ELECTRONIC AND STRUCTURAL PROPERTIES OF ALUMINUM WITH RESPECT TO DENSITY FUNCTIONAL THEORY

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To my lovely children

Table of Contents

Abstract

In this study the electronic and structural properties of Aluminum (Al) were investigated with respect to density functional theory by using Quantum Espresso Package.The local density approximation (LDA) and the generalized gradient approximation (GGA) were used to compute the exchange correlation energy.The total minimum energy of Aluminum is performed as a function of cutoff energy and Monk horst- pack grid size .The results show that, the total minimum energy per atom is monotonically decreasing with increasing cutoff energy due to variational principle.However,there is no systematic trend can be predicted from just increasing the k.point sampling .The total minimum force on Al is computed by displacing Al atom as a function of cutoff energy and k.point grid size by 0.05 Bohr. Moreover, the total minimum force is converged at the cutoff 60 Rydberg and Monk horst-pack mesh of $9 \times 9 \times 1$ k.point.In Addition to this, the equilibrium lattice constant is calculated with different lattice constant.The computational value of the equilibrium lattice is 7.4 Bohr.This result is in good agreement with experimental value. Finally, the four different smearing schemes: Marzari-Vanderbilt, Methfessel -Paxton, Gaussian and Fermi-Dirac are checked for convergence issues of the total minimum energy.The results show that the total minimum energy converges very slowly for Gaussian (Ga) and Fermi-Dirac smearing.
Keywords*:Aluminum,density functional theory,electronic structure,total energy,total force.*

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List of Figures

List of Tables

Chapter 1

Introduction

1.1   General background

Aluminum is the third most abundant element in the earth's crust [1]. Coming after oxygen and silicon. It makes up 8% of the crust's total mass and is the most abundant metallic element [2]. It is never found free in nature and is found in most rocks, particularly igneous rocks as alumina silicate minerals [3, 4]. It is a light metal that is easy to melt, odorless, tasteless, nontoxic, non-magnetic material and has a high electrical conductivity. In the pure metallic state it oxidizes readily in air to form a stable oxide surface that resists further corrosion. Because of these properties Aluminum and its alloys are used extensively in modern industry, technology and everyday life. Its experimental and theoretical study on an atomic scale is still an active field of research. From a fundamental point of view Aluminum is interesting also as a typical nearly-free-electron metal whose basic features can be described by using electron gas concepts beginning with the simplest model [5].

When metals change from the molten to the solid state, they assume crystalline structures. The atoms arrange themselves in definite ordered symmetrical patterns which metallurgists speak of as "lattice" structures. Aluminium, like copper, silver and

gold, crystallizes with the face-centred-cubic arrangement of atoms, common to most of the ductile metals. This means that the atoms form the corners of a cube, with one atom in the centre of each face. The length of the sides of the cube for high purity Aluminium has been determined as 4.049×10^{-8} cm; the shortest distance between two atoms in the Aluminium structure is $\sqrt{2}$ divided by 2×4.049. The face centred cubic structure is one of the arrangements assumed by close packed spheres, in this case with a diameter of 4.049×10^{-8} cm, the corners of the cube being at the centre of each sphere. The metal has an atomic weight of 26.98 and a specific gravity of 2.70, approximately one-third the weight of other commonly used metals; with the exception of titanium and magnesium [6].

In practical applications aluminum is mainly used in the polycrystalline state, although for theoretical simulations and precise experimental studies mono crystalline Al is more suitable. Under low and normal pressure it crystallizes in a FCC (face-centered cube) structure only [7]. Total Energy calculation and molecular dynamic simulation employing density-functional theory represent a reliable tool in condensed matter physics, material science, and physical chemistry. A large variety of applications such as in molecules, bulk materials and surfaces have proven the power of these methods in analyzing as well as predicting non-equilibrium and equilibrium properties. Density-functional theory (DFT) is one of the most popular and successful quantum mechanical approaches to matter. It is nowadays routinely applied for computations of ground state properties of molecules and solids such as the binding energy of molecules and the band structure of solids in physics. The diamond lattice structure is very common in semiconductor materials, such as Si, Al and Ge. AlAs, GaAs and GaP has a zincblende lattice structure which is similar to the diamond

lattice structure. The diamond and zincblende structures are similar except that in diamond structure there is only one type of atom where as in zincblende there are two types of atoms [8].

Calculation of the bulk ground state properties, such as lattice constants, bulk modulus, cohesive energy, and atomic positions, play an important role in the physics of condensed matter [9,10]. Bulk calculations help us to understand, characterize, and predict mechanical properties of materials in surroundings, under extreme conditions [11]. The electronic structure of Aluminum was studied by different scholars analytically. However the electronic and structural properties of Aluminum is not well studied computationally. So the aim of this research is to study electronic and structural properties of Aluminum based on density functional theory using quantum espresso package for the exchange-correlation energy.

1.2 Statement of the problem

It is clear that many body problems are complicated and difficult to solve. That is, the state of motion cannot be solved analytically for systems in which three or more distinct electrons interact. In recent years, there has been remarkable surge activity in the application of density functional techniques to many body systems such as molecular and solid state systems and to problems of chemical interest. The fundamental tenet of density functional theory is that any property of the system of many interacting particles can be viewed as a functional of the ground state density $n_0(r)$; that is one scalar function of position $n_0(r)$, in principle determines all the information in the many body wave functions for the ground state [12]. So the purpose of this study was to investigate the structural and electronic properties of Al with the

help of density functional theory or ab-Initio techniques.

1.3   Objectives

- General objective

The general objective of this study was to calculate the electronic and structural properties of Aluminum with respect to density functional theory.

- Specific objectives

Specific objectives of this study were:

1. To calculate the total minimum energy of Aluminum per atom with respect to cutoff energy ;

2. To calculate the total minimum energy of Aluminum per atom with respect to k.points sampling;

3. To calculate the total minimum force of Aluminum per atom with respect to cutoff energy ;

4. To calculate the total minimum force of Aluminum per atom with respect to k.point sampling;

5. To calculate the lattice constant of Aluminum per atom with respect to cutoff energy;

6. To calculate the total minimum energy of Aluminum with respect to degauss/smearing for different k.point sampling.

1.4 Significance of the study

The significance of this study would help to understand the electronic and structural property of many electron system (Aluminum) using new computational technique known as ab-initio technique.It also helps to practice new problem solving technique.

1.5 Scope of the study

The scope of this study were limited to the calculation of the total minimum energy of Aluminum, total minimum force of Aluminum ,lattice constant of Aluminum with respect to cutoff energy and total minimum energy of Aluminum with respect to smearing for different k.point sampling.

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Chapter 2

Literature Review

2.1   Introduction

Any problem in the electronic structure of matter is covered by Schrödinger equation including the time. In most cases, however, one is concerned with atoms and molecules with out time -dependent interaction, so we may focus on the time - independent Schrödinger equation [13]. 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. The Schrödinger equation for the complex many-atom, many-electron system is not analytically solvable, and numerical approaches have become invaluable for physics, chemistry, and materials science [14].

2.2   Schrödinger's equation

All materials are composed of atomic nuclei and electrons. The macroscopic material properties that we observe only depend on the position of these electrons and ions. Thus knowing only the type of atoms the material is made of is in principle enough to calculate the wave function and energy of the system using the (time independent)

Schrödinger equation.The stationary Schrodinger equation [15] is calculated as:

$$H\Psi = E\Psi \tag{2.2.1}$$

Where H is the Hamiltonian and E the total energy of the system. The solution to this equation gives us the total wave function Ψ which in principle contains all wanted properties of the system and is therefore essential in quantum mechanics. The goal is therefore to find this wave function or equivalently, as in the case of DFT, the density $n(r) = |\Psi|^2$.

For the many-body problem of a system containing N electrons and K nuclei with charge Z_I the Hamiltonian calculated as [16, 17].

$$H = -\sum_{i=1}^{N} \frac{\hbar^2 \nabla_i^2}{2m_e} - \sum_{I=1}^{K} \frac{\hbar^2 \nabla_I^2}{2m_I} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{j>i} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I=1}^{K} \sum_{i=1}^{N} \frac{Z_I e^2}{|r_i - R_I|}$$
$$+ \frac{1}{4\pi\epsilon_0} \sum_{I=1}^{K} \sum_{J>I} \frac{Z_I Z_J e^2}{|R_I - R_J|} \tag{2.2.2}$$

The first to terms represent the kinetic energy of the electrons and nucleons, T_e and T_n. The third term represents the electrostatic repulsion between the electrons,V_{ee}. The fourth term represents the electrostatic attraction between the electrons and nuclei, V_{ne}, and the last term between the nuclei,V_{nn}. m_e is the mass of the electrons, and M_I the mass of the cores. Z_I is the number of protons in each core, I. This looks rather complicated. It turns out that the stationary Schrödinger equation can only be solved analytically for a one-electron system, e.g. the hydrogen atom or the ionized helium atom He^+. So, to be able to continue, certain approximations have to be made. As a first approximation one usually makes the Born-Oppenheimer approximation [18], which is justices by the fact that the nuclei (ions) are much heavier than the

9

electrons, $M_I >> m_e$ In most cases, this justify a time-scale separation by saying that the electrons immediately adapt to changes in the positions of the ions. This means that the electronic and ionic system can be treated separately and for the electrons the ions can be regarded as fixed. We can therefore drop the ionic kinetic energy term and the ion-ion interaction term in the Hamiltonian and only consider the terms involving electrons.

$$H_{BO} = -\sum_{i=1}^{N} \frac{\hbar^2 \nabla_i^2}{2m_e} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{J>i}^{N} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I=1}^{K} \sum_{i=1}^{N} \frac{Z_I e^2}{|r_i - R_I|} \qquad (2.2.3)$$

If we denote the interaction of electron i with the ions $V_{ext}(r_i)$ and use Hartree atomic units $\hbar = m_e = e = \frac{1}{4\pi\epsilon_0} = 1$, we can write the Hamiltonian as

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \sum_{J>i} \frac{1}{|r_i - r_j|} + \sum_i V_{ext}(r_i) \qquad (2.2.4)$$

The Hamiltonian $H(t) = T + V(t) + W$ is assumed to consist of the kinetic energy, spin-independent single-particle potential and some spin-independent particle-particle interaction.

2.3   Density functional theory

Density Functional Theory (DFT) is the model of choice for understanding condensed matter at low energies. It has achieved a certain status as a standard first-principles method. Indeed for many, though not all, significant condensed-matter phenomena DFT is a powerful analytic tool for studying electronic, vibrational, magnetic, superconducting among others [19].

Density Functional Theory (DFT) is a quantum mechanical technique used in Physics and chemistry to investigate the structural and electronic properties of many body

systems. DFT has proved to be highly successful in describing structural and electronic properties in a vast class of materials, ranging from atoms and molecules to simple crystals and complex extended systems (including gasses and liquids). Furthermore DFT is computationally very simple. For these reasons DFT has become a common tool in first-principles calculations aimed at describing or even predicting properties of molecular and condensed matter systems [20, 21, 22].

Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its descendents are based on the complicated many-electron wave function. The main objective of density functional theory is to replace the many-body electronic wave function with the electronic density as the basis quantity. Whereas the many-body wave function is dependent on 3N variables, three special variables for each of the N electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically [8].

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 [23].

2.4 The Hohenberg-Kohn theorems

The Hohenberg-Kohn formalism [23] 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 [24].The energy functional of the density E [n] is:

$$E[n] = \int dr V_{ext}(r)n(r) + F[n] \tag{2.4.1}$$

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 $n_0(r)$:

$$E_0 = E[n_0] \tag{2.4.2}$$

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.

2.5 Kohn-Sham equation

The Density Functional Theory (DFT), in the Kohn-Sham formalism, provides a powerful computational scheme, which allows to determine exactly the ground-state properties even of complex systems of interacting particles, simply solving a single particle like equation.Kohn-Sham density theory [25,26] is widely used for self consistent field electronic structure calculations of the ground state properties of atoms, molecules, and solids. The Kohn and Sham equations as:

$$[-\frac{1}{2}\nabla^2 + \overbrace{V(r)}^{V_{ext}(r)} + V_H(r) + V_{xc}(r)]\psi_i(r) = \epsilon_i\psi_i(r) \tag{2.5.1}$$
$$\underbrace{\phantom{-\frac{1}{2}\nabla^2 + V(r) + V_H(r) + V_{xc}(r)}}_{H_{KS}}$$

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 [22].

2.6 Exchange-correlation energy

The KS DFT provides a practical procedure to solve the many-body problem by breaking the problem into a set of single-particle problems. This formalism is exact but practically still unsolvable since the many-body wave functions are still included in the exchange-correlation term $E_{XC}[n]$, whose exact form is not known.

To make the formalism useful, it is necessary to make some approximations for the exchange-correlation term $E_{XC}[n]$. The most common and straightforward approximation to $E_{XC}[n]$ is the Local Density Approximation (**LDA**) [23].

The idea of the **LDA** is assuming that the exchange-correlation energy per electron of a non-uniform system at any point in space is equal to the exchange-correlation energy per electron in a uniform electron gas having the same density at this point. In LDA the exchange-correlation functional can be written as

$$E_{XC}^{LDA}[n] = \int d\overrightarrow{r} \epsilon_{xc}[n] n(\overrightarrow{n}) \tag{2.6.1}$$

With

$$\epsilon_{xc}[n] = \epsilon_{xc}^{uniform}[n] \tag{2.6.2}$$

By definition, the LDA is local because the exchange correlation energy $\epsilon_{xc}[n]$ at each point in space only depends on the electron density at the same point. The $\epsilon_{xc}[n]$ has been calculated and parameterized through Monte Carlo total energy calculation for a uniform electron gas with a variety of electron densities [27, 28].

Since the LDA is based on uniform electron gas, it is expected to be accurate only for systems in which the electron density varies slowly. It is clearly not suitable for the situations where the electron density undergoes rapid changes, as in the case of covalent bounded solids. To overcome this deficiency of the LDA, another form of exchanged-correlation functional has been developed, that is the Generalized Gradient Approximation (GGA) [29-30].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

$$E_{XC}^{GGA}[n] = \int d\overrightarrow{r} \epsilon_{xc}[n] F_{xc}[n, \overrightarrow{\nabla} n] n(r) \tag{2.6.3}$$

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]. Generally, **GGA** has the following advantages over **LDA** [32, 33-34]:

- 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]

2.7   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 Schroödinger equation for this periodic system, the solution must satisfy a fundamental property known as Bloch's theorem.

2.7.1   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].

$$\Psi_k(r) = e^{i\vec{K}.\vec{r}} u_k(r) \tag{2.7.1}$$

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,

$$u_k(r) = \sum_G c_{i,G} e^{iG.r} \tag{2.7.2}$$

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

$$\Psi_k(r) = \sum_G c_{i,k+G} e^{[i(k+G).r]} \tag{2.7.3}$$

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}.

2.7.2 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

$$\Psi_k(r) = e^{i\overrightarrow{K}.\overrightarrow{r}} u_k(r) \tag{2.7.4}$$

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:

$$u_k(r) = \sum_G c_{i,G} e^{iG.r} \tag{2.7.5}$$

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 , $G.l = 2\pi n$.

Combining the two equations above gives

$$\Psi_k(r) = \sum_G c_{i,k+G} e^{[i(k+G).r]} \tag{2.7.6}$$

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

$$E = \frac{\hbar^2}{2m} |k + G|^2 \tag{2.7.7}$$

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:

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}^2 \tag{2.7.8}$$

The infinite sum then reduces to

$$\Psi_k(r) = \sum_{|G+k|<Gcut} c_{G+k} e^{[i(K+G)r]} \tag{2.7.9}$$

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].

2.7.3   K.points sampling

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 [38-39].

2.7.4 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 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 reduced 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].

2.8   Pseudopotentials

From the earliest developments of plane-wave methods, it was clear that there could be great advantages in calculations that approximated the properties of core electrons in a way that could reduce the number of plane waves necessary in a calculation. The most important approach to reducing the computational burden due to core electrons is to use pseudopotentials. Conceptually, a pseudopotential replaces the

electron density from a chosen set of core electrons with a smoothed density chosen to match various important physical and mathematical properties of the true ion core. The properties of the core electrons are then fixed in this approximate fashion in all subsequent calculations; this is the frozen core approximation. Calculations that do not include a frozen core are called all-electron calculations, and they are used much less widely than frozen core methods.

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 [37].

2.9   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):

$$[-\frac{\nabla^2}{2} + V_{ext}(n(r), r)]\psi_i(r) = \varepsilon_i \psi_i \tag{2.9.1}$$

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

$$V_{ext}(n(r), r) = V_{ion}(r) + V_H(n(r), r) + V_{xc}(n(r), r), \tag{2.9.2}$$

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

$$n(r) = 2 \sum_{i=1}^{n_{occ}} |\psi_i(r)|^2, \tag{2.9.3}$$

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)[44].

2.9.1 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].

Chapter 3

Materials and methods

3.1   Materials

The study was purely theoretically. The main sources of information are the published articles, books, thesis and dissertations. Softwares and computers are additional instruments used to accomplish this project.

3.2   Computational methodology

Our calculations would be based on Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt ultra soft pseudopotentials [46] and the plane wave basis set implemented in the Quantum-ESPRESSO program package [47]. Quantum ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling based on density-functional theory (DFT) [22-25], plane waves basis sets (PW) and pseudo potentials (PP) [48].

It is freely available and distributed as open-source software under the terms of the GNU General Public License (GPL). The present applicability of Quantum ESPRESSO ranges from simple electronic structure calculations to the most sophisticated theoretical spectroscopy such as Nuclear Magnetic Resonance (NMR), Electron Paramagnetic Resonance (EPR), Raman and Scanning Tunneling Microscopy, etc. The simulation tools implemented in Quantum ESPRESSO are used across a wide range of R and D applications. The relevance of this code has been highlighted by its adoption in a number of key research groups, renowned institutions as well as in a number of commercial industries. The most important input parameters in Quantum Espresso are the atomic geometries (number and types of atoms in the periodic cell, bravais-lattice index, crystallographic or lattice constants), the kinetic energy cutoff and the type of pseudo potentials [49].

Chapter 4

Results and discussions

Introduction

In this work , the structural and electronic properties of Aluminum(Al) was calculated within the frame work of the density functional theory. One of the important aspects in studied Aluminum is the total minimum energy. Results are mainly presented in tables and 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 and different smearing for different k.point sampling. The output files of the computations were use to deduce the tables of energy cutoffs, k.points and lattice constants against the total energies and graphs were plotted to obtain the optimized parameters for Al structure with in the both LDA and GGA .

4.1 Total energy of Al per atom with respect to energy cutoffs

The input here has $6 \times 6 \times 6 = 216$ k. point's 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 20 to 150 Ry and lattice constant of 7.50 Bohr.

Table 4.1: The results of the total minimum energy computed with energy cutoffs

Energy cutoffs(Ry)	Total energy(Ry)
20	-4.18846340
30	-4.18947981
40	-4.18986824
50	-4.18993525
60	-4.18993525
70	-4.18993544
80	-4.18993569
90	-4.18993586
100	-4.18993593
110	-4.18993595
120	-4.18993596
130	-4.18993595
140	-4.18993596
150	-4.18993596

4.1.1 Convergence test of total minimum energy of Al with respect to energy cutoffs

Here we see that, the total minimum energy of Al is calculated as a function of energy cutoff. An increment of energy cutoff for wave function is made until the convergence is achieved. As we can see from the Fig4.1, the total minimum energy converge at 50 Ry plane wave cutoff energy and the total ground state energy had its minimum at -4.18993525 Ry . 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.
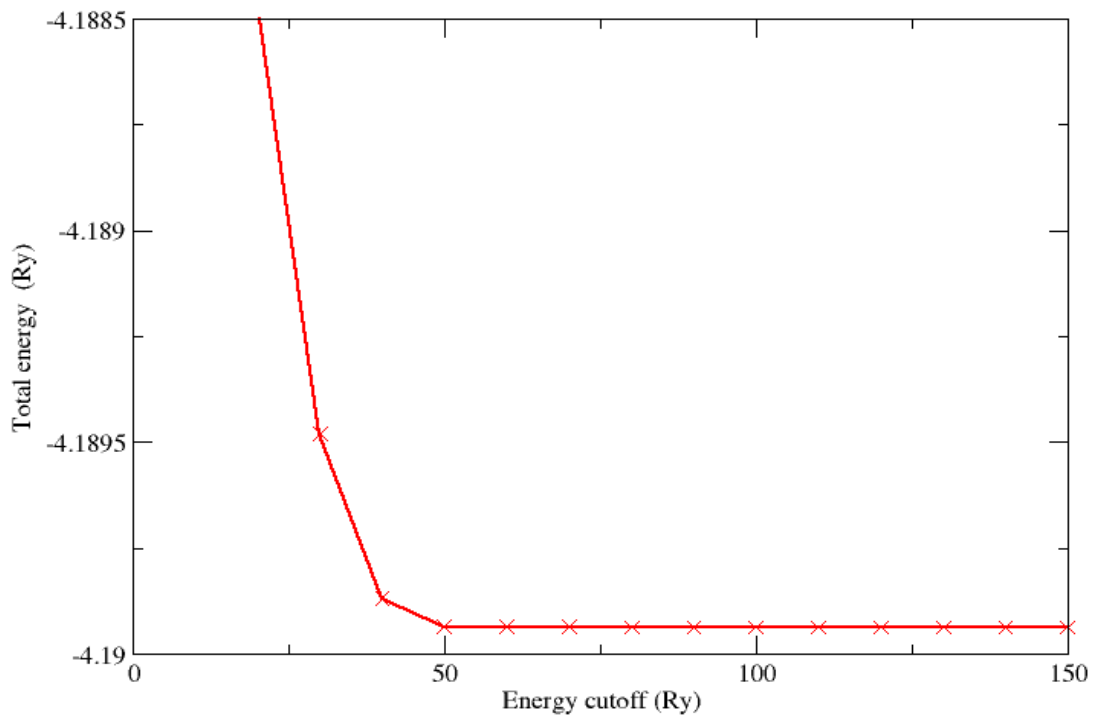
Figure 4.1: Total minimum energy of Al with respect to energy cutoffs

4.2 Total minimum energy of Al with respect to K.point grid sampling

In this case, the calculation was done using different k.point's values from $2 \times 2 \times 1$ to $28 \times 28 \times 1$ mesh with 2.0 points. Here the other variables such as lattice constant, energy cutoff, are keeping fixed.

Table 4.2: The results of the total minimum energy of Al computed with K.points grid

K. points grid	Total energy (Ry)
2	-4.18262858
4	-4.18761179
6	-4.18846340
8	-4.18914036
10	-4.18925069
12	-4.18921005
14	-4.18918761
16	-4.18918792
18	-4.18918878
20	-4.18918870
22	-4.18918833
24	-4.18918860
26	-4.18918852
28	-4.18918864

4.2.1 Convergence test of total energy of Al with respect to K.point grid sampling

Here we can see that, the total minimum energy of Aluminum 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.point's grid size is shown in Figure 4.2. Here it can be observed that the total minimum energy of Aluminum converges at $14 \times 14 \times 14 \times 1$ k.points grid and the total ground state energy has its minimum at -4.18918761 Ry .
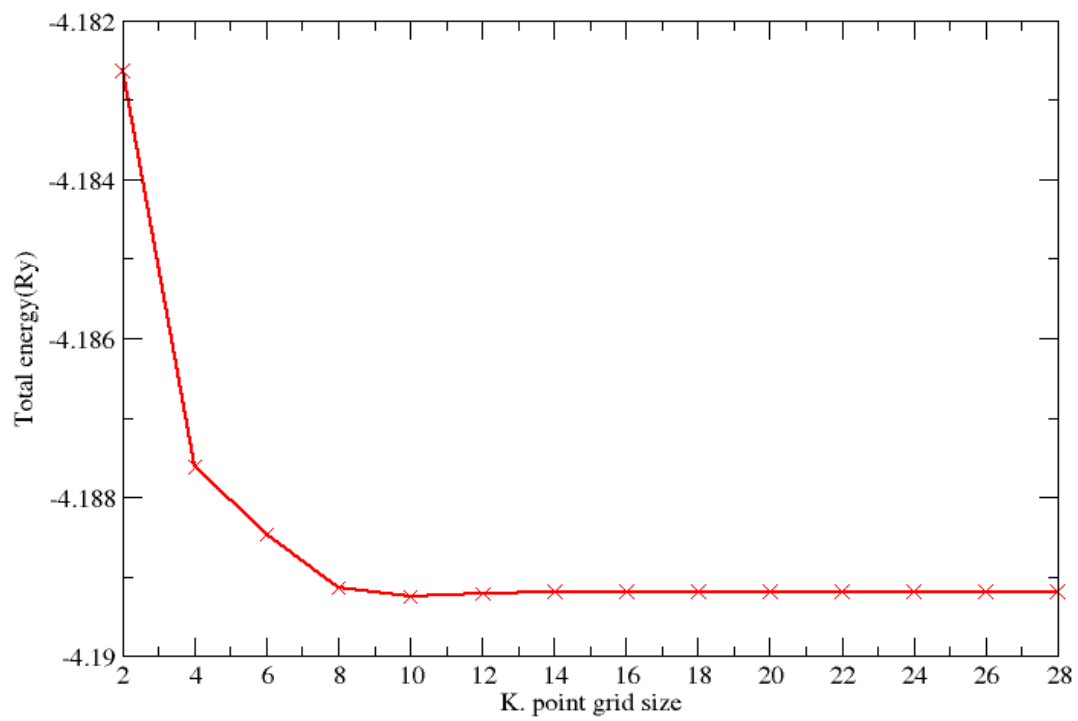
Figure 4.2: Total energy of Al with respect to K.point grid size

4.3 Total minimum forces of Al per atom with respect to energy cutoff

Table 4.3: The result of total forces of Al computed with energy cutoffs

Energy cutoff (Ry)	Total forces (Ry/Bohr)
20	0.449196
30	0.448343
40	0.448857
50	0.448845
60	0.448835
70	0.448834
80	0.448833
90	0.448834
100	0.448832
110	0.448829
120	0.448835
130	0.448833
140	0.448831
150	0.448829

4.3.1 Convergence test of total force of Al with respect to energy cutoffs

In this calculations, we see that the forces on Al are zero in x ,y and z directions.This is because of symmetry,which cancels out forces. However, it is possible to create forces by displacing a aluminum atom + 0.05 Bohr in the z directions (fractional coordinates). Here we calculated total force on Al as a function of plane wave cutoff energy by keeping other parameters fixed. For this calculation, we used the lattice constants a = 7.50 Bohr and $6 \times 6 \times 6 \times 1$ k .points grid. In this simulation convergence is achieved when the energy cutoff is equal to 60 Ry. A total force value at this energy cutoff is 0.448835 Ry/ Bohr.
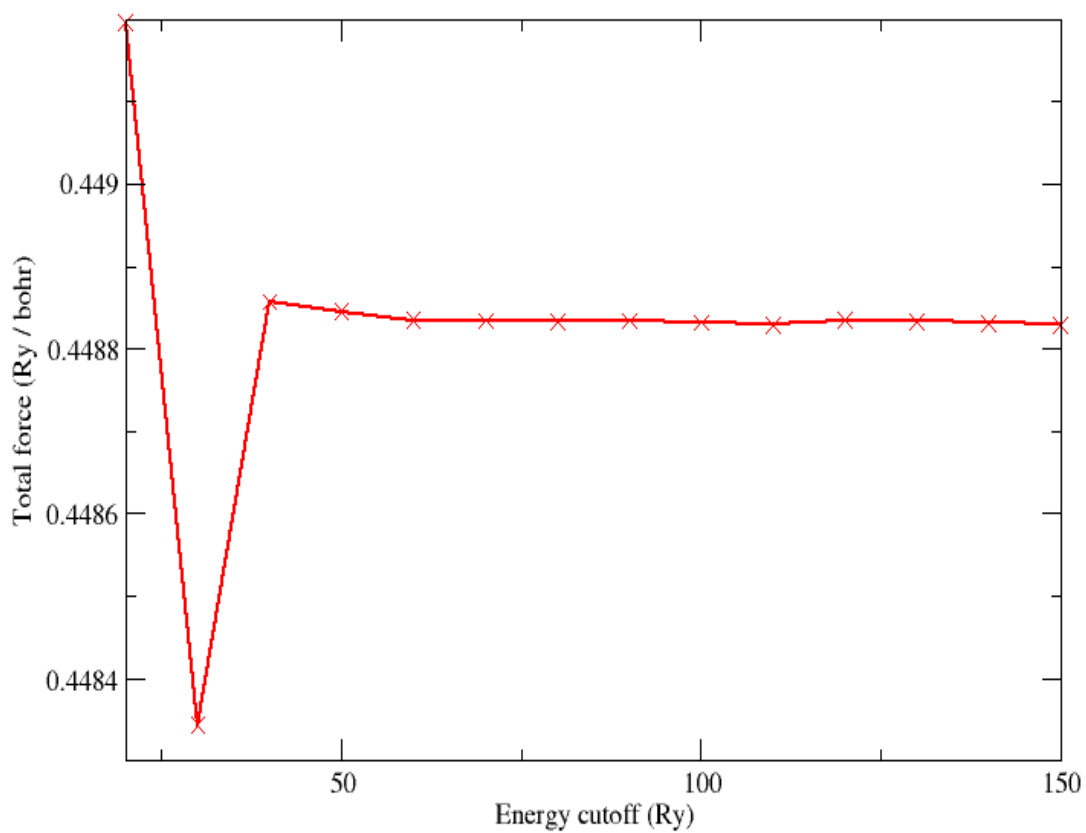
Figure 4.3: Total forces of Al with respect to energy cutoffs

4.4 Total force of Al per atom with respect to K.point sampling

Table 4.4: The result of total force of Al computed with K.point grid

K.points grid	Total forces (Ry/Bohr)
2	0.447652
3	0.451531
4	0.447882
5	0.448995
6	0.449196
7	0.448663
8	0.449014
9	0.448837
10	0.448830
11	0.448876
12	0.448830
13	0.448847
14	0.448847
15	0.448844

In this case, we have calculated the force on 0.05 Bohr displaced Al 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 Fig4.4. As it is observed in Figure, the total force converge at the grid size of $9 \times 9 \times 1$ k.point mesh; and its value is 0.448837 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.
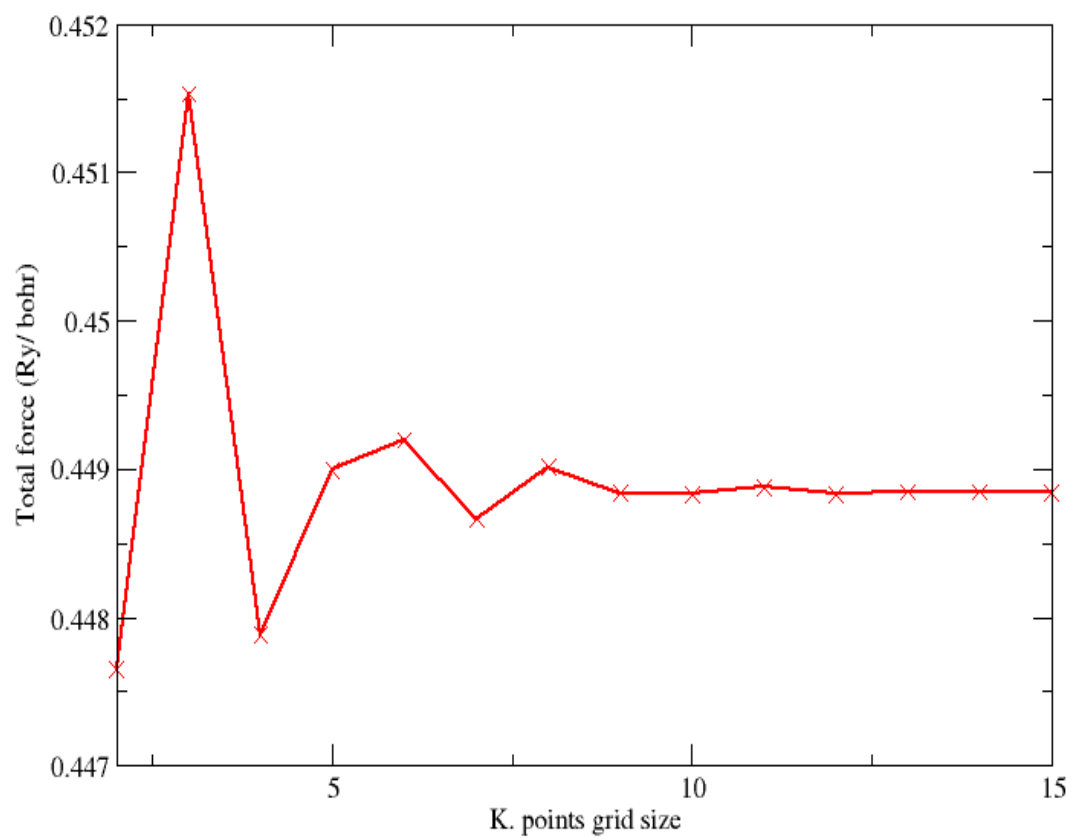
Figure 4.4: Total force of Al with respect to k.point grid size

4.5   The equilibrium lattice constant of Al

Table 4.5: The result of total energy of Al computed versus lattice constant

Lattice constant (Bohr)	Total energy Ry)
6.2	-4.04683272
6.4	-4.09640121
6.6	-413250305
6.8	-4.15777158
7.0	-4.17436079
7.2	-4.18400582
7.4	-4.18809055
7.6	-4.18788244
7.8	-4.18436495
8.0	-4.17844531
8.2	-4.17081838
8.4	-4.16205111
8.6	-4.15256902
8.8	-4.14268531
9.0	-4.13260656

4.5.1   Convergence test of total energy of Al with versus lattice constant

To find the equilibrium lattice constant of aluminum we perform total energy calculation for a series of plausible parameters. In this calculation the energy cutoff and the k.point sampling are made fixed (50 Ry,$14 \times 14 \times 1$ k.point) using the cutoff and k.point grid criteria for energy convergence. The numerical calculation shows that the equilibrium lattice constant is 7.4 Bohr. This result is in good agreement with experimental value.

Figure 4.5: Total energy of Al versus lattice constant

4.6 Total energy of Al with respect to degauss/smearing

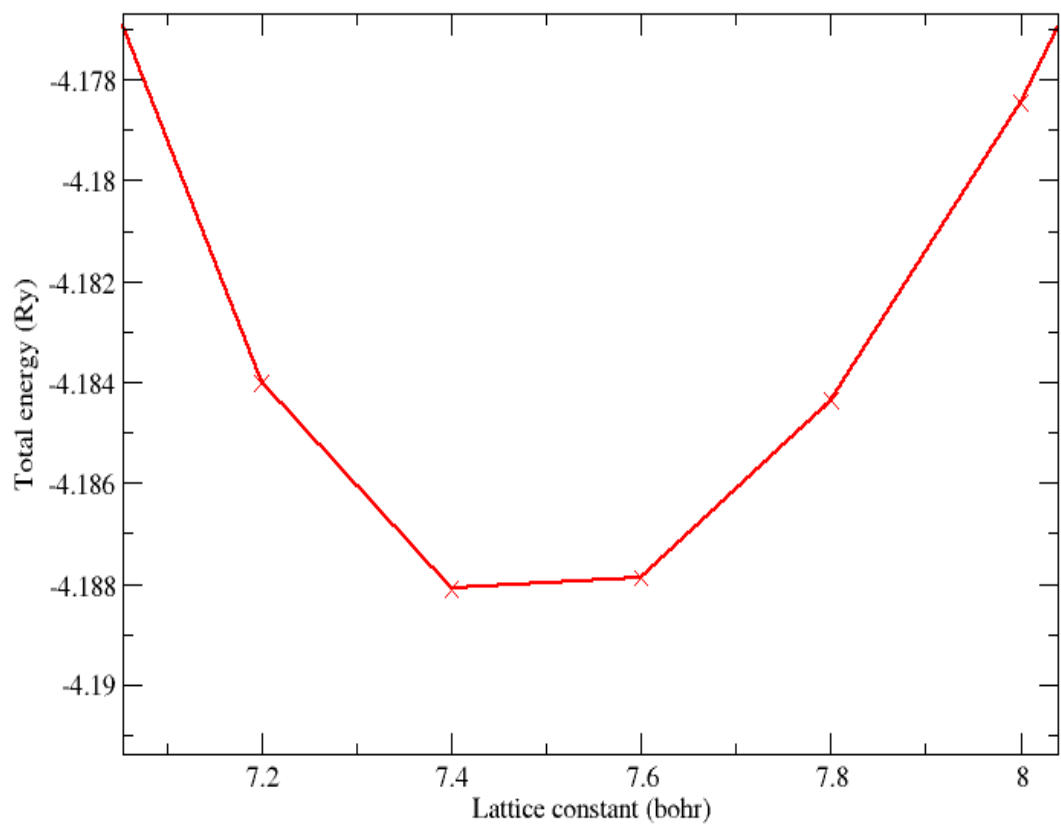Degauss is the electronic temperature; it controls the broadening of the occupation numbers around the Fermi energy and smearing used to select occupation distribution; there are two options: Fermi-Dirac smearing (fd); cold-smearing (cs) including marzari-vanderbilt(m-v), Methfessel-Paxton(M-P) and Gaussian(Ga).

In this calculation, the plane wave cutoffs for wave functions are fixed is 20 Ry and Brillouin Zone integrations have been performed using different smearing from 0.04 up to 0.19 over shifted Monkhorst-Pack meshes of order $6 \times 6 \times 1$ for the face central cubic (fcc). Here we see that, the an increment of the smearing are necessary to obtain fully converged total minimum energy of Al.

4.6.1 Total energy of Al with smearing for $6 \times 6 \times 1$ k.point grid

Table 4.6: The result of total energy of Al computed with smearing

Smearing	Total energy(Ry) in (m-v)	Total energy(Ry) in(m-p)	Total energy(Ry) in (ga)	Total energy(Ry) in (f-d)
0.04	-4.18835466	-4.18857321	-4.19077017	-4.20297416
0.05	-4.18836914	-4.18855767	-4.19200130	-4.21098514
0.06	-4.18846340	-4.18854687	-4.19351577	-4.22073630
0.07	-4.18861398	-4.18854998	-4.19530945	-4.23223843
0.08	-4.18880064	-4.18857333	-4.19737585	-4.24549811
0.09	-4.18900688	-4.18861820	-4.19970845	-4.26051439
0.10	-4.18921827	-4.18867873	-4.20230236	-4.27727878
0.11	-4.18942586	-4.18874550	-4.20515502	-4.29577619
0.12	-4.18962864	-4.18880954	-4.20826601	-4.31598586
0.13	-4.18983216	-4.18886426	-4.21163628	-4.33788211
0.14	-4.19004533	-4.18890584	-4.21526751	-4.36143498
0.15	-4.19027770	-4.18893276	-4.21916159	-4.38661068
0.16	-4.19053804	-4.18894514	-4.22332033	-4.41337204
0.17	-4.19083396	-4.18894416	-4.22774525	-4.44167898
0.18	-4.19117196	-4.18893152	-4.23243757	-4.47148888
0.19	-4.19155781	-4.18890916	-4.23739816	-4.50275710

4.6.2 Total energy of Al with smearing for $8 \times 8 \times 1$ **k.point grid**

Table 4.7: The result of total energy of Al computed with smearing

Smearing	Total energy (Ry)in(m-v)	Total energy (Ry)in (m-p)	Total energy (Ry) in (ga)	Total energy (Ry) in (f-d)
0.04	-4.18928243	-4.18935737	-4.19134283	-4.20317625
0.05	-4.18918156	-4.18925293	-4.19248607	-4.21110005
0.06	-4.18914036	-4.18917191	-4.19392596	-4.22079761
0.07	-4.18916559	-4.18912469	-4.19565145	-4.23226916
0.08	-4.18924049	-4.18910380	-4.19765274	-4.24551230
0.09	-4.18934517	-4.18909673	-4.19992418	-4.26051998
0.10	-4.18946637	-4.18909361	-4.20246343	-4.27728003
0.11	-4.18959914	-4.18908893	-4.20527005	-4.29577532
0.12	-4.18974466	-4.18908047	-4.20834436	-4.31598402
0.13	-4.18990738	-4.18906778	-4.21168692	-4.33787992
0.14	-4.19009300	-4.18905107	-4.21529823	-4.36143279
0.15	-4.19030738	-4.18903071	-4.21917867	-4.38660875
0.16	-4.19055615	-4.18900694	-4.22332852	-4.41337060
0.17	-4.19084461	-4.18897985	-4.22774796	-4.44167826
0.18	-4.19117779	-4.18894947	-4.23243712	-4.47148915
0.19	-4.19156047	-4.18891584	-4.23739603	-4.50275859

4.6.3 Total energy of Al with smearing for $10 \times 10 \times 1$ **k.point and $12 \times 12 \times 1$ k.point grid**

Here there are two tables, first for the total energy of Al with smearing for $10 \times 10 \times 1$ k.point and second for $12 \times 12 \times 1$ k.point grid size as shown below.

Table 4.8: The result of total energy of Al computed with smearing

Smearing	Total energy (Ry) in (m-v)	Total energy (Ry) in (m-p)	Total energy (Ry) in (ga)	Total energy (Ry) in (f-d)
0.04	-4.18935781	-4.18927415	-4.19132533	-4.20317584
0.05	-4.18928439	-4.18922485	-4.19248761	-4.21109918
0.06	-4.18925069	-4.18917768	-4.19393140	-4.22079714
0.07	-4.18926558	-4.18913985	-4.195653665	-4.23226923
0.08	-4.18931934	-4.18911263	-4.19765079	-4.24551278
0.09	-4.18940051	-4.18909484	-4.19991986	-4.26052069
0.10	-4.18950164	-4.18908383	-4.20245874	-4.27728086
0.11	-4.18961992	-4.18907600	-4.20526620	-4.29577620
0.12	-4.18975619	-4.18906818	-4.20834180	-4.31598490
0.13	-4.18991355	-4.18905812	-4.21168557	-4.33788075
0.14	-4.19009632	-4.18904455	-4.21529780	-4.36143353
0.15	-4.19030930	-4.18902694	-4.21917886	-4.38660935
0.16	-4.19055742	-4.18900519	-4.22332908	-4.41337098
0.17	-4.19084561	-4.18897941	-4.22774873	-4.44167831
0.18	-4.19117868	-4.18894978	-4.23243798	-4.47148875
0.19	-4.19156132	-4.18891653	-4.23739694	-4.50275765

Table 4.9: The result of total energy of Al computed with smearing

Smearing	Total energy (Ry) in (m-v)	Total energy (Ry) in (m-p)	Total energy (Ry) in (ga)	Total energy (Ry) in (f-d)
0.04	-4.18919237	-4.18905779	-4.19121756	-4.20316832
0.05	-4.18919624	-4.18907445	-4.192422439	-4.21109815
0.06	-4.18921005	-4.18907679	-4.19389599	-4.22079818
0.07	-4.18924918	-4.18907489	-4.19563540	-4.23227089
0.08	-4.18931389	-4.18907414	-4.19764273	-4.24551460
0.09	-4.18939960	-4.18907486	-4.19991737	-4.26052253
0.10	-4.18950248	-4.18907530	-4.20245896	-4.27728269
0.11	-4.18962143	-4.18907368	-4.20526759	-4.29577802
0.12	-4.18975797	-4.18906874	-4.20834362	-4.31598671
0.13	-4.18991547	-4.18905980	-4.21168752	-4.33788258
0.14	-4.19009832	-4.18904656	-4.21529977	-4.36143541
0.15	-4.19031134	-4.18902900	-4.21918083	-4.38661131
0.16	-4.19055949	-4.18900724	-4.22333104	-4.41337308
0.17	-4.1908469	-4.18898144	-4.22775067	-4.44168062
0.18	-4.19118077	-4.18895181	-4.23243991	-4.47149134
0.19	-4.19156342	-4.18891856	-4.23739886	-4.50276060

4.7 Convergence test of the total minimum energy of Al with smearing for different k.point sampling

In this part, the total minimum energy of Al is calculated as a function of smearing. An increment of smearing for different k.point sampling is made until the convergence is achieved. Here we can see that,the four different colors describe the smearing type methods with different k.point sampling as shown in Figure 4.6 .
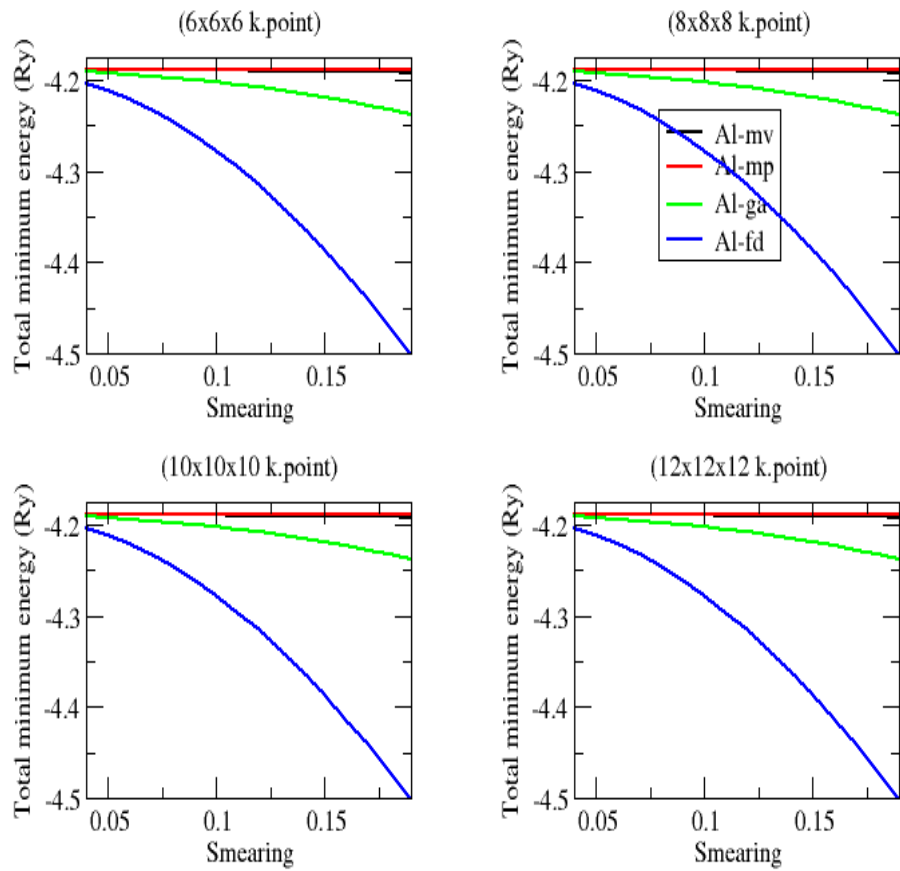
Figure 4.6: The plots of smearing for different k.point sampling

For metals convergence is very slow.The total minimum energy converges very fast using Marzari-Vanderbilt (M-v)or Methefessel-Paxton(M-P) smearing as compared to Gaussian(Ga) or Fermi-Dirac(F-D) smearing for the given values of degauss. Moreover we have checked the convergence of the minimum energy for different values smearings varing the k.point sampling. However, the difference is not considerable.

Chapter 5

Conclusion

The electronic and structural properties of Aluminum (Al) was investigated within the frame work of the density functional theory, plane wave basis sets, and pseudo potentials (ultra-soft). All calculations have been carried out with Quantum Espresso package(software). The total minimum energy calculation is performed as a function of cutoff energy and Monkhorst pack-grid size, respectively fixing the other parameters constant.the total energy convergence test is achieved, at the energy cutoff 50 Ry for the first case and at $14 \times 14 \times 1$ k.point grid size for the second case. The total minimum energy is -4.18993525 Ry for the first case and -4.18918761 Ry for the second case. The total minimum force on Al as a function of cutoff energy and Monkhorst-Pack grid is calculated by displacing Al atom by 0.05 Bohr. Total force convergence test is achieved for the cutoff energy 60 Ry and for Monkhorst-Pack grid at $9 \times 9 \times 1$ k.point grid size. Our numerical calculation shows that the equilibrium lattice constant is 7.4 Bohr. This result is in good agreement with experimental value. Finally, for Al metallic systems, the choice of smearing function is also a major consideration to minimizing the electronic energy in a DFT calculation.The

different smearing calculation was performed with Marzari-Vanderbilt, Methfessel-Paxton , Gaussian and Fermi-Dirac function for four different k.point mesh. The result shows that, the convergence in cold smearing is very fast than Fermi-Dirac smearing.

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