



ELECTRONIC AND STRUCTURAL PROPERTIES OF
IRON USING DENSITY FUNCTIONAL THEORY
(QUANTUM ESPRESSO)

By

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This is to certify that the thesis prepared by **Zeray Gebrehawariat Kidane** Graduate Studies entitled “**Electronic and structural properties of Iron using density functional theory (QUANTUM ESPRESSO)** ” in fulfillment of the requirements for the degree of **Master of Science in physics(Condensed Matter)** complies with the regulations of the University and meets the accepted standards with respect to originality and quality. .

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To my family

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Acronym

• Density functional theory	DFT
• Local density approximation	LDA
• Generalized Gradient approximation	GGA
• Self consistent field	SCF
• Open source package research electronic structure stimulation optimization	ESPRESSO
• Body center cubic	BCC
• Iron	Fe
• Born-Oppenheimer Approximation	BOA
• Hartree Fock theory	HFT
• Kohn Sham	HK
• Exchange-correlation energy	E_{XC}

Abstract

The electronic and structural properties of Iron (Fe) were investigated using density functional theory (QUANTUM ESPRESSO). Iron is the main ingredient used to make steel and the crystalline structure is body center cubic (BCC) at 300 kelvin. The unknown exchange correlation energy was computed by model of local density approximation (LDA) and generalized gradient approximation (GGA). The total minimum energy of Iron is calculated as function cutoff energy and k.point grid. The convergence of total energy is tested and achieved at the energy cutoff 60 Ry for the first case and at $16 \times 16 \times 16$ k.point grid size for the second case. The total magnetization and the total stress of Iron is performed as function of degauss. The result shows that total magnetization of Fe per atom is 1.99 Bohr Mag/cell and the total stress Fe per atom is $-26.50 \text{ Ry}/\text{Bohr}^3$. In addition to this, equilibrium lattice constant is calculated with lattice constant between 4.80 Bohr and 5.55 Bohr. The computational value of the equilibrium lattice is 5.10 Bohr and this result is best agreement when we compare the equilibrium lattice constant with experimental value of 5.217 Bohr. Finally, the four different smearing schemes:- Marzari-Vanderbilt, Methfessel-Paxton, Gaussian and Fermi-Dirac are tested for convergence of the total minimum energy. The result shows that minimum energy converges very fast for Marzari-Vanderbilt, Methfessel-Paxton.

keywords: Iron, density functional theory, electronic structure, total energy, total magnetization

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Chapter 1

Introduction

1.1 Background

From the periodic system, Iron (Fe) is a member of the first row transition series of elements along with Ruthenium and Osmium. From the most abundant elements of the earth's crust, Iron is fourth abundant element and second abundant metal element after aluminium and consisting 6.3% mass of the element [1]. Iron is the main ingredient used to make steel. There is a lot of Fe in the universe because it is the end point of the nuclear reactions in large stars. It is the last element to be produced before the violent collapse of a supernova scatters the Iron into space. Iron is a grey, silvery metal. Pure Fe is soft, very malleable and is able to stretch a lot, while steel (Fe mixed with a little carbon) is stronger and does not stretch as much as Iron [2]. Iron makes chemical compounds with different elements. Usually the different element oxidizes Fe. Sometimes two electrons are taken and sometimes three. Compounds where Fe has two electrons taken are called ferrous compounds. Compounds where Fe has three electrons taken are called ferric compounds. Ferrous compounds have Fe in its +2 oxidation state. Ferric compounds have Fe in its +3 oxidation state. Iron compounds can be black, brown, yellow, green. Ferric oxides

and Ferrous sulfates are common compound [3]. Iron is the most used metal of the earth because it has high strength and is not expensive. Its application go from screwdriver to washing machine, from food containers to family car. Some form of Iron include carbon steel cast Fe, pig Fe and alloy steel [4]. Iron has several vital functions in the body. It serves as a carrier of oxygen to the tissues from the lungs by red blood cell haemoglobin, as a transport medium for electrons within cells and as an integrated part of important enzyme systems in various tissues [5, 6]. Mostly Fe and its alloys are extensively applicable in modern industry [7]. It is strong directional bound, ferromagnetic and symmetrical patten as lattice structures. From the transition series elements Vanadium, Chromium and Iron have the same crystalline structure with body center cubic at 300 kelvin. This means a cube with atom at the edges and an atom with center of every cube. The body centered cubic structure is, low dimension, hexagonal closed packed and low energy [8, 9, 10]. The radius of Fe atom is 0.124nm with lattice constant of $2.87A^0$. The nearest neighbor distance between two atoms in Fe structure is $2.47A^0$. The atom at the origin has 8 nearest neighbors in position and 6 second nearest neighbors in position [11, 12]. The metal has an atomic weight of 55.845 and a specific gravity of 7.87 [13].

Structural properties of bcc Fe have been obtained from total energy electronic structure calculations performed as a function of lattice constant with the use of Density functional theory(DFT) [7]. DFT and its local density approximation seemed to have serious limitations for an accurate description or the prediction of electronic and related properties of atoms, molecules, semiconductors and calculation of energy gap. The initial non-relativistic form of DFT was introduced by Hohenberg and Kohn [14]. Calculations of the bulk structure and the bulk elastic properties play an important

role in the physics of condensed matter. Bulk calculations help us to understand, characterize, and predict mechanical properties of materials in our surroundings, under extreme conditions, as in geological formations and for industrial applications [15]. Many scholars study density functional theory approach to structural and electronic properties. So the target of this research is to study the electronic and structural properties of Fe using density functional theory (quantum ESPRESSO) which is integrated suite of computer codes for electronic-structures calculation [7, 16].

The outline of this research is organized as follows, In chapter(1) we discuss the background information about Iron structure, the application of Iron in industry and also discuss the several vital function in the body. Chapter(2) contains a basic and brief description of the quantum theoretical tools used in this research to compute unknown exchange-correlation energy. Local density approximation and general gradient approximation are the two models to approximate the unknown parameters. Chapter 3 contains materials and methodology which is used to calculate the electronic and structural properties of Fe. Chapter 4 we deals about computational parts, analysis the out come based on convergence criteria and interpret the figures. Finally, the important out comes of this work is conclude in chapter 5.

1.2 Statement of the Problem

The electronic and structural properties of single particle is easy to calculate but it is known that many body problems are difficult to solve. That is, the state of motion cannot be solved analytically for systems in which three or more distinct electrons interact [17, 18]. In particular Hatree-Fock theory and its source are based on the complicated many-electron wave function, where as many-body wave function

is dependent on $3N$ variables, three special variables for each of the N electrons [19]. Now a days, there is more applicability in the fundamental principle of density functional theory in any properties of a system of many interacting particles can be viewed as a functional of the ground states of density, $n_o(r)$, which in principle determine all information in the many-body wave function for the ground states and all excited states. Schrödinger equation is setting of practical values and many applicable rapidly in research in chemistry, physics [20]. Many researchers have been studying the electronic and structural properties of Fe as function of cohesive energy, bulk modulus and density of states. However we are interested to study the electronic and structural properties of Iron per atom as a function of energy cutoff, lattice constant, k.point sampling and smearing for k.point sampling with the help of density functional theory.

Research Questions

1. What is the total minimum energy of Fe per atom with respect to energy cutoff and k.point sampling?
2. what is the total magnetization and total stress of Fe per atom with respect to degauss?
3. What is the equilibrium lattice constant of Fe by consideration of energy cutoff?
4. Why smearing is need for Fe metal?

1.3 Objectives

1.3.1 General objective

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

1.3.2 Specific objectives

The specific objectives of this study are

1. To calculate the total minimum energy of Fe per atom with respect to cutoff energy.
2. To calculate the total minimum energy of Fe per atom with respect to k.point sampling.
3. To calculate the total magnetization of Fe per atom with respect to degauss.
4. To calculate the total stress of Fe per atom with respect to degauss.
5. To calculate the equilibrium lattice constant of Fe with respect to cutoff energy.
6. To calculate the total minimum energy of Fe per atom with respect to different smearing/degauss for k.point sampling.

1.4 Significance of the Study

The significance of this research is to understand and interpret the electronic and structural properties of many electron system in transition metals like Fe by using

new computational technique called density functional theory and it helps to investigate a new practical problem solving techniques. The computational seeks to gain understand of electronic and structural properties of electron principally through use and analysis of mathematical models on high performance computer and to create new knowledge.

1.5 Scope of the Study

The scope of this research is restricted to calculate the total minimum energy of Fe, total magnetization, total stress and equilibrium lattice constant of Fe with respect to different parameter like, energy cutoff, k.point sampling, degauss and smearing for k.point sampling.

1.6 Limitation of the Study

The limitation of the study was lack of time, financial supporting. So in order to solve the problems I use my resource effectively and efficiently.

Chapter 2

Literature Review

2.1 Introduction

Solving the electronic structure problem for molecules, materials and interfaces are fundamental importance to a large number of disciplines including physics, chemistry, and materials science. Since the early development of quantum mechanics, it has been noted, the interactions between atoms and electrons are conducted by the laws of quantum mechanics [21]. Accurate and efficient techniques for solving the basic quantum-mechanical equations for complex many-atom, many-electron systems is developed [22]. DFT reformulates the Schrödinger equation, which describes the behavior of electrons in a system [23].

2.2 Schrödinger Equation

DFT is a useful topic which is begun with the observation of most profound scientific advances development of quantum mechanics [24]. All substances are composed of atomic nuclei and electrons. The macroscopic material properties that we observe depend on the position of these electrons and ions [25].

Any problem in the electronic structure of matter is covered by Schrödinger equation

including the position of the nuclei and the number of the electrons. So we focus on the time-independent Schrödinger equation. For an isolated N-electron atomic or molecular system the Schrödinger equation is given by [17].

$$\hat{H}\Psi = E\Psi \quad (2.2.1)$$

where E is the electronic energy, $\Psi = \Psi(r_1, r_2, \dots, r_N)$ is the wave function or eigenstates of the Hamiltonian and \hat{H} is the Hamiltonian operator. In quantum mechanics electron structure of atom or molecule is concerned, so for single electron wave function can be calculate from Schrödinger equation with single electron moving in potential [26].

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right]\Psi(r) = \epsilon\Psi(r) \quad (2.2.2)$$

For the many-body problem of a system containing N electrons and K nuclei with charge Z_I , the Hamiltonian is given by [26, 27].

$$H = -\sum_{i=1}^N \frac{\hbar^2 \nabla_i^2}{2m_e} - \sum_{I=1}^K \frac{\hbar^2 \nabla_I^2}{2m_I} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{|r_i - r_j|} + \frac{1}{4\pi\epsilon_0} \sum_{I=1}^K \sum_{i=1}^N \frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{4\pi\epsilon_0} \sum_{I=1}^K \sum_{J>I}^K \frac{Z_I Z_J e^2}{|R_I - R_J|} \quad (2.2.3)$$

The first two terms represent the kinetic energy of the electrons and nucleons, T_e and T_n respectively. 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, Born-Oppenheimer approximation have been made [27].

2.3 Born-Oppenheimer Approximation

Born-Oppenheimer approximation plays an essential role in electronic structure calculations. However, as a first approximation which is justified by the fact that the nuclei (ions) are much heavier than the electrons, M_I greater than m_e . In most cases, this justifies a time-scale separation by saying that the electrons immediately adapt to change 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. Therefore we drop the ionic kinetic energy term and the ion-ion interaction term in the Hamiltonian and only consider the terms involving electrons [20, 27].

$$H_{BO} = -\sum_{i=1}^N \frac{\hbar^2 \nabla_i^2}{2m_e} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I=1}^K \sum_{i=1}^N \frac{Z_I e^2}{|r_i - R_j|} \quad (2.3.1)$$

If we denote the interaction of electron i with the ions by V_{ext} and use Hartree atomic units $\hbar = m_e = e = \frac{1}{4\pi\epsilon_0} = 1$, we can write the Hamiltonian as the same operators for any system of particles interacting via the coulomb interaction, just as the kinetics energy operator and the potential due to nuclei of charge Z_i .

$$H = -\frac{1}{2} \sum_i^N \nabla^2 + \sum_i \sum_{j>i} \frac{1}{|r_i - r_j|} + \sum_i V_{ext}(r_i) \quad (2.3.2)$$

The Hamiltonian $H = T + V + W$ is assumed to consist of the kinetic energy, spin-independent single-particle potential and some spin-independent particle-particle interaction [28].

2.4 Density Functional Theory

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 [29]. It is a successful approach to the fundamental equation that describe the quantum behavior of atoms and molecules to simple crystals and complex extended system [29, 30]. It allows one to replace the complicated N-electron wave function $\Psi(r_1, r_2, ..r_N)$ and associated with Schrödinger equation by the much simpler electron density $n(r)$ [24]. Density functional theory as a good modeling method has become a common tool in first-principle calculations aimed at molecular and condensed matter systems [31]. Traditional methods in electronic structure theory, in particular Hartree-Fock theory(HFT) and its descendants are based on the complicated many-electron wave function. The main objective of DFT is to replace the many-body electronic wave function with the electronic density as the basis quantity, where as 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 [19]. The modern formulation of density functional theory originated in a famous paper written by P. Hohenberg and W. Kohn with their two fundamental theorems. In 1965 the major milestone in the development of DFT was introduced. They gave the proofs of these theorems by showing that DFT was an exact theory in same sense as the wave function theory [17, 27, 32].

2.5 Hohenberg-Kohn Theory

The entire field of density functional theory rests on two fundamental mathematical theorems proved by Kohn and Hohenberg and the derivation of a set of equations by Kohn and Sham [33]. Even though an electronic system described by the Hamiltonian (\hat{H}), both the ground-state energy and ground state wave function are determined by minimization of the energy function $E(\Psi)$ and $\hat{H}(\Psi)$ [17, 34]. External potential in principle determines all the properties of the system. So the two Hohenberg-kohn theorems are :-

Theorem I

For any system of interacting particles in an external potential $V_{ext}(r)$, the potential $V_{ext}(r)$ is determined uniquely, not including a constant, ground state particle density $n_0(r)$ [22].

Theorem II

The universal functional of energy $E[n]$ defined in terms of the density $n(r)$. The exact ground state energy is the minimum value of the function and the exact ground state density $n_0(r)$ is the minimum value of the function, $n(r)$.

The Hohenberg-Kohn 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 $n(r)$ is known. 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.

2.6 Kohn-Sham Theory

From the Hohenberg and Kohn theorem, the ground state energy of a many-electron system can be obtained as the minimum of the energy function [17]. 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 is widely used for self consistent field electronic structure calculations of the ground state properties of atoms, molecules, and solids [9, 25, 32]. The Kohn and Sham equations can be written as

$$\left[-\frac{1}{2}\nabla^2 + V(r) + V_H(r) + V_{XC}(r)\right]\Psi(r) = \epsilon_i(r)\Psi(r) \quad (2.6.1)$$

Where the external potential of Kohn-Sham are

$$V_{ext}(r) = V(r) + V_H(r) + V_{XC}(r) \quad (2.6.2)$$

Kohn-Sham density functional theory is the intractable many-body problem of interacting electrons in a static external potential and 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 with in Kohn-Sham density functional theory [17, 28].

2.7 Exchange-Correlation Energy

Kohn-Sham density functional theory is practically established to solve the many-body problem by separate the problem into a set of single-particle problems [36].

The fundamental KS equations represent a practical way of finding the ground-state electron density for a given external potential and a given number of electrons [37]. Kohn and Sham showed that the ground state is found by minimizing the energy of an energy functional and achieved by finding a self-consistent solution of single-particle equations. There is just one critical complication formulation: to solve the Kohn and Sham equations we must specify DFT depends on the adequate knowledge of the exchange-correlation energy functional, $E_{XC}[n(r)]$ [20, 24], But the electron density is constant at all points in space. Solving this uniform electron gas provides a practical way to actually use of Kohn Sham equations. To do this, we set the exchange correlation potential at each position to be the known exchange-correlation potential from the uniform electron gas at the electron density observed at that position and we need good approximations for $E_{XC}[n(r)]$. The most common and straightforward approximation to $E_{XC}[n(r)]$ is the Local Density Approximation (*LDA*) [32].

$$E_{XC}^{LDA}[n(r)] = \int \epsilon_{XC}(n(r))n(r)dr \quad (2.7.1)$$

where LDA is the basis of all approximate exchange-correlation functionals and uniform electron gas is the central idea of this model. From equation 2.6.1 the $\epsilon_{XC}(n(r))$ and $n(r)$ are the exchange-correlation energy per particle of an uniform electron gas of density $n(r)$. The term $\epsilon_{XC}(n(r))$ is express by:

$$\epsilon_{xc}(n(\vec{r})) = \epsilon_x(n(\vec{r})) + \epsilon_c(n(\vec{r})) \quad (2.7.2)$$

where $\epsilon_x(n(\vec{r}))$ and $\epsilon_c(n(\vec{r}))$ are exchange part and correlation part respectively. LDA is fail in systems like heavy fermions and where the electron density undergoes rapid changes. Due to is condition, another form of exchanged-correlation functional has been developed, that is the Generalized Gradient approximations(GGA) [35, 38].

GGA is the only moderate accuracy that the local spin density approximation delivers is certainly insufficient. The first logical step was the suggestion that not only the information about the density $n(r)$ at a particular point r , but to supplement the density with information about the gradient of the charge density, $\nabla n(r)$. In order to account for the non-homogeneity of the true electron density and functionals that include the gradients of the charge density and where the hole constraints have been restored in the above manner are collectively termed as generalized gradient approximations [38]. The *GGA* functional focuses on the local electron density as well as the space variation of the electron density that is represented by the density gradient [39]. The GGA functional can be written as

$$E_{XC}^{GGA}[n(r)_\alpha, n(r)_\beta] = \int F_{XC}(n(r)_\alpha, n(r)_\beta, \nabla n(r)_\alpha, \nabla n(r)_\beta) d\vec{r} \quad (2.7.3)$$

For the above explicit, the integrand f on the densities and their gradients exist. However semi empirical functionals are contain parameters that are calibrated against reference values rather than derived from first principles. In practice, E_{XC}^{GGA} is usually split into exchange and correlation contributions. Generally the hybrid approximations has reduced the LDA errors of atomization energies of standard set of small molecules, improved accuracy values of total energies and gives better energies [28, 35, 38].

2.8 Periodic Super Cell

The shape of unit cell is define by the repeated periodically in space. In the solid state and most of materials like to have their atoms arranged in some kind of regular repeating pattern by lattice vector a_1, a_2, a_3 [40]. In fact, the straightforward application of the supercell method always generates fictitious images of the original

system unit cell [41]. The reciprocal lattice plays fundamental role in most analytical studies of periodic structure with functional periodic of bravais lattice. A perfect crystal is arranged in a regular periodic array and we led to consider the problem of an electron in a potential $U(r)$ with the periodicity of the underlying bravais lattice, $U(r + R)=U(r)$ for all bravais lattice vectors R [40]. Different approximation are choices into methods, namely the size and shape of the supercell are choices the exchange correlation function and pseudopotential to make a significant difference to predicted physical properties [42]. The shape of the cell are the periodic boundary condition which is determines the types of lattice and the contents of the cell determines the lattice basis [43]. When we solve the Schrödinger equation for single electron by periodic system in Free electron Schrödinger equation in special case of $U(r + R)=U(r)$ are independent electron are satisfy a fundamentals properties known as Bloch's theorem [40].

2.8.1 Bloch's Theorem

Bloch's theorem is allows labeling of the one-electron wave function in terms of their crystal momenta. Where set of momenta is allowed with brillouin zone which is determined by lattice translational symmetries [44]. Bloch's theorem is, enables reduction of the eigenvalue problem of the single-particle Hamiltonian that commutes with the translational group [45]. The eigen-states Ψ of one electron and periodic potential are proved the important solution of the Schrödinger equation, so Bloch's theorem is, periodic solid for any electronic wave function can be written as the product of a plane wave $exp^{ik.r}$ times a function $U_k(r)$ with the periodicity of the crystal lattice.

$$\Psi_k(r) = exp^{(ik.r)}U_k(r) \tag{2.8.1}$$

where $U_k(r)$ is periodic in space with the same periodicity as the super cell. That is, $u_k(r + n_1a_1 + n_2a_2 + n_3a_3) = u_k(r)$ for any integers n_1, n_2 and n_3 . Therefore Bloch's theorem is possible to try and solve the Schrödinger equation for each value of k independently [6, 26]. The periodic part of the function can be expanded using a basis set consisting of a discrete set of plane waves. The wave vectors are reciprocal lattice vectors of the crystal and the equation is given by.

$$U_k(r) = \sum_G C_G \exp^{iG \cdot r} \quad (2.8.2)$$

where the reciprocal lattice vectors G are defined by $G \cdot a_i = 2\pi n$ for all a_i , a_i is a lattice vector of the crystal and n_i is an integer for real number. Then for each electronic wave function can be written as combination of plane waves and the equation can be written as.

$$\Psi_k(r) = \sum_G C_K + G \exp^{i(K+G) \cdot r} \quad (2.8.3)$$

The electronic wave functions at any k .point are now expressed in terms of a discrete plane wave basis set. Even though 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} [20, 40].

2.8.2 Energy Cutoff

From the principle of fourier basis function e^{iGr} represented a plane wave traveling in space and perpendicular to the vector G . 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.

$$\Psi_k(r) = \exp^{ik \cdot r} U_k(r) \quad (2.8.4)$$

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.

$$U_k(r) = \sum_G C_G \exp[iG \cdot r] \quad (2.8.5)$$

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 equation 2.7.2 have a simple interpretation as solutions of the Schrödinger equation. Therefore the solutions of kinetic energy is.

$$E = \frac{\hbar^2}{2M} |K + G|^2 \quad (2.8.6)$$

It is reasonable to expect that the solution 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:

$$E_{cut} = \frac{\hbar^2}{2M} G_{cut}^2 \quad (2.8.7)$$

the infinite sum is reduced to

$$\Psi_K(r) = \sum_{|G+K| < G_{cut}} C_{G+K} e^{i(K+G)r} \quad (2.8.8)$$

This expression includes slightly different numbers of terms for different values of \vec{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 [20].

2.8.3 K.point Sampling

The role of k.point sampling was analyzed by Thygesen and Jacobsen. They demonstrated for, a given supercell size, a poor sampling of k.points direction. Even though electron momentum k in supercell is calculate the elastic electron transmission and total energy calculation well understood [47, 48]. To obtain electronic potential and total energy by making easy difficult calculation. If the system is metallic it is a dense set of k.points. 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 computation of total energy converge by density of k.points increase and the error due to the k.point sampling approaches zero. In principle we need to integrate over all possible k.point when constructing the density. Fortunately the wave functions change slowly as we vary k , so we can approximate the integral with a summation to reduced total energy method by using the k.point [49].

$$n(r) = \int |\Psi_k(r)|^2 d^3k \simeq \sum_k |\Psi_k(r)|^2 \quad (2.8.9)$$

2.8.4 Plane wave basis sets

In the plane-wave basis set, the Bloch's function for an electron in a periodic potential is associated with a wave vector k and can be written as the product of a plane wave $exp^{(ik.r)}$ times a function $U_k(r)$ with the periodicity of the crystal lattice [50]. Even though each electronic wave functions are expanded in terms of k.point by discrete plane-wave basis sets [20]. The exact form of the plane-wave expansion is

used plane wave codes and control the spacing of the real-spacing grid. Therefore, the truncation of plane wave expansion is plane wave calculations. Namely, only the reciprocal lattice vectors whose kinetic energy lower than a predefined maximum cutoff energy

$$\frac{1}{2}|\vec{G}|^2 < E_{cut} \quad (2.8.10)$$

Wave function Cutoff Energy are kept in the expansion, while the rest of the coefficients are set to zero. Besides reducing the computational load, this truncation strategy limits the effects of unit cell orientation on the outcome of the calculation. DFT calculations rarely use a completely converged plane-wave basis, but that convergence is usually unnecessary. However, incomplete basis set calculations using different cell sizes require that each calculation use the same E_{cut} [51].

2.9 PseudoPotential

Plane-wave methods is, the most important approach to reducing the computational load due to core electrons [49]. Pseudopotentials replace the electron density from a chosen set of core electrons with a smoothed density. The properties of the core electrons are fixed in approximate fashion in subsequent calculations; this is the frozen core approximation and the calculations include a frozen core and they are used much less widely than frozen core methods. Pseudopotential is developed by considering an isolated atom of one element, but the result can be used reliably for calculations that place the atom in any chemical environment without its further adjustment. It also defines the transferability, a minimum energy cutoff that should be used in calculations including atoms associated with that pseudopotential and requiring high cutoff energies are said to be hard. The most widely used method of pseudopotentials

is work by Vanderbilt, these are the ultrasoft pseudo potentials (USPPs). As their name suggests, it require essentially lower cutoff energies than alternative approaches [20]. Valence electrons are reducing the number of states which need for calculation of Schrödinger equation [20, 49].

$$\left(-\frac{1\nabla^2}{2} + V_{eff}^{ps}\right)\Psi_j^{ps} = E_j\Psi_j^{ps}, \left(-\frac{1\nabla^2}{2} + V_{eff}\right)\Psi_j = \varepsilon_j\Psi_j \quad (2.9.1)$$

2.10 Magnetization

Absolute measurements of magnetization are difficult, so it is normal to calibrate magnetization apparatus with the standard sample. At room temperature, the only available standards are Iron, Nickel and cobalt. So Iron and Nickel are usually used[52]. Magnetization also describe how a material responds to an applied magnetic fields [53]. Degaussing system is a system that is in use on the metal parts or electronic device that are at risk of magnetic field. This system is used to prevent the vessel from dangerous equipment. In Self-consistent-field Calculation we can generate the magnetization for Fe. Since there is single atom per unit cell, the only possible magnetic structure is ferromagnetic [54].

2.11 Stress Theorem

The stress is a generalized force for which the ideas of the force theorem can be applied. The key point is that for a system in equilibrium, the stress tensor is given by.

$$\sigma_{\alpha\beta} = -\frac{1}{V} \frac{\partial E}{\partial \epsilon_{\alpha\beta}} \quad (2.11.1)$$

where α and β are the cartesian indices, and where strain is define to be a scaling of

space [27]

2.12 Self-consistent-field Calculation

From the theory of Hohenberg and Kohn approximation homogeneous system of interacting electrons are developed. These methods are exact for system of slowly varying or high density. Electronic structure is obtained in terms of one-particle states that generally extend throughout the system under consideration. The numerical effort to compute such extended states scales as N^3 (N is the number of occupied electronic states) and self-consistent computing the solutions of Kohn-Sham equation in single particle [33, 55].

$$\left[-\frac{1}{2}\nabla^2 + V_{ext}(n(r), r)\right]\Psi_i(r) = \varepsilon_i\Psi_i(r) \quad (2.12.1)$$

where $\Psi_i(r)$ is a wave function of the particle, ε_i is a Kohn-Sham eigenvalue and external potential equation are express as

$$V_{ext}(n(r), r) = V_{ion}(r) + V_H(n(r), r) + V_{XC}(n(r), r) \quad (2.12.2)$$

The above external potential equation 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 the charge density, $n(r)$. The charge density of a particle is given by [33].

$$n(r) = 2 \sum_{i=1}^{N_{occ}} |\Psi_i(r)|^2 \quad (2.12.3)$$

Here, n_{occ} is the number of occupied states, which is equal to one-half the number of valence electrons in the system. The factor of 2 is comes from spin multiplicity. Equation 2.12.3 can be easily expanded to situations, where the highest occupied states have fractional occupancy or when there is an imbalance in the number of

electrons for each spin component. The most computationally expensive step of DFT is solving the Kohn-Sham equation 2.9.1. Since $V_{ext}(n(r), r)$ depends on the charge density $n(r)$, which in turn depends on the wave function $\Psi_i(r)$. The SCF iteration is a general technique used to solve nonlinear eigenvalue problem. It starts with an initial guess of the charge density [56].

2.12.1 Algorithm Self-Consistent Iteration

The SCF method is an computational procedure which yields a self-consistent set of wave functions and orbital energies [46]. Therefor initial SCF iteration requires solving an eigenvalue problem in order to prepare a good initial subspace and it include the following steps [57, 58].

- Starting from estimation of charge density for $k=1$.
- Evaluate effective potential $V_{eff}(r)=V_{ext}(r) + V_H[(n^k(r))] + V_{XC}[(n^k(r))]$
- Solve $[-\frac{1}{2}\nabla^2 + V_{eff}[(n^k(r))]\Psi_i(r)=\varepsilon_i\Psi_i(r)$, The wave function $\Psi_i(r)$ $i=1,2,3,\dots$
- Evaluate actual density from new wave function,

$$n(r) = 2 \sum_{i=1}^{occ} |\Psi_i(r)|^2$$

- Consistent $\|n^k(r) - n(r)\|^2$ and
- Computes the energy, magnetization and stress, but if the wave function does not satisfy the right boundary condition, we return to step one in order to make another guess for the energy [59].

Chapter 3

Materials and Methodology

3.1 Materials

The study of this research was included theoretical analysis and computational parts. The main source of information are published articles, journals, standard books, network connection and different software like Winedit, Ubuntu, Textworks and also computer is the main instrument to complete this research.

3.2 Computational Methodology

The methodology was based on density functional theory. However in this methodology the exchange-correlation functions are unknown. As the result the local density approximation (LDA) and general gradient approximation (GGA) are used to approximate this unknown functions. Vanderbilt pseudopotential, electrons and system control are the mandatory used to implements the quantum ESPRESSO Program package [16, 20].

To implement the electronic and structure properties of Iron, we use the software of quantum ESPRESSO which is an integrated suite of computer codes and material modeling based on density-functional theory.

The software mentioned above is free, open source software which is General Public Licence (GPL) and fast methodology innovation in the field of electronic structure simulation [16]. It is applicable from simple electronic structure calculation to highly complex theoretical spectroscopy such as K-edge x-ray absorption spectra, ballistic conductance, nuclear magnetic resonance (NMR) and electronic paramagnetic resonance (EPR). The simulation device implemented in quantum ESPRESSO used across a world range and the code have been highlighted by research group. Quantum ESPRESSO uses input parameters like atomic numbers, types of atomic in periodic cell, lattice constant, kinetic energy cutoff, bravais lattice index, k.point sampling and atomic position [16, 27].

Chapter 4

Results and Discussions

Introduction

In this work, the electronic and structural properties of Iron (Fe) were calculated based on the frame work of the density functional theory. One of the important aspect in studied Iron is the total minimum energy. Results are mostly presented in Tables and Figures. The first results are the total minimum energy per atom and second results are total magnetization and total stress per atom with different degauss values for bulk Iron. Then comes the results for the equilibrium lattice constants and different smearing for k.point sampling. The computational output file were use to compare the tables of energy cutoffs, k.points and lattice constants against the total energies, total magnetization, total stress and graphs were plotted to interpret parameters for Fe structure with calculation of SCF for both LDA and GGA.

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

From the input card we used $4 \times 4 \times 4=64$ k.point space; other k.points have the similarity in each cutoff energy because of the symmetry of the space. The calculation was done using different cutoff energy values from 25 Ry to 170 Ry and lattice constant of 5.217 Bohr.

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

Energy coutoff (Ry)	Total energy (Ry)	Energy coutoff (Ry)	Total energy (Ry)
25	-55.54077103	100	-55.541240604
30	-55.54124609	105	-55.541240809
35	-55.54200590	110	-55.541241021
40	-55.54221218	115	-55.541241166
45	-55.54222463	120	-55.541241213
50	-55.54228947	125	-55.541241226
55	-55.54235266	130	-55.541241196
60	-55.54237417	135	-55.541241247
65	-55.54237544	140	-55.541241331
70	-55.54238209	145	-55.541241226
75	-55.54239326	150	-55.541241392
80	-55.54240168	155	-55.541241465
85	-55.55240462	160	-55.541241471
90	-55.54240462	165	-55.541241422
95	-55.54240519	170	-55.541241530

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

In this part of the calculation, we see that, the total minimum energy of Iron is calculated as a function of energy cutoff. An increment of energy cutoff for wave function is made until the the convergence is succeed. From Fig 4.1 we can see that, the total energy converge at 60 Ry plane wave cutoff energy and the ground states energy had its minimum at -55.54237417 Ry. Furthermore, the total minimum energy is monotonically decreasing with increasing energy cutoff for wave function. The nearest ground state of energy is depend on the number of basis function.

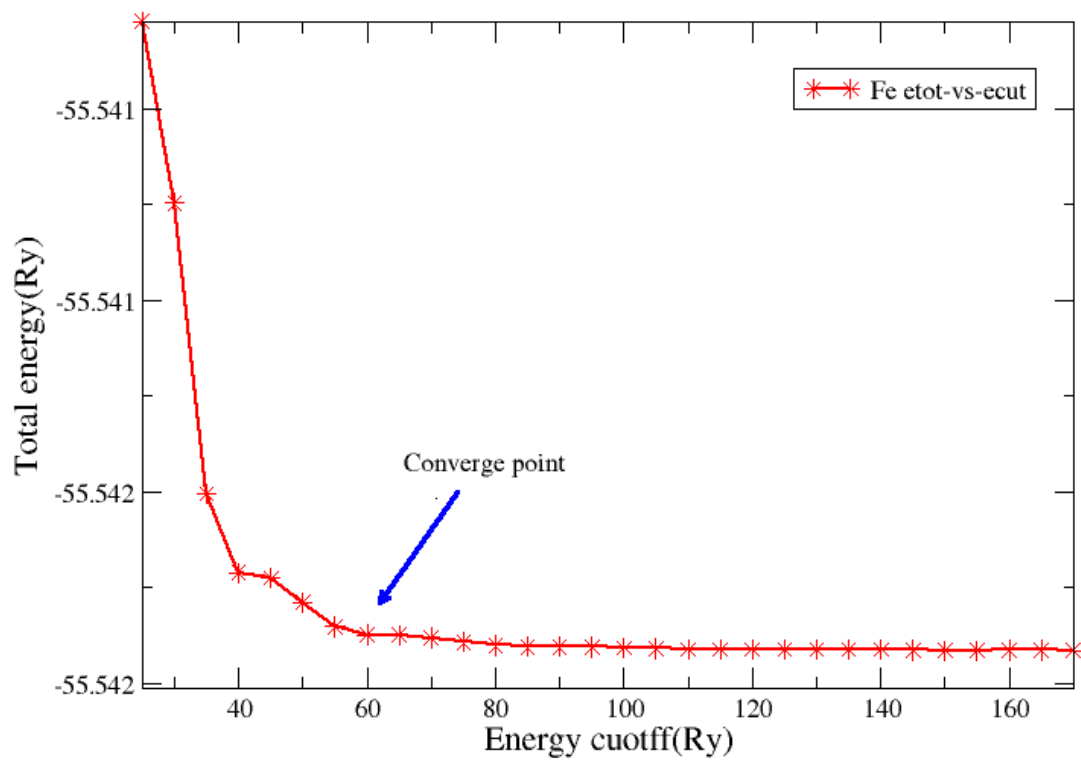


Figure 4.1: Total minimum energy of Fe with respect to energy cutoffs.

4.2 Total energy of Fe per atom with respect to K.point grid sampling

In this case, the calculation was done using different k.point value from $2 \times 2 \times 2$ to $32 \times 32 \times 32$ space with 2.0 point. Then, the other parameter such as lattice constants, energy cutoff are fixed.

Table 4.2: The results of the total minimum energy computed with K.point grid sampling

K.point grid sampling	Total energy (Ry)	K.point grid sampling	Total energy (Ry)
2	-55.50906426	18	-55.54574511
4	-55.54221218	20	-55.54574536
6	-55.54879477	22	-55.54574527
8	-55.54520585	24	-55.54574523
10	-55.54582999	26	-55.54574523
12	-55.54575668	28	-55.54574521
14	-55.545728334	30	-55.54574521
16	-55.54574483	32	-55.54574522

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

As we can see that, the total minimum energy of Fe is calculated as the function of k.point grid size from $2 \times 2 \times 2$ to $32 \times 32 \times 32$. For this calculation, the other parameter like lattice constant, energy cutoff are kept constant. The total minimum energy of Fe versus K.point grid size is shown in Fig 4.2. It can be observed that the total minimum energy of Fe coverage at $16 \times 16 \times 16$ and total ground state energy has its minimum at -55.54574483 Ry. Moreover, in this simulation the total minimum energy is monotonically decreasing with increasing K.point grid until reach normal structure of Fe.

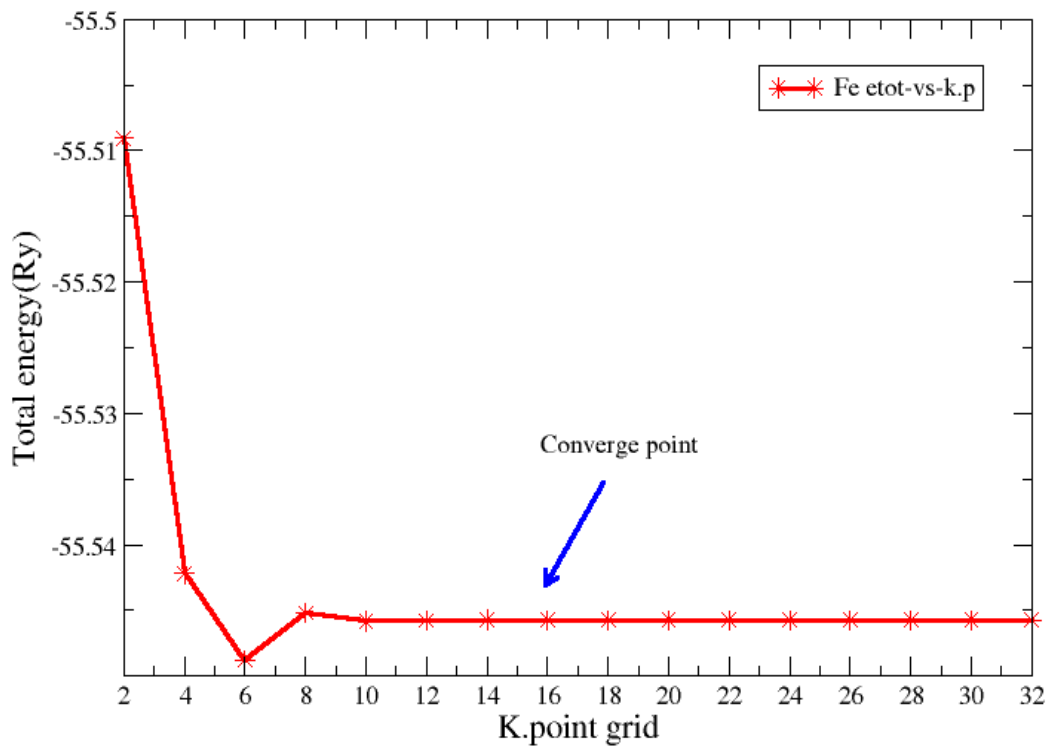


Figure 4.2: Total minimum energy of Fe with respect to K.point grid.

4.3 Total magnetization of Fe per atom with respect to degauss sampling

In this part, the calculation was done using different degauss value from 0.02 to 0.18 with 0.01 space point. The other parameter is fixed such as lattice constant, cutoff energy.

Table 4.3: The results of the total magnetization computed with degauss sampling

Degauss	magnetization (Bohr mag/cell)	Degauss	magnetization (Bohr mag/cell)
0.02	1.99	0.11	0.18
0.03	1.98	0.12	-0.02
0.04	1.95	0.13	0.01
0.05	1.89	0.14	-0.01
0.06	1.80	0.15	-0.01
0.07	1.67	0.16	-0.01
0.08	1.50	0.17	0.00
0.09	1.26	0.18	0.01
0.10	0.86	-	-

4.3.1 Convergence test of total magnetization of Fe with respect to degauss sampling

Fig 4.3 shows that, the total magnetization of Fe is calculated as the function of degauss. From the result total magnetization of Fe per atom is 1.99 Bohr Mag/cell and converge at 0.12 degauss. However the amount of magnetization is decrease with decreasing of degauss. when the values of degauss is above 0.12 there is negative values of magnetization. So the negative values shows the response of imposed magnetic field and the magnetization result is reach to zero. Iron is ferromagnetic materials with negative susceptibility.

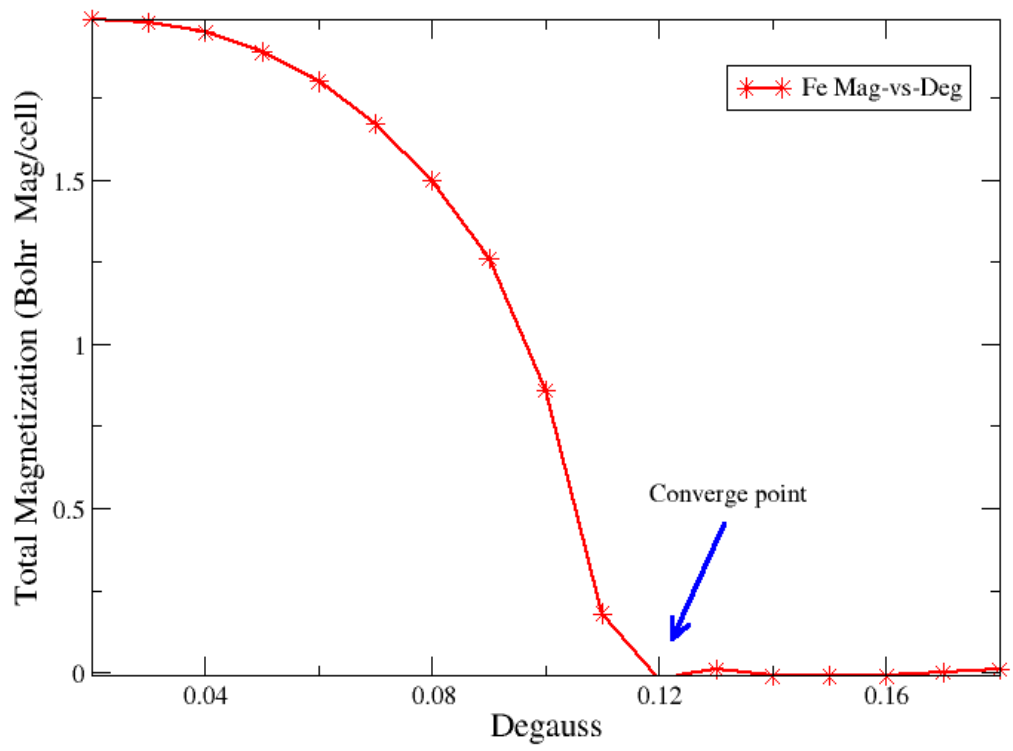


Figure 4.3: Total Magnetization of Fe with respect to degauss.

4.4 The total stress of Fe per atom with respect to degauss sampling

Table 4.4: The results of the total stress computed with degauss sampling

Degauss	$stress(Ry/Bohr^3)$	Degauss	$stress(Ry/Bohr^3)$
0.02	-26.50	0.11	-192.78
0.03	-40.63	0.12	-217.06
0.04	-41.18	0.13	-211.27
0.05	-53.48	0.14	-226.15
0.06	-71.14	0.15	-217.82
0.07	-98.30	0.16	-206.76
0.08	-133.34	0.17	-184.16
0.09	-135.14	0.18	-168.70
0.10	-160.44	-	-

4.4.1 Convergence test of total stress of Fe with respect to degauss sampling

In this part, the total stress of Fe is calculated as the function of degauss sampling, the other parameter's like lattice constant, energy cutoff and k.point are fixed. The result show that, the total stress of Fe per atom is $-26.50 Ry/Bohr^3$ and the stress is decrease with increasing amount of degauss until reach at 0.14 degauss. However the total stress of Fe again increase with respect degauss due to the effect of magnetic field and it is difficult to estimate the converge point. Stress has direct proportional relation with total energy and the negative stress are shows the corresponding positive values of strain.

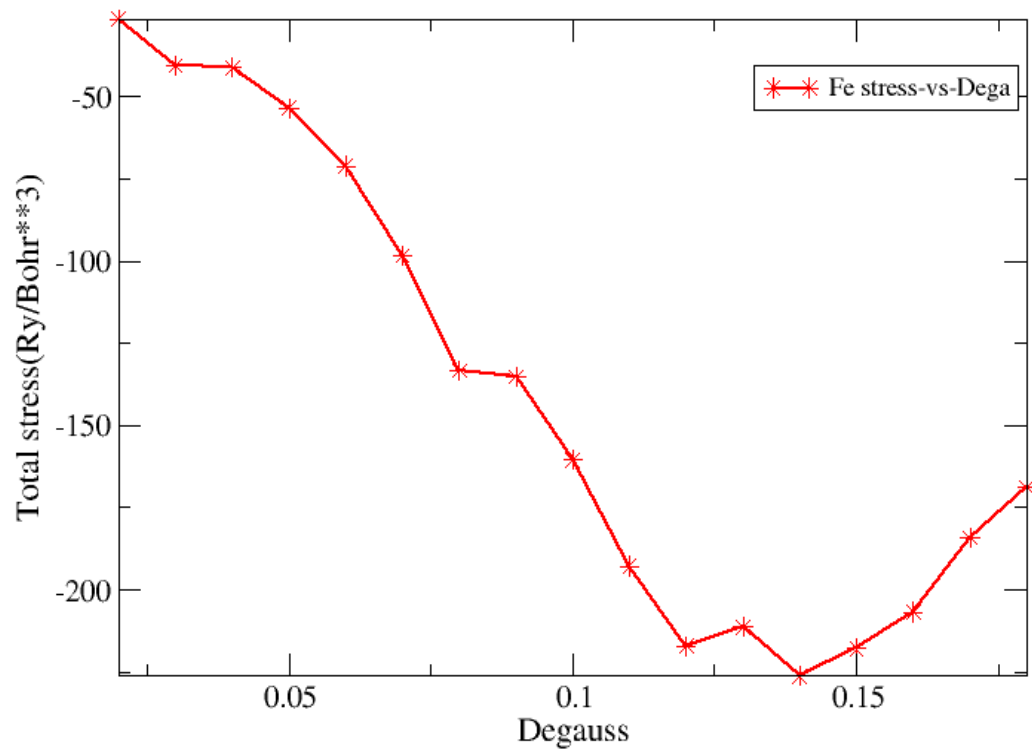


Figure 4.4: Total Stress of Fe with respect to degauss.

4.5 The equilibrium lattice constant of Fe with respect to energy cutoff

The procedure to calculate equilibrium lattice constant of Fe was computing lattice constant between 4.80 Bohr to 5.55 Bohr, in steps of 0.05 Bohr.

Table 4.5: The results of the total minimum energy computed with lattice constant

Lattice constant(Bohr)	Total minimum energy (Ry)	lattice constant (Bohr)	Total minimum energy (Ry)
4.80.	-55.52140018	5.20	-55.54665816
4.85	-55.53027763	5.25	-55.54413666
4.90	-55.53718939	5.30	-55.54074155
4.95	-55.54232848	5.35	-55.53657026
5.00	-55.54584836	5.40	-55.53167544
5.05	-55.54791760	5.45	-55.52615297
5.10	-55.54865435	5.50	-55.52087173
5.15	-55.54819455	5.55	-55.51349166

4.5.1 Convergence test of total minimum energy of Fe with versus lattice constant

To find the equilibrium lattice constant of Iron we performed total energy calculation for a series of arguments parameters. In this calculation the energy cutoff and the k.point sampling made fixed (60 Ry, $16 \times 16 \times 16$ k.point) using the cutoff and k.point grid criteria for energy convergence. From Fig 4.5 we observe that, total minimum energy of Fe was increase with increasing lattice constant. Therefore, the numerical calculation shows that the equilibrium lattice constant is 5.10 Bohr and the result is best agreement when we compare the equilibrium lattice constant with experimental value of 5.217 Bohr.

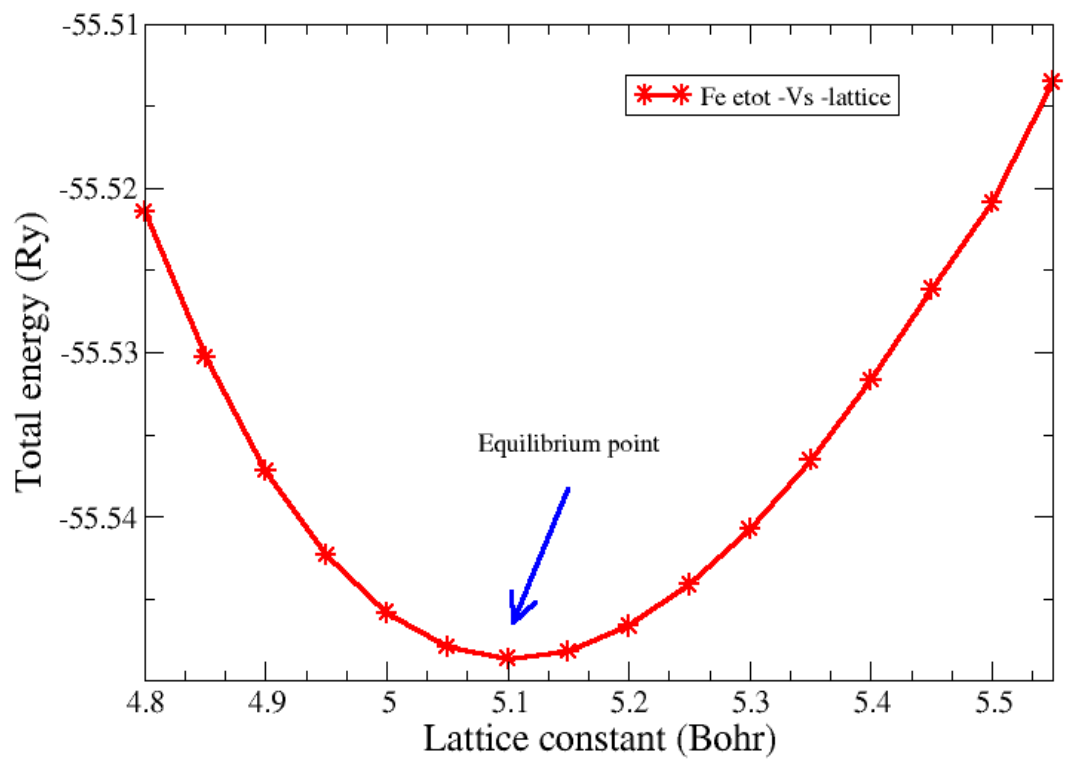


Figure 4.5: Total energy of Fe versus lattice constant.

4.6 Total energy of Fe with respect to different smearing/degauss

Degauss is the electronic temperature; it controls the process of decreasing or eliminating remanent magnetic field and broadening of the occupation number around the Fermi energy. Smearing is used to test unwarranted occupation distribution which depends on the system of the interest. In metal we use either Fermi energy or Cold smearing with large broadening including comparison of smearing methods like Marzazi-Vanderbilt (M-V), Methfessel-Paxton (M-P), Gaussian (Ga) and Fermi-Dirac (F-D). In this calculation, the plane wave cutoffs for wave functions are fixed at 25 Ry and k.point integrations have been performed using different smearing from 0.01 up to 0.10 over shifted Monkhorst-Pack meshes of order $4 \times 4 \times 4$ for the body center cubic (bcc). From Table 4.6 , we see that the an increment of the smearing are important to obtain fully converged total minimum energy of Fe and to interpret the comparison of smearing methods.

4.6.1 Total energy of Fe with respect to smearing for $4 \times 4 \times 4$ k.point grid

In this part, the total energy per atom compute with respect to degauss to compare the smearing in Fe metal.

Table 4.6: The results of the total minimum energy computed with smearing sampling

Smearing	Total energy (Ry) in (M-V)	Total energy (Ry) in (M-P)	Total energy (Ry) in(Ga)	Total energy (Ry) in (F-D)
0.01	-55.53286299	-55.53296591	-55.53438617	-55.54142434
0.02	-55.53409140	-55.53341971	-55.53858486	-55.55992398
0.03	-55.53593429	-55.53474660	-55.54437002	-55.58472227
0.04	-55.53800464	-55.53607592	-55.55138741	-55.61466625
0.05	-55.54077103	-55.53767723	-55.55957059	-55.64927438
0.06	-55.54410172	-55.53966876	-55.56876254	-55.68813513
0.07	-55.54758602	-55.54199143	-55.57883030	-55.73078277
0.08	-55.55081476	-55.54454355	-55.58969297	-55.77675677
0.09	-55.55351333	-55.54722281	-55.60131108	-55.82565117
0.10	-55.55559749	-55.54994885	-55.61366927	-55.87713044

4.6.2 Convergence test of total minimum energy of Fe with smearing for $4 \times 4 \times 4$ k.point sampling

The smearing for $4 \times 4 \times 4$ k.pont sampling is increased until convergence is made. From Fig 4.6 we can see that, the four different colors describe the smearing types method with $4 \times 4 \times 4$ k.point sampling. The convergence of metallic system is very slow. The total minimum energy of Fe converge very fast using Marzari-Vanderbilt (M-V) or Methfessel-Paxton (M-P) as compared to Gaussian (Ga) or Fermi-Dirac (F-D) smearing for the given values of degauss. However Marzari-Vanderbilt (M-V) and Methfessel-Paxton (M-P) are less dependent on degauss and we have checked the convergence of the minimum energy of Fe for different values of smearing with the k.point sampling.

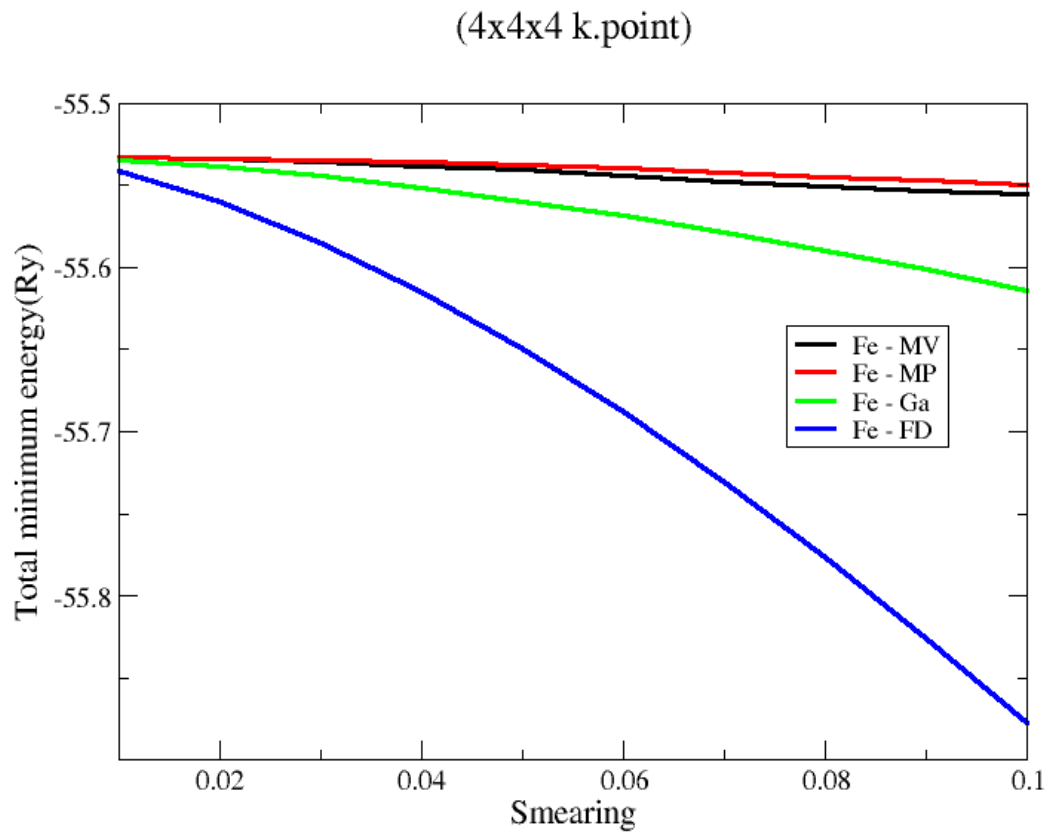


Figure 4.6: The plots of smearing for $4 \times 4 \times 4$ k.point grid.

Chapter 5

Conclusion

The electronic and structural properties of Iron (Fe) was studied with the framework of density functional theory, plane wave basis set, energy cutoff, k.point and pseudopotential (vanderbilt). Iron is the main ingredient used to make steel. There is a lot of Fe in the universe because it is the end point of the nuclear reactions in large star. All parameters have been obtained with quantum ESPRESSO software package by calculation of self consistent field (SCF). The total minimum energy calculation is interpreted as function of energy cutoff and k.point grid, keeping other parameters constant. The total energy convergence test is achieved at the energy cutoff 60 Ry for the first case and at $16 \times 16 \times 16$ k.point grid size for the second case. The total minimum energy is -55.54237417 Ry and -55.54574483 Ry for the second case. The total magnetization of Iron (Fe) is calculated as function of degauss. In this case the total magnetization of Fe per atom is 1.99 Bohr Mag/cell and the magnetization is decrease with increasing of degauss. However when the values of degauss is above 0.12 there is negative values of magnetization. Therefore the negative values show the response of imposed magnetic field and the magnetization result is reach to zero.

The total stress of Fe is calculated as function of degauss sampling. In this calculation the total stress Fe per atom is $-26.50 \text{ Ry}/\text{Bohr}^3$ and the stress is decrease with increasing amount of degauss until reach at 0.14 degauss. However the total stress of Fe again increase with respect to degauss due to the effect of magnetic field. Stress has direct proportional relation with total energy and the negative stress are shows the corresponding positive values of strain. The numerical calculation shows that the equilibrium lattice constant is 5.10 Bohr. This result is best agreement when we compare the equilibrium lattice constant with experimental value of 5.217 Bohr. Finally, for Fe metallic system, the choice of cold smearing is used to minimize the electronic energy in a DFT calculation. The different smearing calculation was performed with Marzari-Vanderbilt, Methfessel-Paxton, Gaussian and Fermi-Dirac for $4 \times 4 \times 4$ k.point sampling. The result shows that the convergence cold smearing is very fast than Fermi-Dirac smearing. However cold smearing is less dependent on degauss.

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