



**FIRST PRINCIPLE CALCULATION OF $Al(100)$
SURFACE USING QUANTUM ESPRESSO
PACKAGE**

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Abstract

In this thesis the first principle calculation of Aluminum surface($Al(100)$) is investigated with density functional theory (DFT) using Quantum Espresso package. Our study is based on Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set implemented in the Quantum-ESPRESSO package. The calculation of the total minimum energy and the total minimum force of $Al(100)$ is calculated as a function of cutoff energy and K-points sampling. The total minimum values are selected at the points of convergence. These convergence values are then used as inputs for the calculation of equilibrium lattice constant, energy band gap and density of state of $Al(100)$. However, this trend can not be predicted from increasing the k-points sampling. Moreover, the equilibrium lattice constant is calculated using results obtained from energy convergence test (i.e., 50 Ry and $17 \times 17 \times 1$). The calculated values of the equilibrium lattice constant are $a = 5.420$ bohr and $c = 6.36$ bohr. They are closer to the experimental value of $a = 5.22$ bohr and $c = 6.48$ bohr. Finally, discussing band structure and density of state of two dimensional $Al(100)$, the electrical property of two dimensional $Al(100)$ is determined based on energy band gap.

Keywords: Aluminum surface, density functional theory, electronic structure, total energy

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Chapter 1

Background of the Study

1.1 Introduction

Aluminum is the third most abundant element in the earth's crust after oxygen and silicon [1]. It has a density of $2.70g/cm^3$. Therefore, a piece of aluminum of volume $10.0cm^3$ has a mass of 27.0 g [2]. By mass Aluminum makes up about 8.3% of the earth crust. It is never found free in nature and found in most rocks, particularly igneous rocks as aluminum silicate minerals. It is a light metal that is easy to melt, odorless, tasteless, nontoxic, non-magnetic materials and has a high electrical conductivity.

Aluminum is remarkable for its low density and its ability to resist corrosion. The Density of aluminum is $2.7g/cm^3$ about 1/3 that of steel much lower than other commonly encountered metals. Its low density compared to the most other metals arise from the fact that its nucleus are much lighter. It is not as strong or stiff as steel, but the low density make up for this in the aerospace industry and for many other applications where light weight is crucial. Pure aluminum is quite soft and lacking in strength. In most application various aluminum alloys are used instead because of their higher strength and hardness. Aluminum is an excellent thermal and electrical

conductor, having 59% the conductivity of copper, both thermal and electrical, while having only 30% of copper density. Aluminum is capable super conductivity, with a super conducting critical temperature of (1-2)Kelvin and critical magnetic field about 100 gauss [3]. It is one of the most important metals in modern engineering industry due to superior physical and mechanical properties. It's corrosion resistance is based on compact and chemically stable passive oxide film that is spontaneously formed on the surface [28]. It is also an interesting one which is commonly used for making an electrode in the low-cost electric devices [4].

Density - function theory (DFT) is one of the most popular success-full quantum mechanical approaches to matter [5]. The Density that minimizes the total energy is the exact ground state density. The basic theory of DFT was proposed by Kohn and Sham who simplified [6]. The first principle calculation is to find the geometric construction, electronic structure, thermodynamic properties, and Optical properties, so on by solving Schrödinger equation with self consistent based on atomic components [7]. The first principle calculation of electronic surface was studied by different scholars analytically. However, the first principle calculation of $Al(100)$ (surface) is not well studied computationally. So the aim of this research was study $Al(100)$ surface based on density functional theory using quantum espresso package.

Electrons and nuclei are the fundamental particles that determine the nature of the matter of our everyday world: atoms, molecules, condensed matter, and man-made structures. The theory of electrons in matter ranks among the great challenges of theoretical physics: to develop theoretical approaches and computational methods that can accurately treat the interacting system of many electrons and nuclei found in condensed matter and molecules.

1.2 Statement of problem

Recently, there is an interest to know the structure and electronic property of materials to design electronic devices for technological applications. On the other hand the Schrödinger equation of many electron problems were difficult to solve analytically as well as the usual numerical methods. This challenge to solve many electron problems can be resolved by modern computational techniques such as density functional theory. So the purpose of this study was to investigate the structural and electronic property of $Al(100)$ surface using density functional theory.

1.3 Objectives

1.3.1 General Objective

The general objective of this thesis was studying the structural and electronic properties of Aluminum surface $Al(100)$ using Density functional theory implementing Quantum Espresso open source code.

1.3.2 Specific objectives

Specific objectives of this study are:

- ▶ To determine the total minimum energy of $Al(100)$ surface per atom with respect to cutoff energy.
- ▶ To determine the total minimum energy of $Al(100)$ surface per atom with respect to k-point sampling.
- ▶ To determine the total minimum force of $Al(100)$ surface per atom with respect to cutoff energy.

- ▶ To study the total minimum force of $Al(100)$ surface per atom with respect to k-point sampling.
- ▶ To estimate the lattice parameters of $Al(100)$ surface corresponding to minimum energy state.
- ▶ To determine the band structure of $Al(100)$ surface using density functional theory.
- ▶ To find the total density of state $Al(100)$ surface using density functional theory.

1.4 Basic Research questions

- . What is the total minimum energy of $Al(100)$ surface per atom with respect to cutoff energy?
- . What is the total minimum energy of $Al(100)$ surface per atom with respect to k-point sampling?
- . What is the total minimum force of $Al(100)$ surface per atom with respect to cutoff energy?
- . What is the total minimum force of $Al(100)$ surface per atom with respect to k-point sampling?
- . What is the lattice constant of $Al(100)$ surface?
- . What is the band structure of $Al(100)$ surface?
- . What is the density of state of $Al(100)$ surface?

1.5 Significance of the study

The Significance of this study was to understanding the electronic and structural property of $Al(100)$ surfaces would helps to use it for different technological applications. Moreover, the information generated may serve as a base line information

for researchers for further development of the study. It also helps to compare the experimental results with respect to our calculation.

1.6 Scope of the Research

Due to time and budget constraint the scope of this study were limited to the calculation of the total minimum energy, total minimum force, theoretical lattice constant, electronic band structure and density state of $Al(100)$ surface.

Chapter 2

Review Related of Literature

2.1 Introduction

First-principles calculations are away of accurately predicting the electronic structure of a material with out the expense and logistics of fabrication and testing [8, 51]. Most materials are termed as solid state materials which can be described as many-body systems consisting of electrons and nuclei which are interacting electromagnetically. Quantum many body problems are reduced to interactions of electron systems with the movement of the potential of the nuclei at fixed positions, this is referred to as first-principles method .Density functional theory is among the common methods where the electronic structure calculations are done at ground state in quantum chemistry and solid state physics. This theory gives solutions to the Schrödinger equation for many-body or many-electron systems as a function of charge density, rather than solving the wave-function. In many-electron (many-body) systems, the exchange-correlation also termed as self-interactions relations, cause electrons to be indistinguishable, leading to the fact that energy and forces are impossible to be solved analytically. DFT provides a balance between computational cost and accuracy that allows quantitative data to be computed for any material model (up to thousands of

atoms). The fundamental problem of describing materials is that of describing the system of interacting electrons and nuclei. The electronic properties of such a system containing N electrons can be obtained by solving the many body Schrödinger equation [49]. Solving the Schrödinger equation to obtain energies and forces, require only the atomic numbers of the constituents as input, and should describe the bonding between the atoms with high accuracy [9].

2.2 First principles calculations

The first principle calculation material properties, relying, upon quantum mechanics and electromagnetism [47]. A first principles approach is one which is founded only on the basic laws of physics [10, 11, 12]. First principle methods are parameters free and based only on fundamental interactions between electrons and nuclei. The first principles methods aim at solving the complicated problem of electron moving in the electrostatic field due to the nuclei. As first approximation, the nuclei are considered fixed and the problem becomes that electrons only whose motion is governed by the Schrödinger equation [13]. Using the first principles total-energy calculations the geometry of the (110) surface has been determined [52]. The aim of the first-principles method is to come up with a solution to the Schrödinger time-independent, non-relativistic equation[47].

$$H\varphi_k r_1 \sigma_1 \dots r_N \sigma_N = E_k \varphi_k r_1 \sigma_1 \dots r_N \sigma_N \quad (2.2.1)$$

2.3 Schrödinger equation for many-body systems

Quantum mechanics is one of the most fundamental theories in physics that governs the motion of micro particles. To begin with, let's look at the time-independent Schrödinger equation for a many-body system with electrons and nuclei. This equation for such systems is given as:

$$H\Psi(r) = E\Psi(r) \quad (2.3.1)$$

H is the Hamiltonian for the many-body system,

$$H = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \frac{\hbar^2}{2M_I} \sum_I \nabla_I^2 + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (2.3.2)$$

Where m_e is the electron mass, M_I is the mass of the ion, \hbar is the plank constant divide by 2π , e is the electron charge, Z_I is the atomic number of the ion, r_i is the position of vector of the electron, R_I is the position vector of the ion and ∇_i^2 , ∇_I^2 are the laplacian operators with respect to r_i and R^I respectively. In *eq.(2.3.2)* Where the electrons are represented by lower case subscripts and the nuclei are represented with upper case subscripts.

According to the Born-Oppenheimer/adiabatic approximation [23], the motion of nuclei and electrons can be decoupled due to the fact that nuclei are much heavier than electrons and they move much slowly than the electrons. The electrons can be considered to respond instantaneously to the motion of the nuclei. Thus, the Hamiltonian for the many-body system in *Eq.(2.3.2)* could be decoupled into two parts.

We can write equation (2.3.2) as

$$H_e = -\frac{\hbar^2}{2me} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|} - \sum_{i,I} \frac{Z_I e^2}{|r_i - R_I|}, \quad (2.3.3)$$

and

$$H_n = -\frac{\hbar^2}{2M_I} \sum_I \nabla_I^2 + U(R) \quad (2.3.4)$$

Where H_e is the Hamiltonian for the electrons, and H_n is the Hamiltonian for the nuclei. The total potential of the nuclei is defined as;

$$U(R) = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J e^2}{|R_I - R_J|} + E(R) \quad (2.3.5)$$

Where $E(R)$ is the total energy of the electrons within the set of coordinates R for the nuclei. The force on each nucleus can be calculated with

$$F_I = \frac{M_I d^2 R_I}{|d\tau^2|} = -\frac{\partial U}{\partial R_I} \quad (2.3.6)$$

The equilibrium geometry of the nuclei is given by the condition that the force acting on individual nucleus is zero [27]. In atomic units, the set of Schrödinger equations for the electrons, i , can be expressed as

$$-\frac{1}{2} \nabla^2 + V_n(r) + V_H(r) + V_{xc}(r) \Psi_i(r) = \varepsilon_i \Psi_i(r) \quad (2.3.7)$$

The kinetic energy of the electron is expressed by $-\frac{1}{2} \nabla^2$, $V_n(r)$ is the potential of the nuclei, $V_H(r)$ is known as the Hartree potential; it is the coulomb interaction between the electron and the mean field of all the electrons. $\Psi_i(r)$ Are the single electron wave functions and ε_i the corresponding single electron Eigenvalues. The unknown many-body interactions are placed on the exchange correlation potential $V_{xc}(r)$ [10].

The most commonly used exchange-correlation functional used for calculating the Al(100) surface in solid is the GGA functional formulated by Perdew, Burke and Ernzerhof (PBE).

2.4 The variational principle for the ground state

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

$$E[\Psi] = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (2.4.1)$$

Where $\langle \Psi | \hat{H} | \Psi \rangle = \int \Psi \Psi^* \hat{H} d\vec{x}$. The variational principle states that the energy computed from a guessed Ψ is an upper bound to the true ground state energy E_o . Full minimization of the functional $E(\Psi)$ with respect to all allowed N-electron wave functions will give the ground state Ψ_o and Energy $E[\Psi_o] = E_o$ that is

$$E_o = \min_{\Psi} E[\Psi] = \min_{\Psi} \langle \Psi | T + V_{Ne} + V_{ee} | \Psi \rangle \quad (2.4.2)$$

For a system of N electrons and given nuclear potential V_{ext} , the variational principle defines a procedure to determine the ground state wave function Ψ_o , the ground state energy $E_o[N, V_{ext}]$ and other properties of interest [19]. In other work, the ground state energy is a functional of the number of electron N and the nuclear potential V_{ext} .

$$E_o = E[N, V_{ext}] \quad (2.4.3)$$

2.5 Quantum Many-body theory

The state of motion can not be solved analytically for systems in which three or more distinct masses interact [10]. To solve this problem we can use different approximation

approaches. In general the N-electron Hamiltonian is given by equation (2.3.2) above. We can write equation (2.3.2) as

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{NN} + \hat{V}_{eN} + \hat{V}_{ee} \quad (2.5.1)$$

2.5.1 Born-Oppenheimer Approximation

There are many approximations that one must make when dealing with many-body problem in the realm of solids. The first one is known as the Born-Oppenheimer approximation. This approximation solves the problem with an assumption that the nuclei is much heavier compared to electrons that are lighter and therefore their movement is slower, then the electronic and nuclear motion are easily separated. Nuclei are treated to be stationary and the electrons move relative to them. *eq.*(2.2.1), can be separated into two independent eigenvalue problems such that the electron and nuclei wave functions are products of the total wave function [49].

$$\varphi(\vec{r}, \vec{R}) = \psi_e(\vec{r}, \vec{R}) \times \psi_{nuc}(\vec{r}, \vec{R}) \quad (2.5.2)$$

The nuclei, which are approximated as ions in this case, are assumed to be stationary. Since the electrons are much less massive and move at much higher velocities than the nuclei, the positions of the electrons are considered variables and the positions of the ions are considered parameters.

In order to examine this situation we define the general Hamiltonian for a many-body system from the standard Hamiltonian. Remember the basic Hamiltonian in this situation is the potential and kinetic energy as in [13]

$$H = T + V \text{ where } T = \frac{-\hbar^2}{2m} \nabla^2 \quad (2.5.3)$$

However the potential, V , changes based on the potential of the system. There are two kinetic energy terms and three potential energy terms that needed to be added. They can be written as equation (2.3.2). Due to their masses the nuclei move much slower than the electrons. We can consider the electrons as moving in the field of fixed nuclei [30]. We can ignore the nuclear kinetic energy and their potential energy is merely constant. Thus, the electronic Hamiltonian (2.5.1) reduces to

$$\hat{H} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} \quad (2.5.4)$$

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

$$\hat{H}\psi_{elec} = E_{elec}\psi_{elec} \quad (2.5.5)$$

$$E_{tot} = E_{elec} + E_{nuc} \quad (2.5.6)$$

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

This allows a great simplification of the equations when dealing with solids.

2.5.2 The Hartree-Fock Approximation

The Born-Oppenheimer approximation begins the outline a many-body Hamiltonian in a useful manner by reducing out various terms. But the many-body problem is a complex one and the Hamiltonian derived in the Born-Oppenheimer is still not suitable for calculations. There are further approximations that must be made to achieve better accuracy and minimize calculation time. That is what is involved in the derivation of the Hartree Energy equations[14]. The Hartree-Fock approximation

is the method whereby the orthogonal orbitals ψ_i are found that minimize energy for this determinantal form of ψ_0 :

$$E_{HF} = \min_{(\psi_{HF} \rightarrow N)} E[\psi_{HF}] \quad (2.5.7)$$

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

$$E_{HF} = \langle \psi_{HF} | \hat{H} | \psi_{HF} \rangle = \sum_{i=1}^N H_i + \frac{1}{2} \sum_{i,j=1}^N (J_{ij} - K_{ij}) \quad (2.5.8)$$

$$H_i \equiv \int \psi_i^*(\vec{x}) \left[-\frac{1}{2} \nabla^2 - V_{ext} \right] \psi_i(\vec{x}) d\vec{x} \quad (2.5.9)$$

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

$$J_{ij} = \int \int \psi_i(\vec{x}_1) \psi_i^*(\vec{x}) \frac{1}{r_{12}} \psi_j(\vec{x}_2) d\vec{x}_1 d\vec{x}_2 \quad (2.5.10)$$

$$K_{ij} = \int \int \psi_i^*(\vec{x}_1) \psi_i(\vec{x}_1) \frac{1}{r_{12}} \psi_j(\vec{x}_2) \psi_j^*(\vec{x}_2) d\vec{x}_1 d\vec{x}_2 \quad (2.5.11)$$

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

The variational freedom in the expression of the energy equation(2.5.8) is in the choice of the orbitals. The minimization of the energy functional with normalization conditions $\int \psi_i^*(\vec{x}) \psi_j(\vec{x}) d\vec{x} = \delta_{ij}$ leads to the Hartree-Fock differential equations:

$$\hat{f} \psi_i = \epsilon_i \psi_i, i = 1, 2, \dots, N \quad (2.5.12)$$

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

$$\hat{f} = -\frac{1}{2} \nabla_i^2 - \sum_A^M \frac{Z_A}{r_{iA}} + V_{HF}(i) \quad (2.5.13)$$

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

$$V_{HF}(\vec{x}_1) = \sum_j^N (\hat{J}_j(\vec{x}_1) - \hat{K}_j(\vec{x}_1)). \quad (2.5.14)$$

$$\hat{J}_j(\vec{x}_1) = \int (\psi_j(\vec{x}_2))^2 \frac{1}{r_{12}} d\vec{x}_2 \quad (2.5.15)$$

The Coulomb operator \hat{J} represents the potential that an element at position \vec{x}_1 experiences due to the average charge distribution of another electron in spin orbital ψ_j . The second term in (2.5.15) is the exchange contribution to the HF potential. It has no classical analog and it is defined through its effect when operating on a spin orbital:

$$\hat{K}_j(\vec{x}_1)\psi_i(\vec{x}_1) = \int \psi_j^*(\vec{x}_2) \frac{1}{r_{12}} \psi_i(\vec{x}_2) d\vec{x}_2 \psi_j(\vec{x}_1) \quad (2.5.16)$$

The Hartree-Fock potential is non-local and it depends on the spin orbitals. Thus, the Hartree-Fock (HF) equations must be solved self-consistently [14].

2.6 Density Functional Theory (DFT)

Physics and chemistry use a theory called Density functional theory (DFT), which is a quantum mechanical theory, to examine the electronic structure of many body systems, especially, atoms, molecules and the condensed phases. DFT is one of the most common and easy methods which can be applied in condensed phases, computational physics, and computational chemistry [29].

Density functional theory is proposed by kohn and Hohenberg in the 190s. It is a method to find the Schrödinger equation that reflects the quantum behavior of

molecule and atoms which finally reflects the properties of materials. The Density functional theory includes two fundamental mathematical theorems [15].

The first theorem is the ground state energy for Schrödinger's equation can be uniquely identified by the distribution of the electron density.

The second theorem define how to get this functional; the electron density which make the total energy of the functional minimum is the true electron density.

Density functional theory is an extremely successful approach for solving many body problems' i.e., it is an exact reformulation of many-body quantum mechanics in terms of the probability density rather than the wave function. When one know the density of states one can estimate the kinetic energy of particles in the system. From the kinetic energy it is possible to estimate the potential. However this estimation is not complete, for example there is something called exchange correlation energy that is not included, and that leads to large systematic errors in the final answers. The exchange correlation energy is actually two terms that have been combined into one energy. Both energies are unknown in the current formalism and must be approximated, so to simplify matters they have been combined. One of the primary goals of density functional theory is to come up with a good approximation of the exchange-correlation energy, which will be discussed more in the Local Density Approximation section[13]. The following are among approximation approaches of density functional theory [31].

2.6.1 The Thomas-Fermi Model

The original density functional theory of quantum systems is the method of Thomas and Fermi proposed in 1927. Although their approximation is not accurate enough for

present-day electronic structure calculations, the approach illustrates the way density functional theory works. In the original ThomasFermi method the kinetic energy of the system of electrons is approximated as an explicit functional of the density, idealized as noninteracting electrons in a homogeneous gas with density equal to the local density at any given point. Both Thomas and Fermi neglected exchange and correlation among the electrons; however, this was extended by Dirac in 1930, who formulated the local approximation for exchange still in use today. This leads to the energy functional for electrons in an external potential $V_{ext}(r)$

$$T_{TF}[n] = C_1 \int d^3r n(r)^{\frac{5}{3}} + \int d^3r V_{ext}(r)n(r) + C_2 \int d^3r n(r)^{\frac{4}{3}} + \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|} \quad (2.6.1)$$

where the first term is the local approximation to the kinetic energy with $C_1 = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} = 2.81$ in atomic units, the third term is the local exchange with $C_2 = -\frac{3}{4}(\frac{3}{\pi})^{\frac{1}{3}}$, and the last term is the classical electrostatic Hartree energy. The ground state density and energy can be found by minimizing the functional $E[n]$ in equation(2.6.1), for all possible $n(r)$ subject to the constraint on the total number of electrons[50]

$$\int d^3r n(r) = N \quad (2.6.2)$$

This is the first density functional theory (1927) [32]. Based on the uniform electron gas, they proposed the following functional for the kinetic energy:

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} \quad (2.6.3)$$

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

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} - Z \int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2} \int \int \frac{\rho(\vec{r}_1)\rho(\vec{r}_2)}{r_{12}}d\vec{r}_1d\vec{r}_2 \quad (2.6.4)$$

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

In order to determine the correct density to be included in equation (2.6.4), they employed a variational principle. They assumed that the ground state of the system is connected to the $\rho(\vec{r})$ for which the energy is minimized under the constraint of $\int \rho(\vec{r})d\vec{r} = N$.

The attraction of density functional theory is evident by the fact that one equation for the density is remarkably simpler than the full many-body *Schrodinger* equation that involves $3N$ degrees of freedom for N electrons. The Thomas-Fermi approach has been applied, for example, to equations of state of the elements. However, the *Thomas–Fermitype* approach starts with approximations that are too crude, missing essential physics and chemistry, such as shell structures of atoms and binding of molecules . Thus it falls short of the goal of a useful description of electrons in matter.

The basic foundations of DFT were provided in 1964 by Hohenberg and Kohn with their two fundamental theorems. In 1965 the major milestone in the development of DFT was introduced by Hohenberg, Kohn and Sham (HKS). They gave the proofs of these theorems by showing that DFT was an exact theory in same sense as the wave function theory [16].

2.7 The Hohenberg-Kohn theorems

The Hohenberg-Kohn formalism [16] of DFT is based on two theorems:

Theorem I

For any system of interacting particles in an external potential $V_{ext}(r)$, the potential $V_{ext}(r)$ is determined uniquely, up to a constant, by the ground state particle density, $n_0(r)$.

Theorem II

The second HK theorem defines energy functional for the system and proves that the correct ground state electron density minimizes this energy functional [17]. The energy functional of the density $E[n]$ is:

$$E[n] = \int dr V_{ext}(r)n(r) + F[n] \quad (2.7.1)$$

Where $F[n]$ is a universal functional of the density and incorporates the kinetic and the potential energy. Once the external potential $V_{ext}(r)$ has been fixed, the energy functional $E[n]$ has its minimum, the ground state energy E_0 , at the physical ground state density $n_0(r)$:

$$E_0 = E[n_0] \quad (2.7.2)$$

The Hohenberg-Kohn (HK) theorems have the limited purpose to prove that a universal functional of the electron density exists; they do not derive its actual expression. A direct minimization of the functional is usually not applicable, because no good expression for the kinetic energy as a functional of n is known, except for simple metals. The Kohn-Sham (KS) scheme, a reformulation of the theory based on the KS orbitals instead of the mere density, is the starting-point of most of the actual

calculations.

2.8 Kohn-Sham Equation

In 1965 Kohn and Sham introduced a method for calculating these terms. Replace our system of interacting electrons with a fictitious system of non-interacting electrons of the same density. The Kohn-Sham approach is the break-through in modern DFT. It is tightly linked to the Hartree-Fock Slater approximation of many fermions theory and considered exchange and correlation energies [18].

The Idea of Kohn and Sham was to treat this as if it is a single-particle problem. the first term represent the Kinetic Energy and the remaining terms the the Kohn-Sham potential [19].

$$V_{KS}(r) = V(r) + \int \frac{n(r')}{|r - r'|} d^3r' + \frac{\delta E_{xc}[n(r)]}{\delta n(r')} \quad (2.8.1)$$

The Kohn-Sham equations are a set of single- particle schrödinger equation with the potential given by Eq(2.8.1). The kohn-sham equations represents a mapping of the the interacting many-body system onto a system of non-interacting electron moving in an effective potential due to all the other electrons [47].

$$\underbrace{\left[-\frac{1}{2}\nabla^2 + \overbrace{V(r) + V_H(r) + V_{xc}(r)}^{V_{ext}(r)} \right]}_{H_{KS}} \psi_i(r) = \epsilon_i \psi_i(r) \quad (2.8.2)$$

Where $V_{ext}(r)$ external potential, ψ_i eigenfunction. Within the framework of Kohn-Sham DFT (KS DFT), the intractable many-body problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the

exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT [30]. The electronic density is obtained by occupying the N solution $\Psi_i(r)$ with lowest energy;

$$n(r) = \sum_{i=1}^N |\psi_i(r)|^2, \quad (2.8.3)$$

Now the electronic density obtained this way can be used to calculate a new Kohn-Sham potential following Eq(2.8.1). we continue this iterative procedure until we reach convergence.

2.9 Exchange -Correlation Energy functional

The simplest approximation for $E_{xc}(\rho)$ is the total density approximation (LDA). This assumes that $E_{xc}(\rho)$ depends only on the charge density at each point and is of the form

$$E_{XC}^{LDA}[\rho] = \int E_{XC}^{LDA}[\rho(r)] d\vec{x}^3 \quad (2.9.1)$$

Where $E_{xc}(\rho)$ is the exchange correlation energy per unit volume. By additionally taking into account the gradient at each point more advanced generalized gradient approximation'(GGA)exchange correlation functional are obtained which are of the form

$$E_{XC}^{LDA}[\rho] = \int E_{XC}^{LDA}[\rho(r), \nabla_\rho(r)] d^3(r) \quad (2.9.2)$$

The most commonly used exchange correlation functional we use for calculating the Al(100) surface in solid is the GGA functional formulated by perdew, Burke and Ernzer hof(PBE). The DFT is however a very convenient method to treat the correlation effects in a mean field manor. The method was presented by Hohenberg, Kohn and Sham [10].

Further more, DFT in the kohn-sham implementation with LDA or GGA approximation for the exchange -correlation functional has been successfully applied to deduce structure,electronic as well as other properties of condense matter systems [47].

2.9.1 The Local Density Approximation

:

The simple approximate exchange-correlation (energy reduction due to a spatial separation between the electrons with the same spin and opposite spin) functional is the local density approximation (LDA).

This is simplest approximation, and can be written as:

$$E^{XC-LDA}[\rho(r)] = \int \rho(r)\epsilon^{XC-unif}(\rho(r))d(r) \quad (2.9.3)$$

Where $\epsilon^{xc-unif}$ is the exchange-correlation energy per particle of the homogeneous electron gas of density ($\rho(r)$), i.e. The exchange-correlation energy density is taken to be exceedingly similar, differing only in how their correlation contributions have been fitted to the many body free electron gas data. The LDA is valid only for slowly varying densities. Experience with calculations of atoms, molecules and solids shows that Eq. (2.7.3) can in general also be applied to these systems.

2.9.2 The Generalized Gradient Approximation

These are the second generation functional(sitting on the second rung of Jacob's ladder) in which the gradient of the density, $\nabla\rho(r)$, at each coordinate is taken into account as well as the density itself:

$$E^{(xc - GGA)}[\rho(r)] = \int \rho(r)\epsilon^{(xc - unif)}(\rho(r))\nabla_{\nabla}(r)d(r) \quad (2.9.4)$$

Thus GGAs are "semi-local" functional, comprising corrections to the LDA while ensuring consistency with known sum rules. The **GGA** functional depends on the local electron density as well as the spatial variation of the electron density that is represented by the density gradient. The **GGA** functional can be written as

$$E_{XC}^{GGA}[n] = \int d\vec{r} \epsilon_{xc}[n] F_{xc}[n, \vec{\nabla} n] n(r) \quad (2.9.5)$$

The $E_{XC}^{GGA}[n]$ is the exchange correlation energy per particle of an electron gas and F_{xc} is a functional of the electron density and its gradient. The GGA method gives better total energies, especially for small molecules, but computationally it is more time consuming than LDA [31, 33]. Generally, **GGA** has the following advantages over **LDA** [34, 35]:

- GGA improves ground state properties for light atoms, molecules and clusters.
- GGA predicts the correct magnetic properties of 3d transition metals such as body centered iron.
- Though GGA seems to be superior compared to LDA, it has several drawbacks. A GGA method fails to accurately treat the hydrogen bond. This defect is clearly manifested through expansion and hence softening of bonds [[35]]

2.10 Periodic supercells

We defined the shape of the cell that is repeated periodically in space, the supercell, by lattice vectors a_1 , a_2 , and a_3 . If we solve the Schrödinger equation for this periodic system, the solution must satisfy a fundamental property known as Bloch's theorem.

2.10.1 Bloch's theorem

Bloch's theorem states that in a periodic solid each electronic wave function can be written as the product of cell-periodic part and wave like part [36].

$$\Psi_k(r) = e^{i\vec{K} \cdot \vec{r}} u_k(r) \quad (2.10.1)$$

Where $u_k(r)$ is periodic in space with the same periodicity as the supercell. That is, $u_k(r + n_1 a_1 + n_2 a_2 + n_3 a_3) = u_k(r)$ for any integers n_1, n_2 , and n_3 . This theorem means that it is possible to try and solve the Schrödinger equation for each value of k independently.

The cell-periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$u_k(r) = \sum_G c_{i,G} e^{iG \cdot r} \quad (2.10.2)$$

Where the reciprocal lattice vectors G are defined by $G \cdot l = 2\pi n$ for all l where l is a lattice vector of the crystal and n is an integer. Therefore each electronic wave function can be written as a sum of plane waves,

$$\Psi_k(r) = \sum_G c_{i,k+G} e^{i(k+G) \cdot r} \quad (2.10.3)$$

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

2.10.2 Energy cutoffs

Our lengthy discussion of k space began with Bloch's theorem, which tells us that solutions of the Schrödinger equation for a supercell have the form

$$\Psi_k(r) = e^{i\vec{K} \cdot \vec{r}} u_k(r) \quad (2.10.4)$$

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

$$u_k(r) = \sum_G c_{i,G} e^{iG \cdot r} \quad (2.10.5)$$

where the summation is over all vectors defined by $G = n_1 b_1 + n_2 b_2 + n_3 b_3$ with integer values for n_i . These set of vectors defined by G in reciprocal space are defined so that for any real space lattice vector l_i , $G \cdot l_i = 2\pi n$.

Combining the two equations above gives

$$\Psi_k(r) = \sum_G c_{i,k+G} e^{i(k+G) \cdot r} \quad (2.10.6)$$

According to this expression, evaluating the solution at even a single point in k space involves a summation over an infinite number of possible values of G. This does not sound too promising for practical calculations! Fortunately, the functions appearing in Eq. (2.7.6) have a simple interpretation as solutions of the Schrödinger equation: they are solutions with kinetic energy

$$E = \frac{\hbar^2}{2m} |k + G|^2 \quad (2.10.7)$$

It is reasonable to expect that the solutions with lower energies are more physically important than solutions with very high energies. As a result, it is usual to truncate

the infinite sum above to include only solutions with kinetic energies less than some value:

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}^2 \quad (2.10.8)$$

The infinite sum then reduces to

$$\Psi_k(r) = \sum_{|G+k| < G_{cut}} c_{G+k} e^{i(K+G)r} \quad (2.10.9)$$

This expression includes slightly different numbers of terms for different values of k . The discussion above has introduced one more parameter that must be defined whenever a DFT calculation is performed the cutoff energy, E_{cut} . In many ways, this parameter is easier to define than the k .points , as most packages will apply sensible default settings if no other information is supplied by the user. Just as with the k .points , it is good practice to report the cutoff energy used in your calculations to allow people to reproduce your results easily [37].

2.10.3 K.points sampling

In computational area, the calculation of many properties of materials needs the evaluation of integrals over the Brillouin zone in reciprocal spaces. These integrals are typically approximated using a discrete set of points which we called K-points.

The required amount of k-point depends on the material and size of the unit cell:

- Metals required many points
- Insulators semiconductors and molecular crystals typically required fewer k-points
- To determine suitable k-points convergence study in which we systematically increase the quality of the k-space sampling unit the quality that you are interested (e.g energy or lat tice parameter) is converged.

The solution that is used most widely was developed by Monkhorst and pack in 1976. Using these methods, one can obtain an accurate approximation for the electronic potential and the total energy of an insulate or semiconductor by calculating the electronic states at a very small number of k.points. The electronic potential and total energy are more difficult to calculate if the system is metallic because a dense set of k.points is required to define the Fermi surface precisely. The magnitude of any error in the total energy due to inadequacy of the k.points sampling can always be reduced by using a denser set of k.points. The computed total energy will converge as the density of k.points increases, and the error due to the k.point sampling approaches zero.

In principle, a converged electronic potential and total energy can always be obtained provided that the computational time is available to calculate the electronic wave functions at sufficiently dense set of k.points. The computational cost of performing a very dense sampling of k.space can be significantly reduced by using the k.point total energy method [39].

2.10.4 Plane wave basis sets

Bloch's theorem states that the electronic wave functions at each k.point can be expanded in terms of a discrete plane-wave basis sets.

In principle, an infinite plane wave basis set is required to expand the electronic wave function. However, the coefficients $C_{i,K+G}$ for the plane waves with small kinetic energy. $\frac{\hbar^2}{2m}|K+G|^2$ are typically more important than those with large kinetic energy. Thus, the plane wave basis set can be truncated to include only plane waves that have kinetic energies less than some particular cutoff energy. If a continuum of plane wave basis states were required to expand each electronic wave function, the basis set

would be infinitely large number matter how small the cutoff energy. Application of the Bloch theorem allows the electronic wave functions to be expanded in terms of a discrete set of plane waves. Introduction of any energy cutoff to discrete plane wave basis set produces a finite basis set.

The truncation of plane wave basis set at a finite cutoff energy will lead to an error in the computed total energy. However, it is possible to reduce the magnitude of the error by increasing the value of cutoff energy. In principle, the cutoff energy should be increased until the calculated total energy has converged [40].

2.11 Geometry optimizations

Geometry optimization is used to find minima on the potential energy surface, with these minimum energy structures representing equilibrium structure. Optimization also is used to locate transition structures, which are represented by saddle points on the potential energy surface. Optimization to minima is also referred to as energy minimization. During minimization, the energy of molecule is reduced by adjusting atomic coordinates. Energy minimization is done when using either molecular mechanics or quantum mechanics methods or it must precede any computational analyses in which these methods are applied [20].

2.12 Plane-waves and pseudo potentials

In calculation of solids or condensed matter [21], which will be the main types of systems that (DFT) is applied to in this thesis, plane-waves basis set is a very common choice. In many cases, combined plane-wave is the pseudo potential approach for treating the strong interactions between core electron and nuclei. In this we will be

briefly discuss plane waves and pseudo potentials.

2.12.1 Pseudo potential

Pseudo potentials are well established that most physically interesting properties of solids are determined by the valence electrons rather than the core electrons. Meanwhile, the deeply bound core electrons within plane-wave basis sets, require a huge amount of basis functions for their description. To relieve this problem, the pseudo potential approximation replaces the strong ionic potential with a weaker pseudo potential. In general, there are two main purposes of the pseudo potential formalism. First, to use a much weaker pseudo potential to replace core electrons which due to their deep potential need to be described by many plane-wave basis functions. Second, to eliminate the rapid oscillations of the valence electron wave function in the core region. The most common general form of a pseudo potential is,

$$V_{ps} = \sum_{lm} | Y_{lm} \rangle V_l(r) \langle Y_{lm} | \quad (2.12.1)$$

Where Y_{lm} are the spherical harmonics.

A pseudopotential is developed by considering an isolated atom of one element, but the resulting pseudopotential can then be used reliably for calculations that place this atom in any chemical environment without further adjustment of the pseudopotential. This desirable property is referred to as the transferability of the pseudopotential. The details of a particular pseudopotential define a minimum energy cutoff that should be used in calculations including atoms associated with that pseudopotential. Pseudopotentials requiring high cutoff energies are said to be hard, while more computationally efficient pseudopotentials with low cutoff energies are soft. The most widely used method of defining pseudopotentials is based on work by Vanderbilt; these are

the ultrasoft pseudopotentials (USPPs). As their name suggests, these pseudopotentials require substantially lower cutoff energies than alternative approaches [22, 37].

2.13 Self-consistent-field calculation

In (1897-1958) D. R. Hartree came up with the first idea of getting Self Consistent Field (SCF) solutions to a many-electron problem as a strategy to break the state. D. R. Hartree was helped by his father, William Hartree, in solving the numerical problems involved in solving the SCF problem [41, 42, 43]. Here we focus discussion on SCF in DFT calculations, the most time-consuming part of an SCF calculation is in matrix diagonalization, which consists of computing the self-consistent solutions of the following Kohn-Sham equation (in atomic units):

$$\left[-\frac{\nabla^2}{2} + V_{ext}(n(r), r)\right]\psi_i(r) = \varepsilon_i\psi_i \quad (2.13.1)$$

Where $\psi_i(r)$ is a wave function, ε_i is a Kohn-Sham eigenvalue. The external potential

$$V_{ext}(n(r), r) = V_{ion}(r) + V_H(n(r), r) + V_{xc}(n(r), r), \quad (2.13.2)$$

includes the ionic potential V_{ion} , the Hartree potential V_H and the exchange-correlation potential V_{xc} . In DFT the external potential depends only on $n(r)$ the charge density.

The charge density is given by

$$n(r) = 2 \sum_{i=1}^{n_{occ}} |\psi_i(r)|^2, \quad (2.13.3)$$

where n_{occ} is the number of occupied states (half the number of valence electrons in the system) and the factor of two comes from spin multiplicity. Self-consistent iterations for solving this problem consist of starting with an initial guess of the charge density $n(r)$, then obtaining a guess for V_{ext} and solving Kohn-Sham equation for wave function $\psi_i(r)$ to update charge density and external potential. Then Kohn-Sham equation is solved again for the new wave function and the process is carried

on until the difference between two consecutive external potential is below a certain tolerance (equivalently, the wave functions are close to stationary) [42, 43, 44].

2.13.1 Algorithm Self-Consistent Iteration

The SCF method is an iterative procedure which yields a self-consistent set of wave functions and orbital energies. It consists of the following steps.

1. An initial guess for the charge density.
2. Solve $[-\frac{\nabla^2}{2} + V_{ext}(n(r), r)]\psi_i(r) = \varepsilon_i\psi_i(r)$ for wave function $\psi_i(r)$, $i = 1, 2, ..$
3. Compute new charge density $n(r) = 2 \sum_{i=1}^{n_{occ}} |\psi_i(r)|^2$
4. Solve for new Hartree potential V_H .
5. Update V_{xc} and V_{ion} .
6. If the wave function does not satisfy the right boundary condition, we return to step 3 in order to make another guess for the energy $\varepsilon_i(r)$. If the wave function satisfies the right boundary condition, the calculation returns to step 2 and the newly obtained $\psi_i(r)$ plays the role of wave functions [45].

2.14 Quantum ESPRESSO

Quantum ESPRESSO Software package is a first-principle calculation software based on the density functional theory applying of the plane-wave basis set and the pseudo-potential method. It includes two major modules: PWscf and CPMD. In addition, there are two auxiliary graphical interface modules for input parameter setting and generation of potentials. It can compute Fermi surface(metals), electro-acoustic coupling and super conducting properties(including, isotropic,anisotropic

super-conducting features).

The advantage of quantum ESPRESSO are functional modularity (easy to add new modules) and free open source. Quantum espresso is a variety of numerical and algorithms aimed at a chemically realistic modeling of materials from the nano scale upwards, based on the solution of the density functional theory(DFT). It is an integrated suite of computer codes for electronic structure calculations and materials modeling based on DFT, plane waves and pseudo potentials(norm conserving, ultra-soft and projector augmented wave) to represent the electron-ion interactions. The ESPRESSO stands for opEn source package for research in Electronic structure, simulation and Optimization. The codes are constructed around the use of periodic boundary conditions, which allows for a straightforward treatment of infinite crystalline systems.

Quantum espresso can do several important basic computations such as calculation of the Kohn-Sham(KS) orbital's and energies for isolated systems, and of their ground state energies , complete structural optimizations of the atomic coordinates, ground state of magnetic or spin polarized systems,..etc [46].

2.14.1 The Accuracy of K-points sever in Quantum ESPRESSO

In computational material area, various properties of materials are determined by integrals over the Brillouin Zone in reciprocal space. K-points are a set of discrete points to approximate these integrals. we try to test the efficiency of K-point server in Quantum ESPRESSO to see if it can reduce the computing space and save time while maintaining accuracy. To test for the effectiveness of our k-points server, we used density functional theory(DFT) as implemented inQuantum ESPRESSO to calculate the converged energies of randomly selected materials.

To determine the number of k-point required to calculate a converged energy value, we generated k-point grids for different values.

2.14.2 Brillouin zone

Quantum ESPRESSO (QE) support for the definition of high symmetry lines inside the Brillouin zone (BZ) is still rather limited. However QE can calculate the coordinates of the vertexes of the BZ and of particular points inside the BZ. The principal direct and reciprocal lattice vectors, as implemented in the routine `latgen`, are illustrated here together with the labels of each point. These labels can be given as input in a band or phonon calculation to define paths in the BZ. This feature is available with the option `tpiba b` or `crystal b` in a bands calculation or with the option `q` in band form in the input of the `matdyn.x` code. Lines in reciprocal space are defined by giving the coordinates of the starting and ending points and the number of points of each line. The coordinates of the starting and ending points can be given explicitly with three real numbers or by giving the label of a point known to QE. For example:

```
X10
gG25
0.50.50.51
```

indicate a path composed by two lines. The first line starts at point X, ends at point G, and has 10 k points. The second line starts at G, ends at the point of coordinates (0.5, 0.5, 0.5) and has 25 k points. Greek labels are prefixed by the letter g: gG indicates the G point, gS the S point etc. Subscripts are written after the label: the point P1 is indicated as P1. In the following section you can find the labels of the points defined in each BZ. There are many conventions to label high symmetry points inside the BZ. The variable `point label type` selects the set of labels used by

QE. Other choices can be more convenient in other situations. The names reported in the web pages http://www.cryst.ehu.es/cryst/get_kvec.html are available for some BZ. You can use them by setting (point label type = BI), others can be added in the future. This option is available only with $ibrav = 6$ and for all positive $ibrav$ with the exception of the base centered monoclinic ($ibrav = 13$), and triclinic ($ibrav = 14$) lattices. In these cases you have to give all the coordinates of the k-points[48].

$ibrav=6$, simple tetragonal lattice The primitive vectors of the direct lattice are:

$$a_1 = a(1, 0, 0), a_2 = (0, 1, 0), a_3 = a(0, 0, c/a) \quad (2.14.1)$$

while the reciprocal lattice vectors are:

$$b_1 = 2\pi/a(1, 0, 0), b_2 = 2\pi/a(0, 1, 0), b_3 = 2\pi/a(0, 0, c/a) \quad (2.14.2)$$

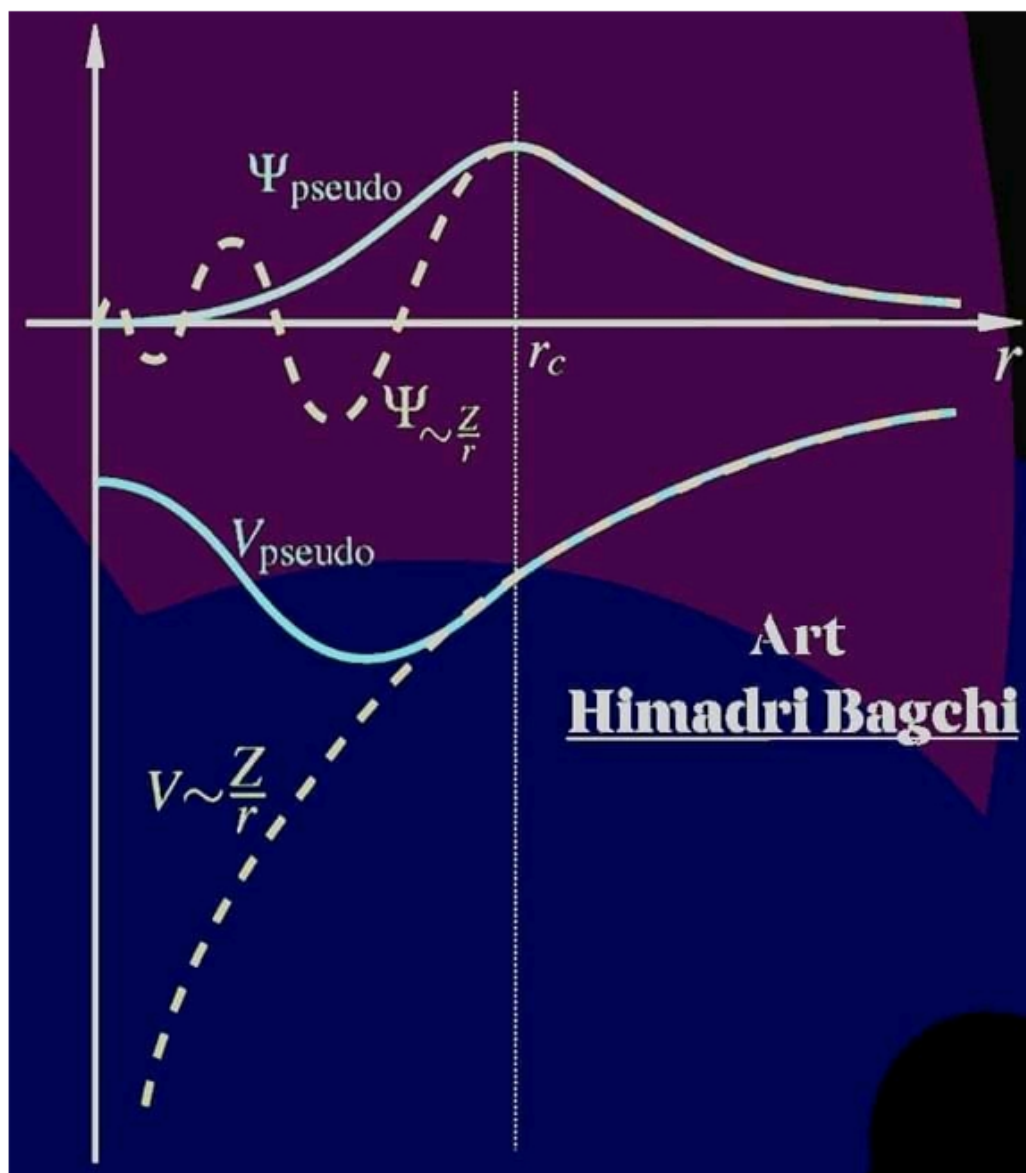


Figure 2.1: Schematic illustration of the replacement of the all-electron wavefunction and core potential by a pseudo-wavefunction and pseudopotential.

Chapter 3

Research Methodology

3.1 Materials

The Structural and electronic properties of Al(100) surface has been studied theoretically using density functional theory. Materials used to accomplish this research include published articles, books, thesis and dissertations. Quantum ESPRESSO software is used to calculate out puts to be analyzed. Latex software is used to write the research.

3.2 Methodology

First principle calculation with in density functional theory are carried out using the PWscf code of Quantum-ESPRESSO distribution. The perdw-Zunger functional with in the Local density approximation (LDA) is used. For the Brillouin-zone integration, we use a monkhorst-pack set of special \mathbf{K} -points. A normcon-serving pseudo-potential is used for Al with electron in a $3s^23p^1$ configuration. Al(100) surface were constructed using supercell with a thin slab. for the slabs considered, each layer in the unit cell contains one in-equivalent atom. For Al(100) a tetragonal cell is used with a base formed by $a_o/\sqrt{2}[110]$ and $a_o/\sqrt{2}[\bar{1}\bar{1}0]$, where the inter-layer spacing is

$a_{0/2}$ and ABAB stacking is used, where a_o is the equilibrium lattice parameter [52]. Quantum ESPRESSO package is an integrated suite of computer codes for first principle calculations and materials modeling based on density -functional theory DFT, plane waves basis sets (PW) and pseudo potential [24]. It is free under the conditions of the GNU General public license GPL [18]. We will be using the Quantum -Espresso package as our first-principles code. Quantum-Espresso is a full ab initio package implementing electronic structure and energy calculations, linear response method. Inside this package, PWSCF is the code we will use to perform total energy calculations. PWSCF uses both norm-conserving pseudo potentials(pp) and ultra soft pseudo potentials(US-PP), with density functional theory(DFT) [25]. The most important of input parameters in Quantum Espresso are the atomic geometrics (Number and types atoms in the periodic cell, brave's-lattice index, crystallographic or lattice constants), the kinetic energy cut off and the type of pseudo potentials [26]. Firstly, an initial guess for the electron density $\rho(r)$ is assumed, which is required for the calculation of $V_{eff}(r)$, the diagonalization of the Kohn-Sham equations, and the succeeded evaluation of $\rho(r)$ along with total minimum energy. As long as the convergence criterion is not fulfilled, the numerical procedure is continued with the last $\rho(r)$ instead of the initial guess. When criterion is satisfied, various output quantities [6] are computed.

Each of these input parameters have meanings that need to be considered. We can find a more detailed description for all the input parameters of pw.x in the official PW documentation of QE. The most relevant lines for the calculations related to this are the following:

The line

```
calculation = scf
```

indicates that is a self-consistent calculation(SCF) to find the total energy of the system. The line

```
prefix = al
```

is a tag the code uses to identify this calculation. The line

```
Pseudo_dir = ./pseudo/
```

indicates the path to the place where the pseudopotential file is located. we provide the necessary pseudopotential (Al.pz.vbc.UPF)

The line

```
outdir = ./tmp/
```

indicates the path to the directory to be created by the code.

The line

```
ibrav = 6
```

indicates the Bravais-lattice index. In this case $ibrav = 6$ means that we are dealing with the tetragonal primitive unit cell.

The line

```
celldm(1) = 5.42
```

is the value of the lattice parameter in Bohr atomic units. The line

```
celldm(3) = 6.36
```


is the value of lattice parameter in Bohr atomic units. The line
`nat = 4` indicates the number of atoms in the unit cell. The line
`ntyp = 2`
indicates the number of types of atoms in the unit cell. The line
`ecutwfc = 15.D0`,

indicates the value of the kinetic-energy cutoff in Rydberg units. This value
determines how many plane waves will be used in the expansion of kohn-sham wave-
functions during the iterative of the kohn-sham equations.

The line
`occupations = 'smearing'`,

indicates the system to use the smearing method. The line
`smearing = m-v` ,

it tells the system the type of distribution to use when smearing.

The line
`conv-thr = 1.D-10`,

indicates the convergence threshold in Rydberg units during the iterative solution of
the kohn-sham equation. When this threshold is reached, the calculation will stop.

The line
`mixing_beta = 0.7D0`,

it tells the system that when it gets results to feed them back into the calculations
with a percent equal to the mixing beta parameter

The line

ATOMIC SPECIES

Al 26.98 Al.pz.vbc.UPF

indicates the label of the atom, its mass and the name of the pseudopotential file.

The line

K.poitsautomatic

6 6 1 0 0 0

indicates the **K** points sampling of the Brillouin zone.

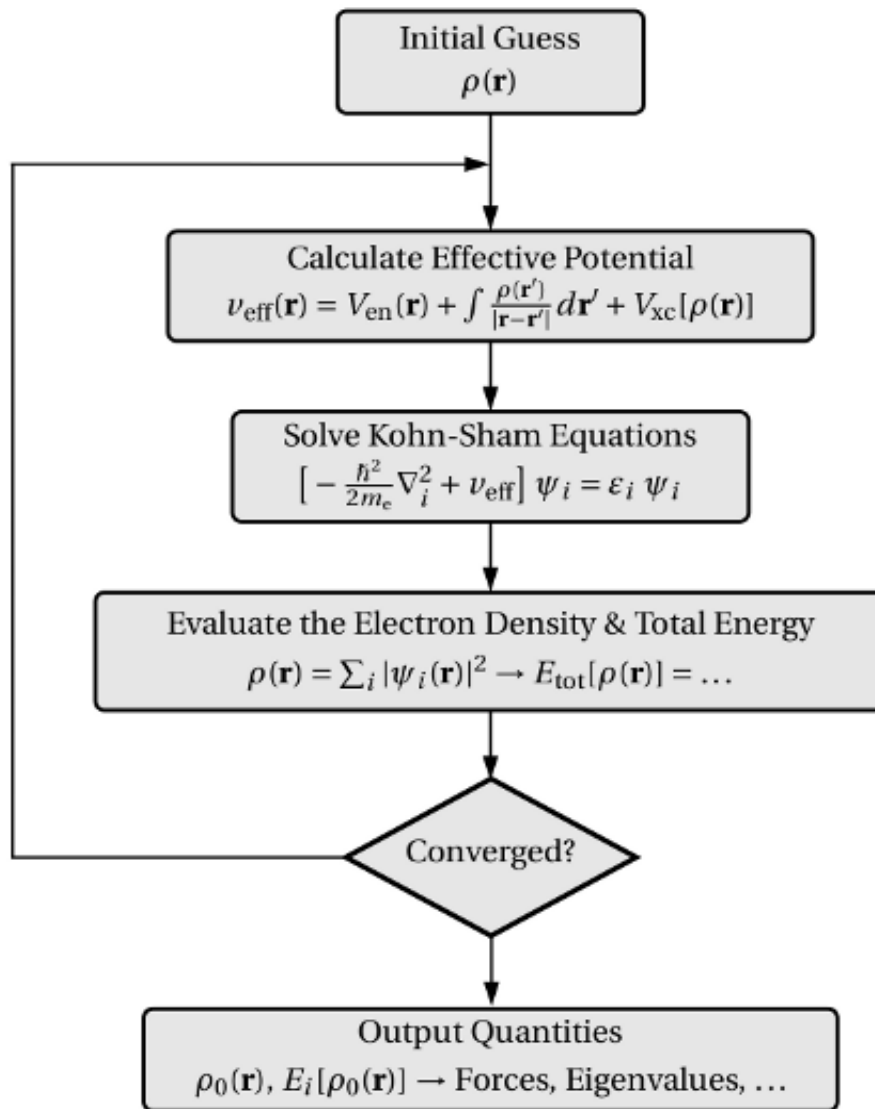


Figure 3.1: *Self Consistent Field of flow chart of the iteration scheme.*

Chapter 4

Results and discussions

Introduction

In this work , the structural and electronic properties of $Al(100)$ surface was calculated within the frame work of the density functional theory. One of the important aspects in studied Aluminum surface is the total minimum energy. Results are mainly presented in figures. The first results are the total energy per atom and second results are forces values for bulk Aluminum. Then comes the results for the equilibrium lattice constants, band structure and density of state with LDA Approximation.

4.1 Structural Calculation of Al(100) surface Parameters

The software xcryden can import QUANTUM ESPRESSO input files and visualize the geometrical structures of Al(100) surface. The primitive cell of Al(100) is shown in Figure 4.1. A single-layer of Al is composed of hexagons with $Al - Al - Al - Al$ atoms situated at a positions of:

ATOMIC-POSITIONS

Al: (0.50000000 0.50000000 0.5000000000000000)

Al: (0.50000000 0.50000000 3.5355339059327378)

Al: (0.00000000 0.00000000 2.8284271247461898)

Al: (0.50000000 0.50000000 2.1213203435596428)

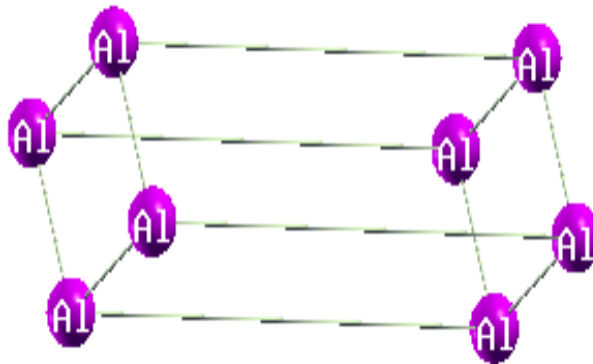


Figure 4.1: *Geometrical Structure of tetragonal Al(100) surface*

4.2 Convergence Test of Total energy of $Al(100)$ surface per atom with respect to energy cutoffs

To compute The Total energy of $Al(100)$ surface with respect to energy cutoff, The input file is initially adjusted to have $6 \times 6 \times 1 = 36$ k-points mesh; some of these k-points have the same energy because of the symmetry of the crystal. The calculation was done using different cutoff values, from 15Ry to 160Ry with 5Ry interval and lattice constant of $a = 5.42$ Bohr and $C = 6.36$ bohr.

. Here we see that, the total minimum energy of $Al(100)$ surface is calculated as a function of energy cutoff. An increment of energy cutoff for wave function is made until the convergence is achieved (i.e., the plane where the energy becomes nearly constants). The energy cutoff versus total energy graph is shown in figure 4.2. From the graph we can observe that the total minimum energy converges at 55 Ry plane wave cutoff energy and the total ground state energy had its minimum at -16.578404406 Ry whose plot is shown below. Moreover the total minimum energy is monotonically decreasing with increasing energy cutoffs for wave function. The accuracy of the ground state energy depends on the number of basis functions. However, we can get energy that close to ground state energy as the number of basis functions approaches infinity.

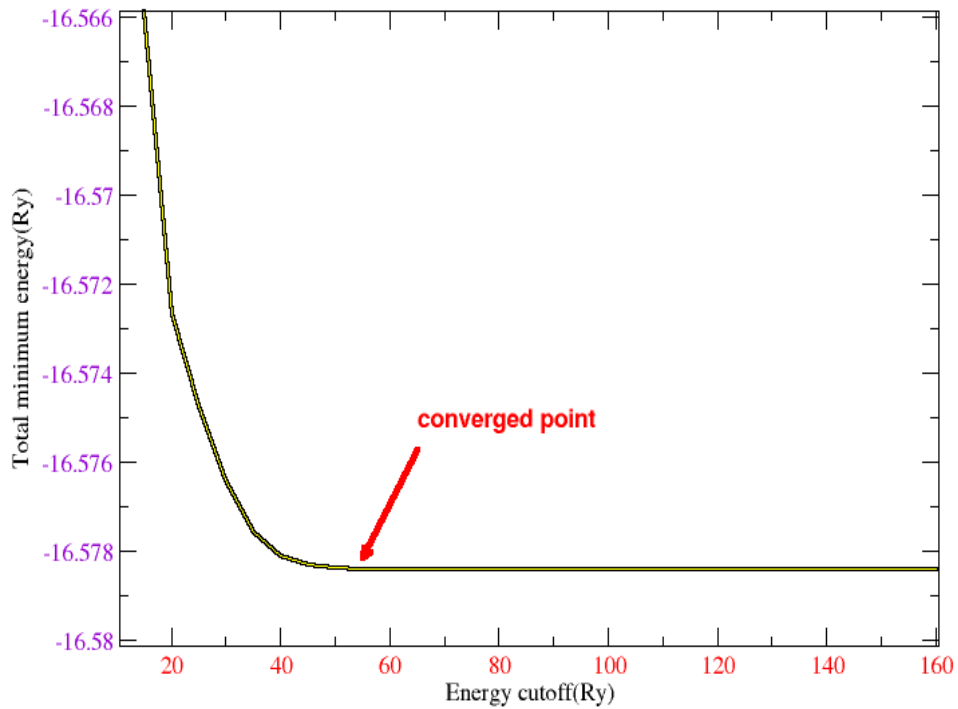


Figure 4.2: *Total energy of Al(100) with respect to energy cutoff*

4.3 Convergence Test of Total minimum energy of Al(100) with respect to K.point grid sampling

To compute the Total energy of Al(100) surface per atom with respect to K.point values are used starting from $2 \times 2 \times 1$ up to $36 \times 36 \times 1$ with step by step. Keeping the cutoff energy at 15 Ry and lattice constant of $a=5.42$ bohr, $C=6.36$ bohr. A convergence test of total energy for k.point sampling was performed on Al(100) surface. The total minimum energy of Aluminum(100)surface was calculated using

various sets of ranging from $2 \times 2 \times 1$ up to $36 \times 36 \times 1$. In each of these cases the plane wave kinetic energy cutoff $15Ry$ was used. The Total energy of Al(100) surface is calculated as a function of k.points grid size using *PWSCF* code. For this calculation, the other variables (lattice constant, energy cutoff) are kept constant. The total energy of Al versus k.points grid size is shown in Figure 4.3. Convergence of the Total energy is achieved at $17 \times 17 \times 1$ k-points grids and the total energy at this point is -16.56548126 Ry whose plot is shown below.

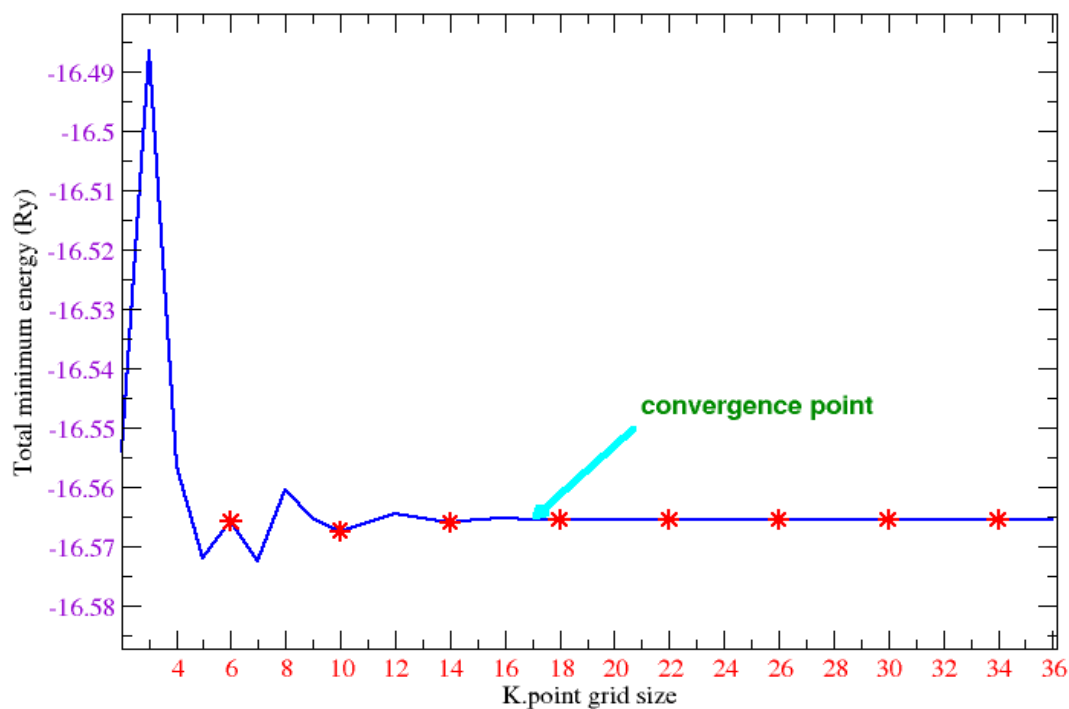


Figure 4.3: Total energy of Al with respect to K.point grid size

4.4 Convergence Test of Total minimum forces of Al(100) surface per atom with respect to energy cutoff

Initially, the net forces acting on Al(100) surface are zero in x, y and z directions. This is because of the result symmetry, which cancels out forces. However, it is possible to create forces by displacing a aluminum atom +0.5 Bohr in the x, y and

z directions (fractional coordinates), net force is created. Here we calculated total force on $Al(100)$ surface as a function of plane wave cutoff energy by keeping other parameters fixed. For this calculation, we used the lattice constants $a = 5.42$ Bohr, $C = 6.36$ bohr and $6 \times 6 \times 1$ k-points grid. In this simulation convergence is achieved when the energy cutoff is equal to $42Ry$. A total force value at this energy cutoff is $0.00676894Ry/Bohr$. The graph of energy cutoff against total force acting on $Al(100)$ surface is shown in figure 4.4.

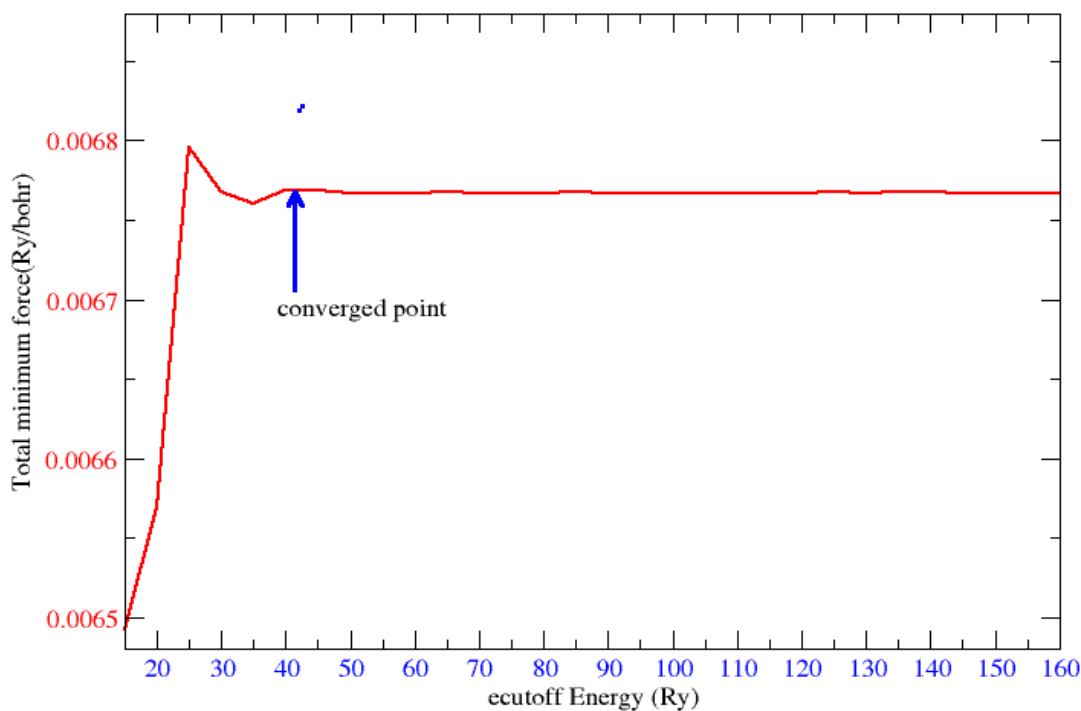


Figure 4.4: *Total forces of Al with respect to energy cutoffs*

4.5 Convergence Test of Total force of Al(100) surface per atom with respect to K.point sampling

In this case, we have calculated the force on 0.5 Bohr displaced Al(100) surface as a function of k-point grid size, by keeping other parameters (lattice constant, energy cutoff) constant. The calculated force with respect to k.point grid is shown above in table 4.4. Moreover the trend of total force for increment of grid size is described

in Figure 4.5. As it is observed in Figure, the total force converge at the grid size of $17 \times 17 \times 1$ k-point mesh; and its value is 0.00650925 Ry/ Bohr. Generally, it is true that different structural geometries will require different k-point meshes in order to reach convergence. However, the change in required k-point density for a slight shift in atoms is expected to be large than the change in required k-point density if we completely change the crystal symmetry for basic centered cubic to face centered cubic.

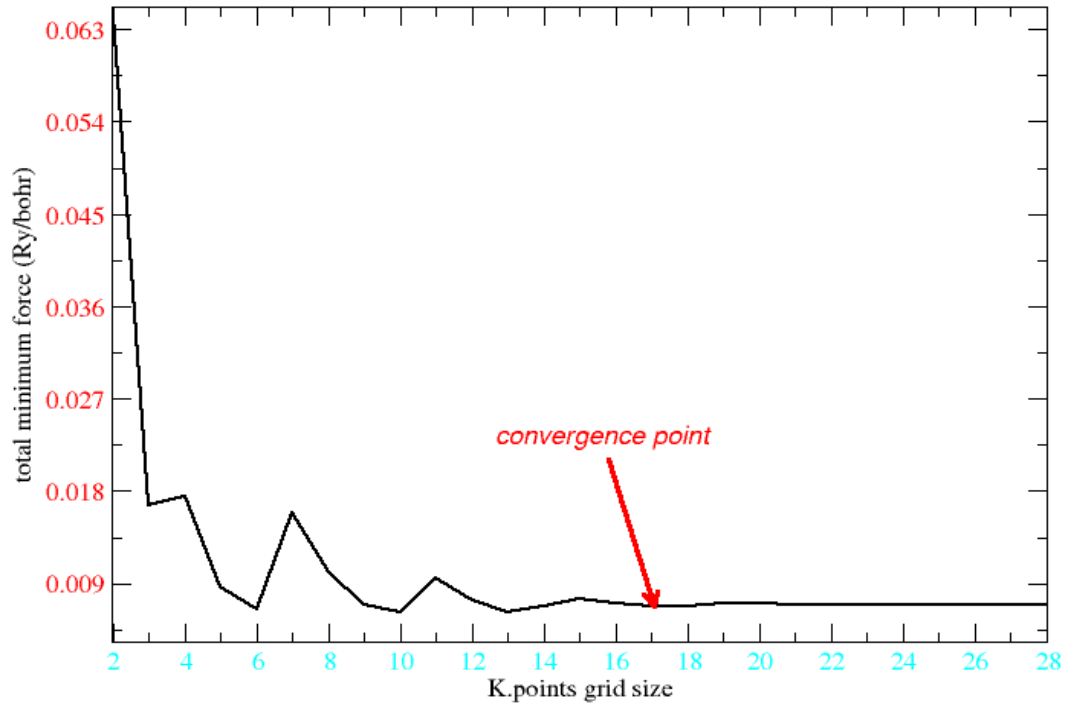


Figure 4.5: Total force of Al(100) surface with respect to k.point grid size

4.6 The equilibrium lattice constant of Al(100) surface with respect to total minimum energy

The equilibrium lattice constant of Al(100) surface was calculated by keeping the cut off energy at 50 Ry and k-point grids at $17 \times 17 \times 1$. In this calculation the total energy of Al(100) was computed by changing the lattice parameter from 4.42 bohr to 6.42 bohr in step of 0.1 and $(C \times a)/a_{const}$ values calculated.

The structure of Al(100) shown in figure 4.1 is tetragonal. so the two dimensional

a and b are equal and represented by initial values of $a = 5.42$ Bohr and the third dimension is represented by C of initial values $C=6.36$ Bohr. The total energy of Al(100) surface was computed for different values of lattice parameters ranging from 4.42 bohr to 6.42 bohr under a constant cutoff energy 50 Ry and k-point grids $17 \times 17 \times 1$. The result of out put shows that the total energy is decreasing until the lattice parameter is 5.32 bohr and then start increasing from 5.35 bohr up to 6.42 bohr lattice. This shows that the total energy is converged at a lattice value $a=5.32$ bohr. Similarly to calculate value of C , the value of $a = 5.42$ bohr was adjusted to be constant and computation was made for each value of C from 5.369 bohr to 7.799 bohr. The lattice constant (c) versus total energy graph is shown in figure 4.6. The graph shows that the equilibrium lattice constant of c is 6.48 bohr . The equilibrium lattice constant $a = 5.22$ bohr and $c = 6.48$ bohr which were found from the computation are closer to the experimental value of $a = 5.42bohr$ and $c = 6.36bohr$. this was better shown in the plot below.

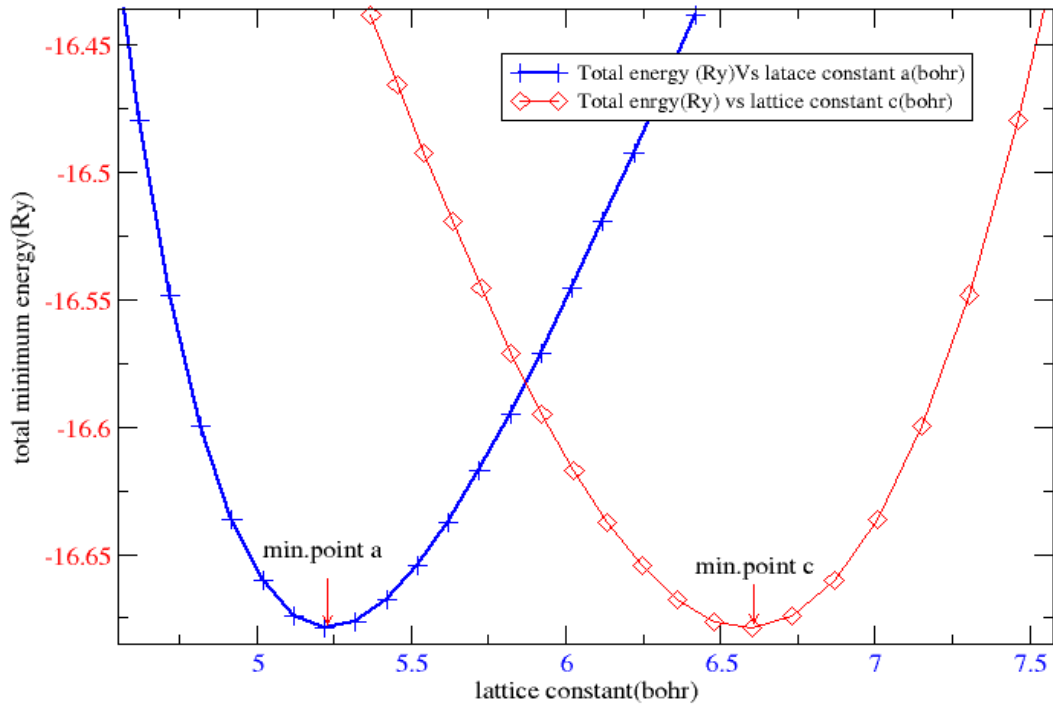


Figure 4.6: *Total energy of Al(100) surface versus lattice constant*

4.7 The equilibrium lattice constant of Al(100) surface per atom with respect to total minimum force

In this case, the calculation was done using different lattice constant a values from 4.42 bohr to 6.42 bohr and lattice constant C values calculated from 7.799 bohr to 5.36935 bohr. Here the other variables such as k -point, energy cutoff, are kept fixed.

This is show that the total forces converged at 0.00182 Ry/bohr, lattice value

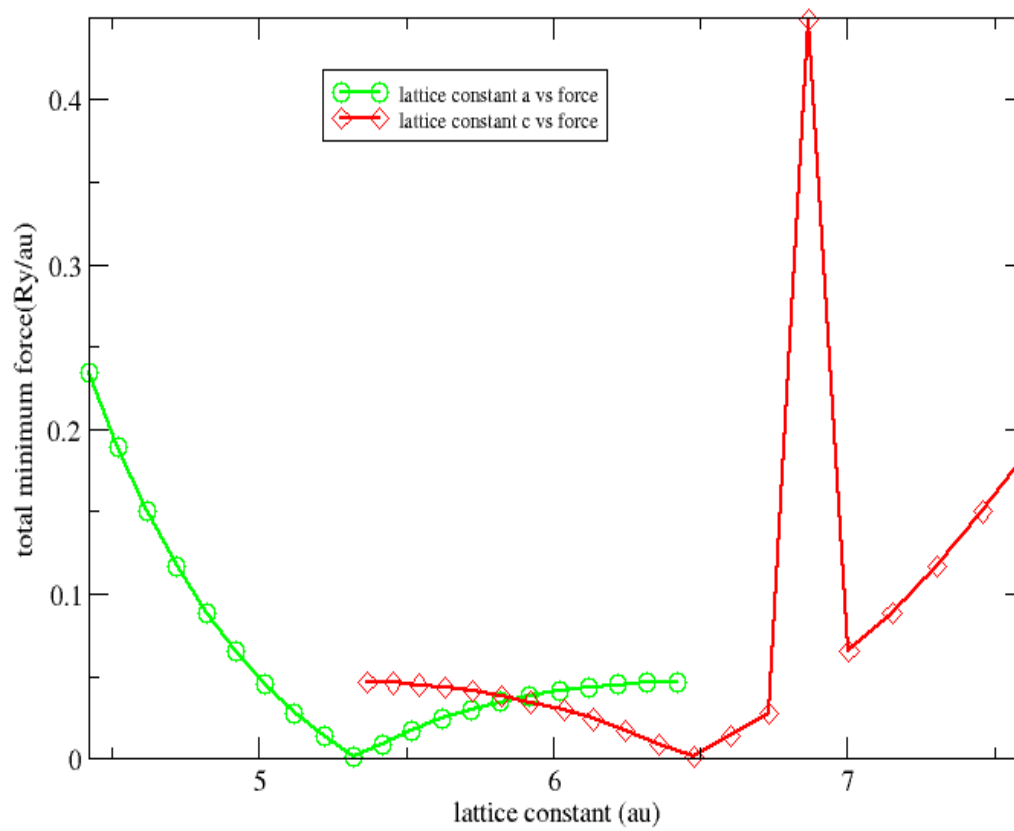


Figure 4.7: *Total force of Al(100) surface versus lattice constant*

$a = 5.3$ bohr and similarly total force are converged at 0.001120045 Ry/bohr at lattice value $c = 6.48$ bohr.

4.8 Band Structure of Al(100)surface

The band structure is a visual representation of the energy levels that the electrons can have inside the solid. These calculations are done almost entirely within the Quantum Espresso suite of programs. If the objective is just to complete a band structure calculation, that is accomplished by calculating an integral over the Brillouin zone of the crystal. However, Quantum Espresso does the numerical integration in an earlier step so then all that is needed is to designate the points desired for plotting. The Brillouin zone of Al(100) is a two dimensional tetragonal. The band structure and outline of the Brillouin zone is well known. The figure 4.8 is the authors depiction of the Brillouin zone, and Table below outlines the coordinates of the key points in the Brillouin zone. The table outlines the coordinates in multiples of $a; b; c$ from equation 2.14.2

Table 4.1: Brillouin Zone Coordinates Table

Coordinates	X	Y	Z
Γ	0.00000	0.00000	0.00000
X	0.00000	0.50000	0.00000
M	0.50000	0.50000	0.00000
Γ	0.00000	0.00000	0.00000

In this work, the energy cutoff and the BZ sampling were chosen to converge the total energy with a value of 15 Ry and we generated 71 K-points in crystal coordinate. From the Figure 4.9 we can observe that there is no band between balance band and

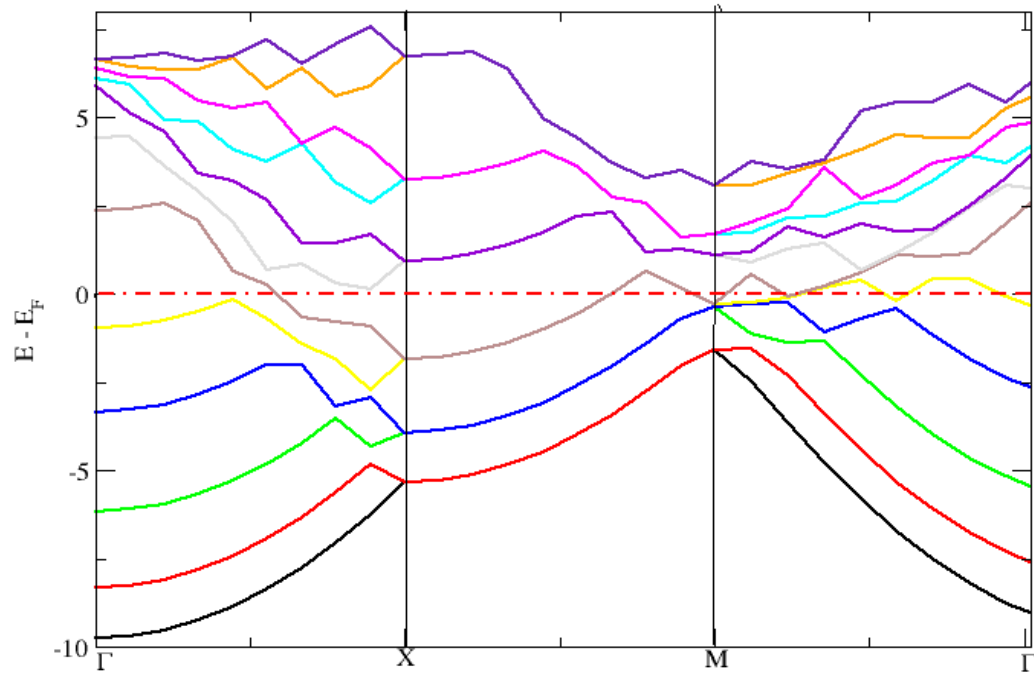


Figure 4.8: *Band Structure of primitive unit cell of 2D of Al(100) surface*

the calculation band of Al(100) surface. It looks like a metallic or semi-metallic structure with zero band gap.

4.9 Density of State (DOS) of Al(100) surface

The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy. Fermi level is indicated at -3.89 eV. The calculate Density of state is continuous from valence band to conduction band with out any discontinuity and confirms that Al(100) is a metallic system.

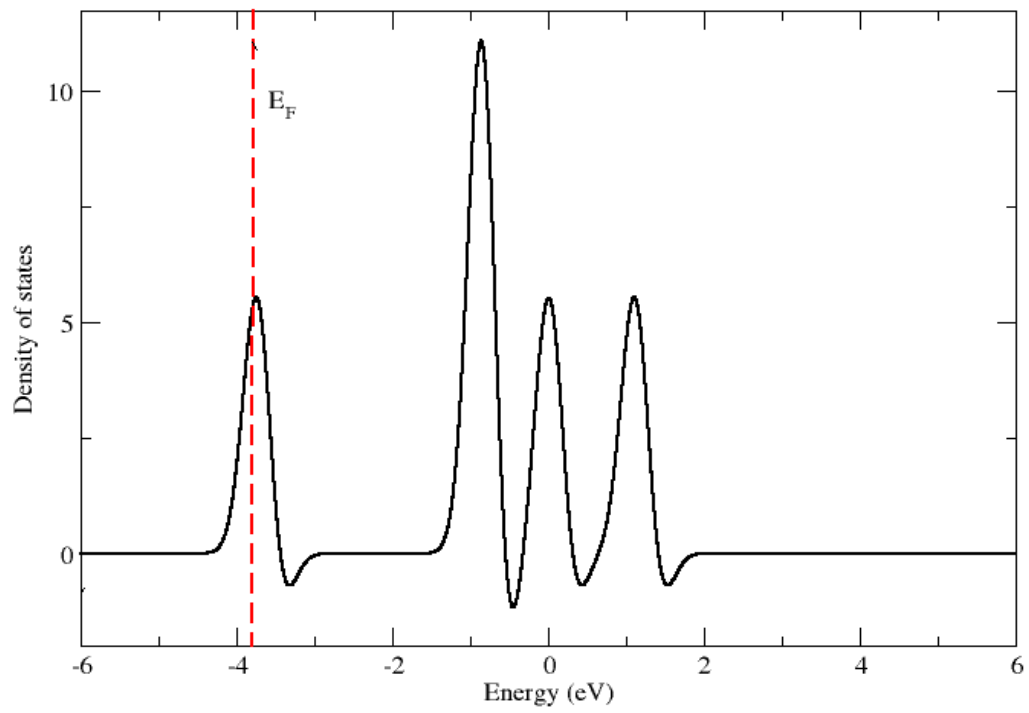


Figure 4.9: *Band Structure of primitive unit cell of 2D of Al(100) surface*

Chapter 5

Conclusion

The electronic and structural properties of Al(100) surface was investigated with in the frame work of the density functional theory, plane wave basis sets, and pseudo potentials (ultrasoft). All calculations have been carried out with Quantum Espresso package (software). The total energy calculation is as a function of cut-off energy and Monkhorst pack-grid size, respectively, fixing the other parameters constant. The total energy convergence test is achieved, at the energy cut-off 55 Ry for the first case and at $6 \times 6 \times 1$ k-point grid size for the second case. The total energy is -16.56548126 Ry . As a function of cutoff energy and Monkhorst-Pack grid is calculated by displacing Al atom by $+0.5bohr$. Total force convergence test is achieved for the cutoff energy 42 Ry and for Monkhorst-Pack grid at $6 \times 6 \times 1$ k-point grid size. The optimized Lattice constants of Al(100) surface have been determined to be $a = 5.22$ Bohr, $c = 6.48$ Bohr, and $c/a = 6.24$ bohr with respect to our computational calculation. The experimental values of Al(100) surface is ($a = 5.42$ Bohr, $c = 6.36$ Bohr, and $c/a = 6.36$ bohr). The band structure calculation shows that there is overlap between the conduction band and the valance band. That is there is no band gap between the valence band and conduction band. This result tells Al(100) surface

is a metallic system. Moreover the absence of discontinuity in the total Density of state near the Fermi level (from valence band to conduction band) Confirms Al(100) is a metallic system.

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