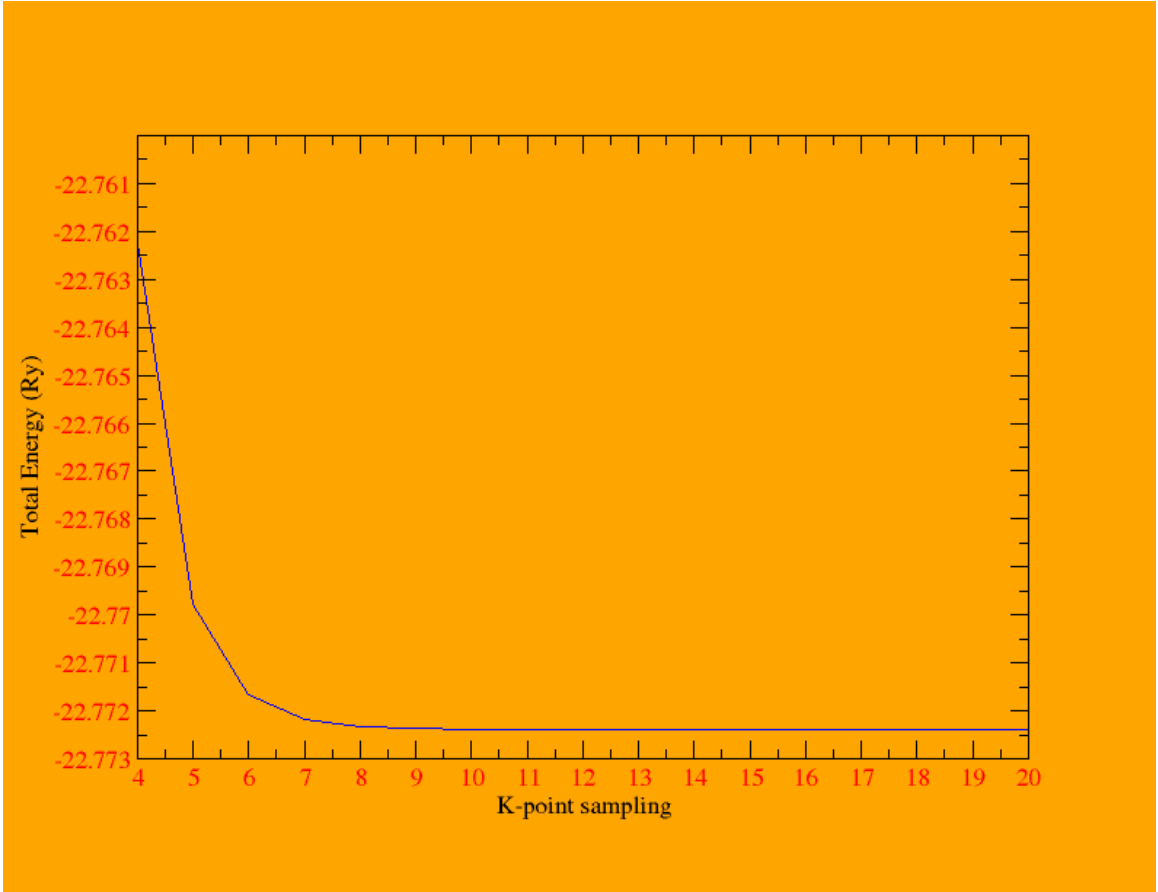


Figure 4.2: Total energy of carbon versus  $\vec{k}$ -points grid

As it can be observed that the total energy of carbon converges at  $9 \times 9 \times 9$   $\vec{k}$ -points grid, for the fixed lattice constant and cutoff energy.

### 4.2.3 Convergency of force with respect to cutoff energy

In the previous calculations, the forces on carbon are zero in x, y, and z directions. However it is possible to create forces by displacing one of the atom in a unit cell

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which is previously located at  $(0.25, 0.25, 0.25)$  along the Z axis with a displacement of  $0.05bohr$ . We calculated force on carbon as a function of cutoff energy by keeping other parameters fixed. For this calculation, we used the lattice constants  $a = b = c = a_o = 6.6$  and from the previous calculation of total energy with respect to  $\vec{k}$ -points sampling, we used the  $\vec{k}$ -points grid at  $9 \times 9 \times 9$  respectively. Fig.4.3 shows the convergency of force with respect to cutoff energy.

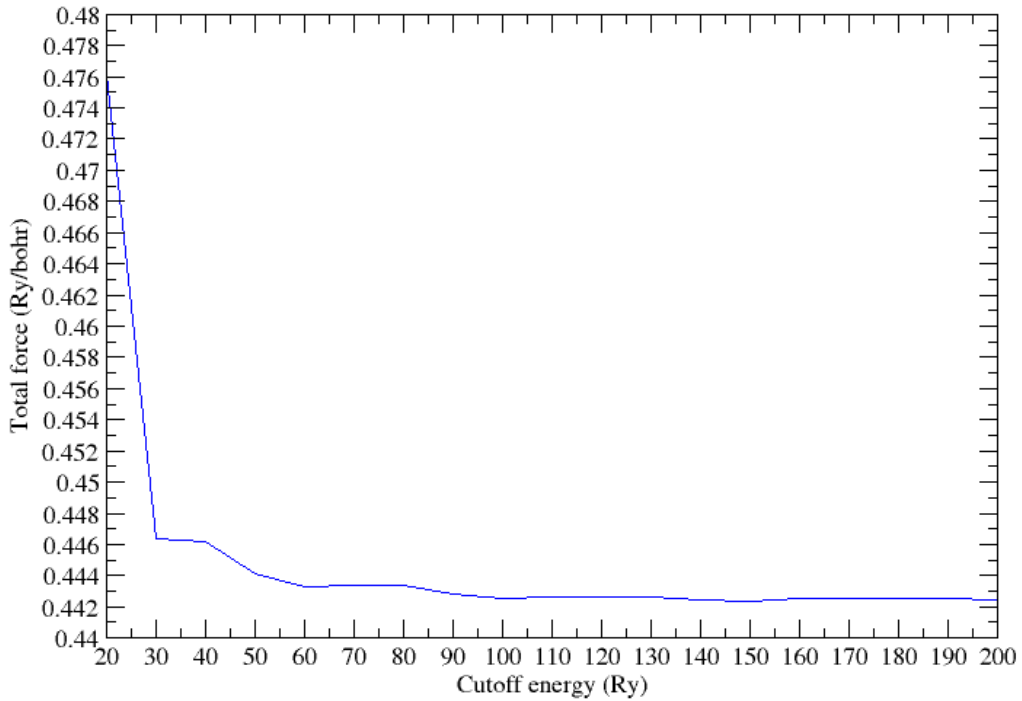


Figure 4.3: Force of carbon versus cutoff energy

It is clearly shown that convergence is achieved when the cutoff energy is equal to 100 Ryd. The force at this cutoff energy is 0.442528 Ryd/bohr.

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#### 4.2.4 Convergency of force with respect to $\vec{k}$ -points grid size

In this part, we have calculated the force on the displaced carbon atom as a function of  $\vec{k}$ -points. By fixing the other parameters such as a lattice constant  $a = b = c = a_o = 6.6$  bohr and cutoff energy is 170 Ryd. Figure 4.4 shows the convergency of force with respect to  $\vec{k}$ -points grid size.

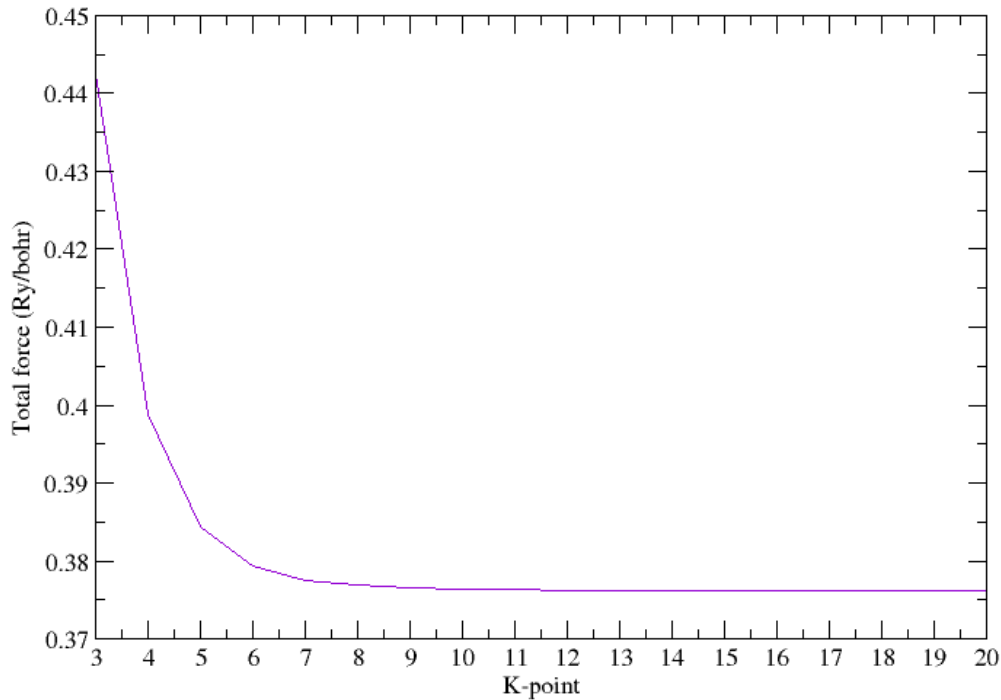


Figure 4.4: Force of carbon versus  $\vec{k}$ -points grid size

From the Figure it is clear that the convergency of force at 170 Ryd was achieved at grid size of  $9 \times 9 \times 9$ .

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### 4.2.5 Structural (Equilibrium lattice constant) property of carbon

In this part of the calculation, the theoretical value of equilibrium lattice constant of carbon at which the minimum energy can be found, is done by varying the lattice constant from 6 to 7 Bohr in steps of 0.05 bohr. From the previous calculation of convergency test of total energy we fixed the cutoff energy at 170 Ryd and the  $\vec{k}$ -point at  $14 \times 14 \times 14$ . Fig.4.5 shows the equilibrium lattice constant of carbon.

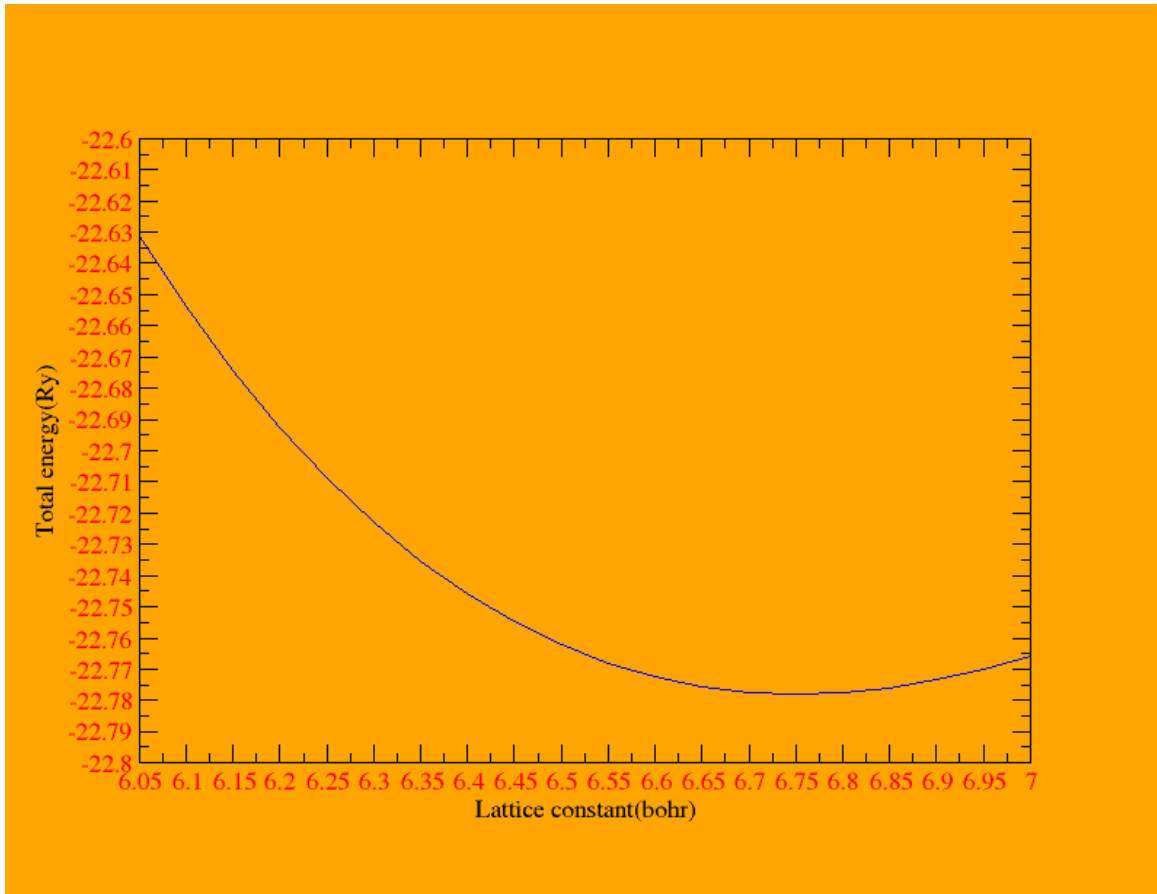


Figure 4.5: Total energy of carbon versus lattice constant

It is clearly shown in the above graph that the minimum energy of carbon, which

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is face-centered cubic (FCC) diamond structure, is found for theoretical value of equilibrium lattice constant  $a = 6.75bohr$  which is very close to the experimental value of lattice constant for carbon (diamond structure) of  $6.740331832 = 6.74bohr$  [24].



# Chapter 5

## Conclusion

The structural and electronic properties of carbon have been theoretically studied, within the frame work of the density functional theory, plane wave basis set and pseudo-potentials. The norm conserved pseudo-potentials with Perdew Zunger (PZ) version of local density approximation (LDA) and the ultra-soft pseudo potentials with Perdew-Bureke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA) exchange-correlation functional are employed respectively. The total energy calculation using a unit cell containing 2 atoms is performed as a function of cutoff energy and Monk Horst Pack mesh grid respectively fixing the other parameters constant. Energy convergence is achieved, at the energy cutoff 170 Ryd for the first case and at  $9 \times 9 \times 9$   $\vec{k}$ -point grid for the second case. The total force on carbon as a function of cutoff energy and Monk Horst Pack mesh is calculated by displacing one of the carbon atom in a cell, which is located at (0.25,0.25,0.25) along the z-axis with a displacement of 0.05 bohr. Total force convergence is achieved for the cutoff energy 100 Ryd and for Monk Horst Pack mesh at  $9 \times 9 \times 9$   $\vec{k}$ -point grid. Our numerical calculation shows that the theoretical value of equilibrium lattice constant is at  $a = b = c = a_o = 6.75$  bohr. This result is in good agreement with experimental

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results which is  $a = b = c = a_o = 6.74$  bohr.

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

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

Name: Dr.Menberu Mengesha

Signature: \_\_\_\_\_

Place and date of submission:

Department of Physics

Jimma University

September, 2017



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Course Code	Course Title	Cr. hr	Number Grade	Rank **	Remark
<b>Phys799</b>	<b>MSc. Thesis</b>	<b>6</b>	<b>85.95</b>	<b>Excellent</b>	

\*\* Excellent, Very Good, Good, Satisfactory, Fail.

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