



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

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A Thesis Submitted to

The Department of Physics

IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

JIMMA UNIVERSITY

JIMMA, ETHIOPIA

JUNE, 2018

JIMMA UNIVERSITY
DEPARTMENT OF
PHYSICS

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Dated: June, 2018

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Title: **electronic and structural properties of nickel using
density functional theory (quantum espresso)**

Department: **Physics**

Degree: **M.Sc.** Convocation: **June** Year: **2018**

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Abstract

Nickel is a metal which is widely distributed in nature; and it is found in animals, plants, and soil. The density functional theory (DFT) simulation tools were employed to investigate energies, magnetization and geometrical structure of nickel (Ni) using quantum ESPRESSO package. A number of convergence test were performed, to establish the optimal value of various parameters in the numerical calculations. Firstly, the total minimum energy of nickel per atom is calculated as a function of cut-off energy, and k-points. Secondly, the optimal lattice constant and the magnetic ordering were calculated for bulk nickel. Here to find the equilibrium lattice constant of nickel, the total energy calculation with a series possible parameters of lattice constant have been performed. Moreover, the total magnetization of an atom is computed as a function of smearing(Marzari-Vanderbilt). In addition to these, Fermi-Dirac function was employed to describe the probability of electronic state occupations. Also the calculations were repeated with Gaussian, Marzari-Vanderbilt and Methfessel-Paxton functions. The total minimum energy per atom is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-point sampling. The computational value of the equilibrium lattice constant is 6.47 Bohr. This result is in good agreement with experimental value. Furthermore, the negative magnetization observed in low fields has been ascribed to two oppositely ordered ferromagnetic super exchange interactions. Moreover, the convergence in cold smearing is very fast than Fermi-Dirac smearing.

keywords: Nickel, Density Functional Theory, Total Minimum Energy, Electronic Structure and Total Magnetization.

Acknowledgements

I would like to express my great thanks to Almighty God! for his help in all my way. First and foremost, I would like to express my deep gratitude thanks to my advisor, Dr. Menberu Mengesha (Associate professor), who is a wonderful mentor. I am extremely thankful for his support, guidance, patience and precious encouragement the whole time during my study. I would like to thank my co-Adviser Mr. Solomon H/marium (Assistant professor) for his support, encouragement and advice. I would like to thank my family, especially my wife, for her motivation and endless support throughout my study. I would like to express my appreciation to every one, who made the successful completion of Msc.

Chapter 1

Introduction

1.1 General Background

Swedish mineralogist Axel Fredrik Cronstedt was first identified nickel as an element in 1751, but he did not name it until 1754. The name comes from the German word kupfernickel, meaning "Old *Nick's* Copper". For the first time pure nickel was obtained apparently by Richter. Nickel is widely distributed in nature and is found in animals, plants, and soil. It is the 24th most abundant element, forming about 0.008% of the earth's crust and 6% of the earth's core. Nickel is a metal which belongs to group 10/VIIIB of the periodic table. It has (atomic number, 28; atomic weight, 58.69 and density, 8.9 g/cm³). The electronic configuration of the nickel (Ni) is represented by [Ar]3d⁸4s². Nickel has five types of isotopes such as: ⁵⁸Ni, ⁶⁰Ni, ⁶¹Ni, ⁶²Ni, and ⁶⁴Ni; the ⁵⁸Ni is the most abundant. The most important oxidation state of nickel is +2, although the +3 and +4 oxidation states are known. Pure nickel has properties that make it very desirable for combining with other metals to form alloys. Such as: hard-ness, silvery-white and shiny surfaces, high melting point, ductility, malleability, some what ferromagnetic behavior, fair conductor of heat and electricity and etc. Some of the metals that can be alloyed with nickel are: iron, copper, chromium,

molybdenum and zinc. Mostly, nickel is used to make stainless steel. Nickel alloys have a number of unique properties, or combinations of properties, that allow them to be used in variety of specialized industrial and commercial applications depending on the primary metal which they are alloyed with and their nickel content. For example, the high resistivity and heat resistance of nickel chromium alloys lead their use to electric resistance of heating elements. The magnetic properties of nickel-iron alloys are used in electronic devices and for electromagnetic shielding of computers and communication equipments. Nickel is a relatively un reactive element. At room temperature, it does not combine with oxygen or water or dissolve in most acids. At higher temperatures it becomes more active. Nickel is emitted to the atmosphere from both natural and anthropogenic sources. Environmental exposure to nickel occurs through inhalation, ingestion, etc. The general population is exposed to low levels of nickel because it is widely present in air, water, food, and consumer products. Nickel is one of the three naturally occurring elements that is strongly magnetic. The other two elements are iron and cobalt. But nickel is less magnetic than iron and cobalt. Nickel crystallizes with the face-centered cubic arrangement atom. This means that the atoms form the corners of a cube, with one atom in the center of each face [1-2].

The total energy of face centered cubic nickel can be calculated by a plane-wave basis set as a function of volume. Density functional theory (DFT) or ab-initio computations would be applied to the nickel atom; to examine its different properties. Density Functional Theory is the most widely applied "ab-initio" method used for real materials in: physics, chemistry, and material science. It is the model of choice for understanding condensed matter at low energy. Its success derives from the ability to produce accurate results [3-4].

1.2 Statements of the problem

It is clear that many body problems are complicated and difficult to solve. The state of motion can not be solved analytically for systems in which three or more masses are interact. In recent years, solved by the application of density functional theory techniques of many body systems, such as molecular and solid state systems and problems of chemical interest. The basic purpose of density functional theory is that any property of the systems of many interacting particles can be viewed as a functional of the ground state density $n_o(r)$; in principle determines all the information in the many body wave functions for the ground state. Nickel metal is more active at higher temperature. If it is heated above T_c , the spontaneous magnetic ordering breaks down in a second order phase transition, leaving the metal in paramagnetic state. The changes in the electronic structure and the amount of short range magnetic order above T_c of nickel atom are subjects of a long and still debate. The electronic and structural properties of nickel based on Density Functional Theory is not well studied. Therefore, decided to study the electronic and structural properties of nickel. So the aim of this study is to investigate the electronic and structural properties of nickel with the help of density functional theory using quantum ESPRESSO package.

1.3 Objectives

1.3.1 General Objective

►The general objective of this study is to investigate the electronic and structural properties of nickel using density functional theory (QUANTUM ESPRESSO).

1.3.2 Specific Objectives

The specific objectives of this study were:

- ▶ To calculate the total minimum energy of nickel per atom with respect to cut-off energy;
- ▶ To calculate the total minimum energy of nickel per atom with respect to K-points sampling;
- ▶ To calculate the lattice constant of nickel with respect to cut-off energy and K-points sampling;
- ▶ To calculate the total magnetization of nickel per atom with respect to smearing (Marzari-Vanderbilt);
- ▶ To calculate the total minimum energy of nickel per atom with respect to different smearing occupational functions.

1.4 Significance of the study

The significance (purpose) of this study is to investigate the electronic and structural properties of nickel (Ni) or many electron-system using computational methods, ab-initio or density functional theory techniques. This study also used to identify the applications of metallic nickel and nickel compounds. Metallic nickel and nickel compounds have many industrial and commercial applications, including, use in stainless steel and other nickel alloys. These alloys are used in making metal coins and jewelry and in industry for making items such as valves, heat exchangers, catalysts, batteries, pigments, ceramics, etc.

1.5 Scope of the study

The scope of this study is limited to the calculation of the total minimum energy of nickel, with respect to cut-off energy, k-points, lattice constants, and smearing for different functions and total magnetization of nickel per atom with respect to smearing (Marzari-Vanderbilt).

1.6 Abbreviations, Units and Words

1.6.1 Abbreviations

Some abbreviations that used in this study are:

Ry-Rydberg(used in the implementation of the DFT)

DFT-Density Functional Theory

LDA-Local Density Approximation

GGA-Generalized Gradient Approximation

1BZ-First Brillouin Zone

FCC-Face Centered Cubic

Ni-Nickel

PWscf-plane-wave self-consistent-field

GGA-PBE-generalized gradient approximations of Perdew-Burke-Ernzerhof

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STRUCTURE, SIMULATION, AND OPTIMIZATION**

E_{xc} -The exchange-correlation energy

KS-Kohn-Sham

HF-Hartree-Fock

1.6.2 Units

In this study the following units are used:

1Ry-length unit=0.52917725Å

1RY-energy unit=13.60569253ev

1.6.3 Words

In this study the following words are used:

K-points: The number of points in the reciprocal space that the program is supposed to sample, i.e. the points in which the actual self consistent minimization of the energy would be performed.

Energy-cutoff: Limits the amount of plane waves that the program would use during the minimization procedure.

Atomic Species: Specified the symbols of the atoms with their corresponding masses (as written on the periodic table).

Atomic Positions: Specified the atomic coordinates of the atoms.

Chapter 2

Literature Review

2.1 Introduction

DFT is used to study the electronic and structural properties of atoms, molecules or bulk materials. The DFT provides a frame work to obtain the electronic structural and the total energy using the concepts of quantum mechanics. The DFT is used to study the electronic and structural properties of atoms, total minimum energy, cut-off energy, k-points, total minimum force on the atoms, etc. The DFT can be used to address a vast variety of systems and problems in physics, chemistry, biology, and material science [5].

2.2 Density Functional Theory

DFT is a successful approach (a reliable tool) for studying or finding solutions to the fundamental equation of the quantum behavior of atoms and molecules at low energies. DFT in principle, is an ab initio method, meaning that it does not use any experimental results on chemical bonding. It works with the electron density. There are significant advantages to a computational theory based on electron densities. The first is in relation to computational efficiency; the electron density depends on three

spatial variables in contrast to the $4N$ variables that wave function theory depends on (three spatial and one spin per electron). Therefore, large system can theoretically be modeled. In addition, electron correlation is conceptually easier to include in DFT. It is a simpler quantity to deal with. It has achieved a certain status as a standard first principle method. First-principles calculations based on DFT have achieved great success in studying the equilibrium properties of matter, although there are still many challenges to DFT. One of the most famous issues is how we solve the problems when encountering electronic degeneracies. Such an issue usually does not pose a problem to the equilibrium conditions. It is well known that electronic degeneracies cannot exist in the ground state of a nonlinear atomic geometry. In DFT we only need to find the charge distribution through out our system. Then we can describe single electrons moving in a crystal mean field of all ions and other electrons. In this way, we can calculate solids up to a few thousand atoms . DFT is a formally exact representation of the N electrons Schrödinger equation. The extent to which DFT has contributed to the chemical, physical and biological sciences is reflected by the 1998 Nobel prize in chemistry, which was awarded to Walter Kohn for the development of DFT, along with John Pople for the development of quantum chemistry [6-7].

2.3 The Schrödinger Equation

The ultimate goal of most approaches in solid state physics and quantum chemistry is the solution of the time independent, non-relativistic Schrödinger equation. The electronic Schrödinger equation of a system of N electrons reads:

$$\hat{H}\Psi(r_1, \dots, r_N) = E\Psi(r_1, \dots, r_N) \quad (2.3.1)$$

where \hat{H} is the Hamiltonian of the system, E is energy, r_N is coordinate of the electron with index N and $\Psi(r_1, \dots, r_N)$ is the many particle wave function.

$$\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{T}_n + \hat{V}_{nn} \quad (2.3.2)$$

$$\hat{T}_e = \sum_i^{N_{elec}} -\frac{1}{2} \nabla_i^2 \quad (2.3.3)$$

$$\hat{V}_{ne} = \sum_a^{N_{nuc}} \sum_i^{N_{elec}} \frac{Z_a}{|R_a - r_i|} \quad (2.3.4)$$

$$\hat{V}_{ee} = \sum_i^{N_{elec}} \sum_{j>i}^{N_{elec}} \frac{1}{|r_i - r_j|} \quad (2.3.5)$$

$$\hat{T}_n = \sum_a^{N_{nuc}} -\frac{1}{2} \nabla_a^2 \quad (2.3.6)$$

$$\hat{V}_{nn} = \sum_a^{N_{nuc}} \sum_{b>a}^{N_{nuc}} \frac{Z_a Z_b}{|R_a - R_b|} \quad (2.3.7)$$

in atomic units.

2.4 Born-Oppenheimer approximation

By Born-Oppenheimer approximation the nuclear kinetic energy is zero (nuclei much slower than the electrons) and their potential energy is merely a constant (nuclear positions are fixed). Then the Hamiltonian reduces to:

$$\hat{H} = \hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} \quad (2.4.1)$$

where,

\hat{T}_e is the kinetic energy of the electrons,
 \hat{V}_{ne} is the electron-nuclei coulomb potential
 \hat{V}_{ee} is the electron-electron coulomb potential
 \hat{T}_n is kinetic energy of the nuclei
 \hat{V}_{nn} is nuclei-nuclei coulomb potential
 Z_a is the atomic number of nucleus a,
 R is nuclear coordinates
 r is electronic coordinates
 ∇_i^2 is the laplace operator of particle i,[8-11].

2.5 Hartree-Fock method

The HF method is a well defined starting point for the theoretical formulation of many body systems. It is an alternative to DFT approaches. It is the simplest ab-initio calculation. In this method exchange energy is exact. The major disadvantage of HF calculation is the electron correlation effect is not taken into consideration, i.e. non classical electron-electron interactions beyond the coulomb and exchange interactions. A many electron wave function must be antisymmetric with respect to the interchange of the coordinate (both space and spin) of any two electrons. In general, the periodic HF method is best suited for the study of highly ionic and large band gap crystals, because such systems are the least sensitive to the lack of electron correlation [12].

2.6 Theorems of Hohenberg and Kohn

The foundation of the DFT method is the Hohenberg-kohn theorem, which states that for each given electronic density $n(r)$, there is one and only one corresponding

potential. All properties of the many body system are determined by the ground state density.

2.6.1 First theorem of Hohenberg and Kohn

The ground-state energy of a many-body system is a unique functional of the particle density. In principle, all properties of the ground state can be expressed as functionals of the ground state spin density matrix ρ_o . Therefore, the ground state wave function Ψ_o (which can be determined by density functional theory) minimizing the energy functional:

$$E[\Psi] = \langle \Psi | \hat{H} | \Psi \rangle \quad (2.6.1)$$

Using $\Psi_o[\rho_o]$ one can determine all properties by calculating:

$$\langle \hat{O} \rangle[\rho_o] = \langle \Psi_o[\rho_o] | \hat{O} | \Psi_o[\rho_o] \rangle \quad (2.6.2)$$

where \hat{O} is an arbitrary operator. This is in particular true for the ground state energy $E[\rho_o]$ or the expectation value of the kinetic energy $\langle \hat{T} \rangle[\rho_o]$ or for the interaction energy of the electrons $\langle \hat{U} \rangle[\rho_o]$.

2.6.2 Second theorem of Hohenberg and Kohn

The functional of $E[n(\vec{r})]$ has its minimum relative to variations $\delta_n(\vec{r})$ of the particle density at the equilibrium density $n_o(\vec{r})$. The Raleigh-Ritz variational principle is used to minimize the energy and find the ground state energy and density.

$$E_o = E[n_o(\vec{r})] = \min E[n(\vec{r})] \quad (2.6.3)$$

$$\frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})} \Big|_{n(\vec{r})=n_o(\vec{r})} = 0 \quad (2.6.4)$$

this theorem defines the following functional of the spin density matrix ρ

$$F[\rho] = \min \langle \Psi | \hat{T}[\rho] + \hat{U}[\rho] | \Psi \rangle. \quad (2.6.5)$$

The minimum is with respect to the wave function Ψ but for a given spin density matrix ρ only those wave functions are valid which build Ψ . The functional of the total energy is

$$E[\rho] = F[\rho] + \int \text{tr}(\rho_r W[\rho(r)]) d^3r \quad (2.6.6)$$

For a given potential matrix W , minimizing the above equation, yields the ground state energy E_o and the ground state spin density matrix ρ_o . If $F[\rho]$ (universal functional) is known, the problem is a minimization problem for ρ [13,14].

2.7 Kohn-Sham Equations

The Kohn-Sham approach of DFT is the most used quantum mechanical method for the calculation of the geometrical and electronic properties of molecules, surfaces, and solids. It is an approach for approximating the functional by mapping the interacting many electron system of non-interacting electrons. Replace original many body problem with an independent electron problem. Calculations on very large systems (up to several thousands of atoms) are possible, since DFT has a relatively low cost which is due to the mapping of a system of interacting electrons to a system of fictitious non-interacting electrons with same electron density. The price to pay for this computational efficiency is the need to choose an approximate functional to represent the exchange correlation energy. Therefore the accuracy of the results of a good calculation (i.e. use of a soft ware with an accurate implementation of the KS equations) relies only on the chosen exchange-correlation functional. Only the

ground state density and energy are required to be the same as in the original many body system. In the theory of Kohn and Sham the problem of calculating the ground state properties of the system of interacting electrons is reduced to the problem of calculating these properties via a hypothetical system of non-interacting electrons in an effective potential with the respective single-electron wave functions.

$$\Psi_i(r) = \begin{pmatrix} \Psi_i^\uparrow(r) \\ \Psi_i^\downarrow(r) \end{pmatrix} \quad (2.7.1)$$

the spin-density matrix ρ is:

$$\rho_{\alpha,\alpha'} = \sum_{i=1}^N \Psi_i^\alpha(r) \left(\Psi_i^{\alpha'}(r) \right)^* \quad (2.7.2)$$

with $\alpha = \uparrow, \downarrow$ can be defined. It is useful to introduce the particle density as well

$$n(r) = \sum_{i=1}^N (|\Psi_i^\uparrow(r)|^2 + |\Psi_i^\downarrow(r)|^2) \quad (2.7.3)$$

Kohn and Sham use a model system (subscript s) where N mutually non-interacting particles are in an effective potential (matrix). The effective Schrödinger equation reads in atomic units:

$$\left[\frac{-1}{2} \nabla^2 + [W_{eff}[\rho](r)] \right] \Psi_i(r) = E_i \Psi_i(r) \quad (2.7.4)$$

In order to calculate the DFT, quantities accurately molecular Kohn-Sham (KS) solutions have been obtained from ab-initio wave functions [15,16].

2.8 The exchange-correlation energy

The exchange-correlation energy E_{xc} of a many-electron system is the key quantity of DFT. With in the Kohn-Sham theory E_{xc} is defined as afunctional of the electron density ρ in the KS expression for the total electronic energy $E[\rho]$,

$$E[\rho] = T_s[\rho] + V[\rho] + W_H[\rho] + E_{xc} \quad (2.8.1)$$

where T_s is the kinetic energy of a non-interacting particle system with density ρ . V is the energy of electron-nuclear attraction and W_H is the coulomb or Hartree energy. E_{xc} can be further subdivided into the exchange E_x and correlation E_c energies.

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \quad (2.8.2)$$

Accurate values of the exchange and correlation energies obtained for chemically interesting systems are essential for analysis of the effect of electron correlation with in Kohn-Sham theory and in order to test and calibrate various DFT approximations (Local Density Approximation (LDA) and Generalized Gradient Approximation (GGA)).

2.8.1 The Local Density Approximation (LDA)

A first family of exchange-correlation functionals is the LDA functionals. The idea of these functionals is the first look at the case of a homogeneous electron gas. In such a system, one considers electrons moving in, a uniform external potential. In DFT, the electronic density rather than the wave function is the basic variable.

$$E_{xc}^{LDA}[n] = \int n(r)\epsilon_{xc}[n(r)]d\vec{r} \quad (2.8.3)$$

There is no known formula to calculate from the density the total energy of many electrons moving in an external potential. Hohenberg and Kohn proved that there exists a universal functional of the density, called $G[\rho]$, such that the expression:

$$E[\rho_r] = \int V_{ext}(r)\rho_r d^3r + \frac{1}{2} \int \frac{\rho_r \rho_{r'}}{|r - r'|} d^3r d^3r' + G[\rho] \quad (2.8.4)$$

has its minimum value that correct ground-state energy associated with $V_{ext}(r)$. Here, the first term on the right-hand side represents the energy due to an external potential,

including the electron-nuclear potential, while the second term is the classical coulomb energy of the electronic system. The functional $G[\rho]$ is valid for any number of electrons and any external potential, but it is unknown and further steps are necessary to approximate it. Another disadvantages of the LDA is that the Hartree coulomb potential includes interactions of each electron with it self, and the spurious term is not canceled exactly by the LDA self-exchange energy, in contrast to the Hartree-Fock method where the self-interaction is canceled exactly.

2.8.2 The Generalized Gradient Approximation (GGA)

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 idea behind these functionals was to improve the approximation of LDA by considering not only the electron density, but also the local gradient of the density. The GGA functional can be written as

$$E_{xc}^{GGA}[n] = \int n(r)\epsilon_{xc}[n(r), \nabla_n]d\vec{r} \quad (2.8.5)$$

The $E_{xc}^{GGA}[n]$ is the exchange correlation energy per particle of an electron gas. The GGA method gives better total energies[17-19].

2.9 The Pseudopotential

A smooth effective potential that reproduces the effect of the nucleus plus core electrons on valence electrons. Many of the physical and chemical properties of molecules and solids are derived due to the interactions between the valence electrons. The pseudopotential approximation is motivated by the fact that the behavior of the valence electrons in the bonding region primarily determines the electronic structure and

the structural properties of many materials. In a pseudopotential formulation, the effect of the core electrons and that of the nuclear potential are combined to form an effective ionic pseudopotential. The pseudopotentials are commonly constructed, so that outside of a core region the valance pseudowave functions match the corresponding states derived from an all-electron calculation, inside the region they are smooth functions. This formulation makes pseudopotential calculations quite efficient, since the core orbital do not need to be recomputed. The relaxation corrections takes into account the relaxation of the electronic system up on the excitation of an electron [20,21].

2.10 Periodic super cells

We would define the shape of the cell that is repeated periodically in space, the super cell, by lattice vectors \vec{a}_1 , \vec{a}_2 , and \vec{a}_3 . If we solve the Schrödinger equation for this periodic system, the solution must satisfy a fundamental property known as Bloch's theorem [22,23].

2.10.1 Bloch's theorem

A Bloch's function is the generalization of a plane wave for an electron in periodic potential. 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.

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

where $u_k(r)$ is periodic in space with the same periodicity as the super cell. That is,

$$u_k(\vec{r} + n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3) = u_k(r) \quad (2.10.2)$$

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,

$$u_k(r) = \sum_G C_{i,G} e^{i\vec{G}\cdot\vec{r}} \quad (2.10.3)$$

where $C_{i,G}$ are expansion coefficients, the reciprocal lattice vectors G are defined by:

$$\vec{G}\cdot\vec{a} = 2\pi n \quad (2.10.4)$$

for all \vec{a} , where \vec{a} is a lattice vector of the crystal and n is an integer. Therefore each electronic wave function can be written as a sum of plane waves,

$$\Psi_k(r) = \sum_G C_{i,k+G} e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \quad (2.10.5)$$

The electronic wave functions at each k -point can be expressed in terms of a discrete plane wave basis set. In principle the Fourier series is infinite. However, in practice we can not 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})[24,25].

2.10.2 Energy cutoffs

Energy cutoff limit the number of plane wave components. The minimum length scale depends on the elements in the system. Energy monotonically decreases to the ground state energy as E_{cut} increases. Our discussion of k -space would begin with Bloch's theorem, which tells us the solutions of the Schrödinger equations for a super cell that have the form

$$\Psi_k(r) = e^{i\vec{k}\cdot\vec{r}} u_k(r) \quad (2.10.6)$$

where $u_k(r)$ is periodic in space with the same periodicity as the super cell. 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:

$$u_k(r) = \sum_G C_{i,G} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad (2.10.7)$$

where the summation is over all vectors defined by:

$$\vec{G} = n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3 \quad (2.10.8)$$

with integer values n_i . The set of vectors defined by \vec{G} in reciprocal space are defined so that for any real space lattice vector, combining the two equations above gives:

$$\Psi_k(r) = \sum_G C_{i,k+G} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad (2.10.9)$$

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 use for practical calculations. they are solutions with kinetic energy:

$$E = \frac{\hbar^2}{2m} |\vec{k} + \vec{G}|^2 \quad (2.10.10)$$

It is reasonable to expect that the solutions with lower energies are more physically important than solutions with very high energies. As a result, it is usual to truncate the infinite sum above to include only solutions with kinetic energies less than some value:

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}^2 \quad (2.10.11)$$

The infinite sum then reduces to:

$$\Psi_k(r) = \sum_{|\vec{G} + \vec{k}| < G_{cut}} c_{G+k} e^{i(\vec{k} + \vec{G}) \cdot \vec{r}} \quad (2.10.12)$$

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}) [26,27].

2.10.3 K-points sampling

The solution that is used most widely was developed by Monk-horst pack in 1976. A regular grid in k -space. The symmetry of the cell may be used to reduce the number of k -points which are needed. Using these methods, one can obtain an accurate approximation for the electronic potential and the total energy of an insulators 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 computational cost of performing a very dense sampling of k -space can be significantly reduced by using the k -point total energy method [28,29].

2.10.4 Plane wave basis

The plane wave method originates from calculations of extended bulk surface systems. Systematic convergence with respect to single parameter E_{cut} . The obvious choice for periodic and works well for a periodic systems. Non-local, cover all space equally. In principle , an infinite plane wave basis set is required to expand the electronic wave function. However, the coefficients, $\vec{K} + \vec{G}$ for the plane waves with small kinetic energy, $\frac{\hbar^2}{2m}|\vec{K} + \vec{G}|^2$ 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. Application of the Bloch's theorem allows the electronic wave functions to be expanded in terms of a discrete set of plane waves. Introduction of any energy cutoff to discrete plane wave basis set produces a finite basis set. The structural and magnetic properties of ferromagnetic nickel is computed by using a plane wave basis set [30,31].

2.11 Magnetic System

When a magnetic field is applied, the electrons acquire extra energy term due to interaction of their spins with the field. Molecules and materials possessing a net magnetic moment are at the core of many modern technology logical devices, such as electrical power generators and transformers, computers, telephones, etc. The measurable imbalance of electron spins align with and against the field is a weak effect known as Pauli paramagnetism. There are different magnetic systems, such as ferromagnetic and anti-ferromagnetic systems.

2.11.1 Ferromagnetic system

If the spins align parallel to the field, then its magnetic energy is negative (electrons are at a lower energy than they were in the absence of a field). Ferromagnetism arises from parallel orientation of the magnetic moments of atoms in the absence of an external field. This can lead to large and permanent magnetization. Iron, nickel and some of the rare earths (gadolinium, and dysprosium) exhibit ferromagnetic properties. Usefulness of a particular ferromagnetic substance depends on factors such as: size of magnetization produced, how easily it can be magnetized and demagnetized, how readily it responds to an applied field.

2.11.2 Anti-ferromagnetic system

Another phenomenon of magnetism is anti-ferromagnetic ordering. If the spins align anti-parallel (opposite direction) to the field, it may go to a higher energy state and change spin, as long as the promotion energy is not more than the gain in magnetic energy [32-35].

Chapter 3

Materials and Methodology

3.1 Materials

The study is purely theoretical. The main source of information were the published articles, books, the published thesis and manuscripts and dissertation carried out based on the project title. Softwares and computers are additional instruments, which will be used to accomplish the study.

3.2 Methodology

DFT calculations were performed with the generalized gradient approximations of Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional, Vanderbilt ultra soft pseudo potentials and the plane wave basis sets are implemented in the Quantum ESPRESSO program package. Quantum ESPRESSO is an integrated module of computer codes for electronic and structural calculations and materials modeling depending on the frame work of the DFT, plane wave basis sets (PW) and pseudo potentials to represent the electron-ion interactions. It is free, open-source software distributed under the terms of the GNU General Public Licence (GPL). The most important input parameters in Quantum Espresso are: number of atoms in unit cell,

types of atoms in the periodic cell, bravais-lattice index, lattice parameters, the kinetic energy cutoff, k-points, atomic positions and atomic species. The structure of the normal phase of Ni was optimized until the total energy has been converged. Also several sets of Monkhorst-pack k-point grid samplings were tested. Plane waves are easy lattice-periodic basis functions but in general not possible to expand the crystal wave function in plane waves because of the strong oscillation near the cores (almost infinitely many plane waves) would be required. The pseudopotential method avoids the problem. A very famous one is the ultrasoft pseudopotential. The ultrasoft pseudopotential is constructed to be smoother, which has the advantage that an even smaller amount of plane waves are needed for the expansion. A popular implementation of the ultrasoft pseudopotential method is the open source plane-wave self-consistent-field (PWscf). The PWscf or the iterative approach to self consistency using different techniques in the frame work of the plane wave pseudopotential method with regards to the ultrasoft pseudopotentials are implemented. PWscf can use the LDA or the GGA exchange correlation functionals, including spin polarization. 1BZ integration in metallic systems is performed by smearing techniques, such as the Fermi-Dirac, Gaussian, Methfessel-Paxton, and Marzari-Vanderbilt cold smearing.[36-41].

Chapter 4

Results and Discussion

Introduction

DFT calculations are used to study the electronic and structural properties of nickel. One of the important aspects in studying nickel is the total minimum energy. The results are mainly presented in tables and figures. The first result is the total energy of Ni per atom with respect to energy cutoffs. Then, with different k-point sampling, lattice constants and different smearing occupational functions. Furthermore, the computations were used to calculate the total magnetization against the smearing (Marzari-Vanderbilt).

4.1 Total minimum energy of Ni per atom with respect to energy cutoffs

Here the input was $4 \times 4 \times 4$ k-points (64 atoms); some of these k-points have the same energy due to the symmetry of the crystal. The calculation was done using different energy cutoff values, from 20 Ry to 250 Ry and lattice constant of 6.48 Bohr. See Table 4.1.

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

| Energy cutoffs(Ry) | Total energy(Ry) |
|--------------------|------------------|
| 20 | -85.72192242 |
| 30 | -85.72386001 |
| 40 | -85.72407458 |
| 50 | -85.72411497 |
| 60 | -85.72414280 |
| 70 | -85.72414685 |
| 80 | -85.72415325 |
| 90 | -85.72415452 |
| 100 | -85.72415624 |
| 110 | -85.72415733 |
| 120 | -85.72415759 |
| 130 | -85.72415823 |
| 140 | -85.72415848 |
| 150 | -85.72415859 |
| 160 | -85.72415883 |
| 170 | -85.72415896 |
| 180 | -85.72415900 |
| 190 | -85.72415909 |
| 200 | -85.72415918 |
| 210 | -85.72415921 |
| 220 | -85.72415924 |
| 230 | -85.72415928 |
| 240 | -85.72415930 |
| 250 | -85.72415932 |

4.1.1 Convergence test of total minimum energy of Ni per atom with respect to energy cutoffs

The convergence of the total energy of Ni with respect to the plane wave cutoff energy was investigated. An increment of energy cutoff for wave function is made until the convergence is achieved. The total minimum energy converge at 100 Ry plane wave cutoff energy and the total ground state energy had its minimum at -85.72415624 Ry. Moreover, the total minimum energy is monotonically decreasing with increasing energy cutoffs for wave function as shown in Fig.4.1. The accuracy of the ground state energy depends on the number of basis functions. Moreover, when the number of basis functions approaches infinity, energy is close to the ground state energy.

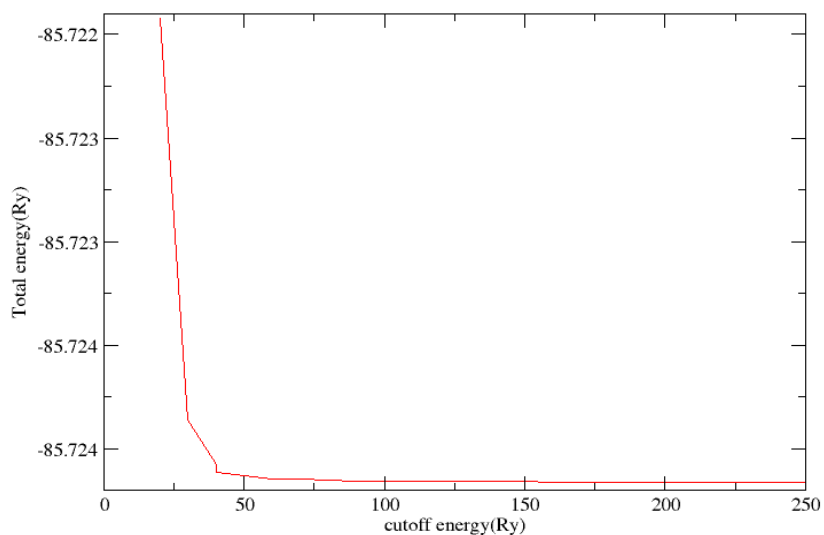


Figure 4.1: Total minimum energy of Ni per atom with respect to energy cutoffs

4.2 Total minimum energy of Ni per atom with respect to K-point grid sampling

In this case, the calculation was done using different k- point's values from $2 \times 2 \times 2$ to $20 \times 20 \times 20$ mesh with 2.0 points. Here the other variables such as lattice constant and energy cutoff are kept fixed. The results are described in Table 4.2.

Table 4.2: The results of the total minimum energy of Ni per atom computed with K-points grid

| k-points grid | Total energy(Ry) |
|--------------------------|------------------|
| $2 \times 2 \times 2$ | -85.73903574 |
| $4 \times 4 \times 4$ | -85.72339901 |
| $6 \times 6 \times 6$ | -85.72236471 |
| $8 \times 8 \times 8$ | -85.72256755 |
| $10 \times 10 \times 10$ | -85.72240765 |
| $12 \times 12 \times 12$ | -85.72242470 |
| $14 \times 14 \times 14$ | -85.72241243 |
| $16 \times 16 \times 16$ | -85.72241022 |
| $18 \times 18 \times 18$ | -85.72241031 |
| $20 \times 20 \times 20$ | -85.72240921 |

4.2.1 Convergence test of total minimum energy of Ni per atom with respect to K-point grid sampling

A convergence test of total energy for k-point sampling was performed on Ni. The total energy of the Ni atom was calculated using various sets of k-points ranging from $2 \times 2 \times 2$ to $20 \times 20 \times 20$. In each of these cases the plane wave kinetic energy cutoff of 24 Ry was used. The total minimum energy of Nickel is calculated as a function of k-points grid size using PWscf code. For this calculations, the other variables (lattice constant, energy cutoff) are kept constant . Convergence of the total energy

with respect to the discrete Brillouin zone sampling was achieved for $10 \times 10 \times 10$ Monkhorst-Pack grid. This corresponds 110 irreducible k-points. The Brillouin zone integration has been performed with the smearing technique of Marzari-Vanderbilt. The total ground state energy has its minimum at -85.72240765 Ry as given in Fig.4.2.

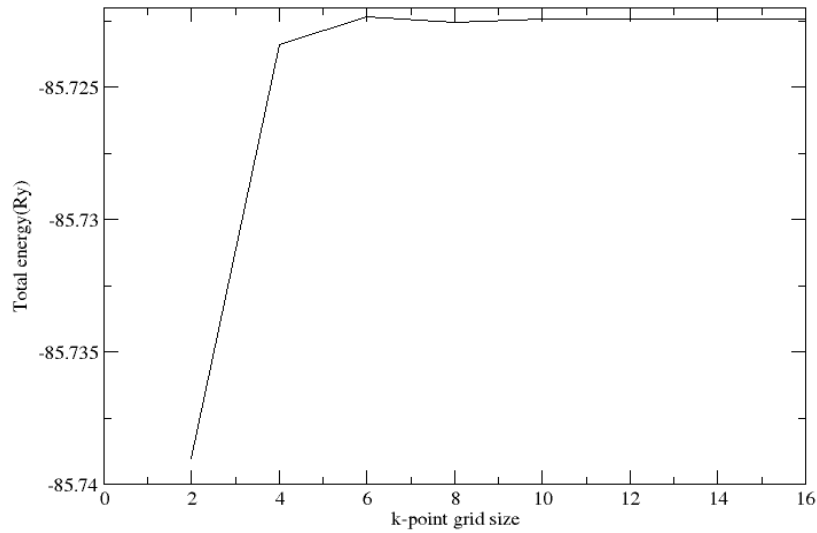


Figure 4.2: Total minimum energy of Ni per atom with respect to k-point grid size

4.3 The equilibrium lattice constant of nickel (Ni) atom

The optimal lattice constant was calculated for Ni atom. The face centered cubic (fcc) crystal structures were used. For the calculation of the crystal, a plane wave kinetic energy cutoff of 100 Ry and a Monkhorst-Pack grid of $10 \times 10 \times 10$ were used. The results are clearly shown in Table 4.3.

Table 4.3: Total minimum energy of Ni per atom with respect to lattice constant

| Lattice constant(Bohr) | Total energy(Ry) |
|------------------------|------------------|
| 6.41 | -85.72277342 |
| 6.42 | -85.72290751 |
| 6.43 | -85.72301423 |
| 6.44 | -85.72309465 |
| 6.45 | -85.72314920 |
| 6.46 | -85.72317869 |
| 6.47 | -85.72318290 |
| 6.48 | -85.72316575 |
| 6.49 | -85.72312571 |
| 6.50 | -85.72306186 |
| 6.51 | -85.72297070 |
| 6.52 | -85.72285664 |
| 6.53 | -85.72272064 |
| 6.54 | -85.72256427 |
| 6.55 | -85.72238402 |

4.3.1 Convergence test of total energy of Ni per atom with respect lattice constant

To find the equilibrium lattice constant of Nickel the total energy calculation was performed for a series of possible parameters. In this calculation the energy cutoff and the k-point sampling are made fixed (100 Ry, $10 \times 10 \times 10$ k-point) using the energy cutoff and k-point grid criteria for energy convergence. The numerical calculation shows that the equilibrium lattice constant is 6.47 Bohr. This result is in a good agreement with the experimental value (the experimental value is 6.48). See Fig.4.3.

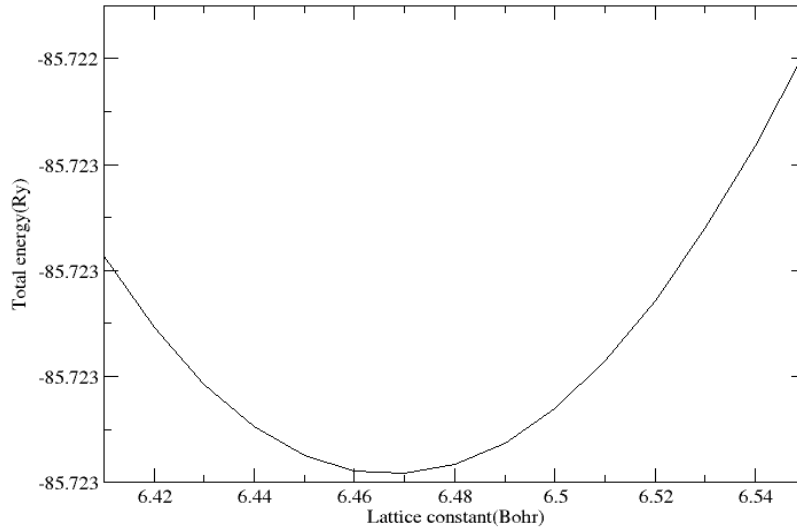


Figure 4.3: Total minimum energy of Ni per atom with respect to lattice constant

4.4 The Total Magnetization Of Ni Per Atom With Respect To Smearing (Marzari-Vanderbilt)

The fcc crystal structures of nickel were used. It is an itinerant ferromagnetic, which means that its magnetic moments are carried by the conduction band electrons. Magnetization is defined as the magnetic moment per unit volume; or when placing magnetic materials in magnetic fields, that material will generate magnetic changes. This is called magnetization. To calculate the magnetization, the kinetic energy cutoff of 24 Ry, lattice constant of 6.48 Bohr, and a Monkhorst-pack grid of dimensions $4 \times 4 \times 4$ super cells (64 atoms) are kept constant. The results are shown in Table 4.4.

Table 4.4: Total magnetization of nickel with respect to smearing (Marzari-Vanderbilt)

| Smearing | Total magnetization(Bohr mag/cell) |
|----------|------------------------------------|
| 0.01 | 0.69 |
| 0.02 | 0.73 |
| 0.03 | 0.79 |
| 0.04 | 0.81 |
| 0.05 | 0.78 |
| 0.06 | 0.71 |
| 0.07 | 0.54 |
| 0.08 | 0.18 |
| 0.09 | -0.03 |
| 0.10 | -0.05 |
| 0.11 | 0.04 |
| 0.12 | 0.03 |
| 0.13 | 0.01 |
| 0.14 | 0.01 |
| 0.15 | 0.02 |

4.4.1 Convergence test of total magnetization of Ni per atom with respect to smearing (Marzari-Vanderbilt)

The total magnetization convergence test was achieved, at smearing/degauss=0.11. The magnetization is negative at 0.09 and 0.10 smearing values as shown in Fig.4.4. Electrons near the Fermi level are responsible for the magnetic properties of Ni. Faraday induction generates an induced magnetization, which points in the opposite rather than in the same direction as the applied external field for the appearance of negative magnetization. A heating-induced demagnetization of the nickel, implying a gradual rise of the spin temperature. Ferromagnetism disappears at the curie temperature. If nickel metal is heated above T_c , the spontaneous magnetic ordering breaks down in a second-order phase transition, leaving the metal in a paramagnetic state. As

the ferromagnetic phase approaches the curie point, the electrical resistance rises as thermal energy starts to overcome the double exchange. A strong magnetic field realigns the spin, restoring the metallic state and thus decreasing the resistivity. A sufficiently large magnetic field in the reverse direction must be applied before the magnetization process can be reversed. After the re magnetization, the system is again in the ground state.

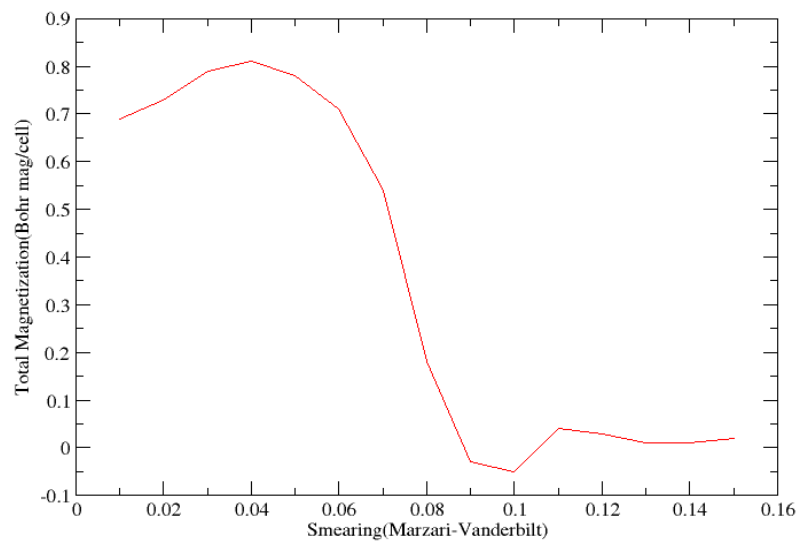


Figure 4.4: Total minimum magnetization of Ni per atom with respect to smearing(Marzari-Vanderbilt)

4.5 Total minimum energy of Ni per atom with respect to degauss/smearing

Here the total minimum energy of Ni is calculated as a function of smearing using PWscf. In this calculation, the plane wave cutoff energy for wave functions is fixed, and is 24 Ry and Brillouin Zone integrations have been performed using different smearing from 0.01 to 0.15 over Monkhorst-Pack meshes of order $4 \times 4 \times 4$ for the fcc nickel. Degauss is the electronic temperature; it controls the broadening of the occupation numbers around the Fermi energy and smearing used to select occupation distribution. In this context, Fermi-Dirac function was employed to describe the probability of electronic state occupations. The calculations were repeated with Gaussian, Marzari-Vanderbilt, and Methfessel-Paxton functions. See Table 4.5.

Table 4.5: Total minimum energy of Ni with respect to smearing for different smearing functions

| smearing | T.Ener(Ry)in M.V | T.Ener(Ry)in F.D | T.Ener(Ry)in M.P | T.Ener(Ry)in G |
|----------|------------------|------------------|------------------|----------------|
| 0.01 | -85.72342197 | -85.72661662 | -85.72353732 | -85.72393918 |
| 0.02 | -85.72339901 | -85.73731589 | -85.72335423 | -85.72531828 |
| 0.03 | -85.72300555 | -85.75329361 | -85.72336610 | -85.72786061 |
| 0.04 | -85.72179269 | -85.77246524 | -85.72336703 | -85.73171065 |
| 0.05 | -85.72024865 | -85.79495111 | -85.72341974 | -85.73692166 |
| 0.06 | -85.71856145 | -85.82058635 | -85.72369023 | -85.74262758 |
| 0.07 | -85.71674934 | -85.84910627 | -85.72425217 | -85.74873308 |
| 0.08 | -85.71481267 | -85.88025345 | -85.72502245 | -85.75528686 |
| 0.09 | -85.71254522 | -85.91380611 | -85.72563492 | -85.76233564 |
| 0.10 | -85.70983078 | -85.94960551 | -85.72609730 | -85.76989808 |
| 0.11 | -85.70675294 | -85.98752553 | -85.72646126 | -85.77798406 |
| 0.12 | -85.70338557 | -86.02747017 | -85.72677094 | -85.78657991 |
| 0.13 | -85.69979627 | -86.06936639 | -85.72705877 | -85.79566930 |
| 0.14 | -85.69603853 | -86.11315816 | -85.72735761 | -85.80523419 |
| 0.15 | -85.69217105 | -86.15880180 | -85.72768414 | -85.81525649 |

4.5.1 Convergence test of the total minimum energy of Ni with respect to smearing for different smearing functions

When applied in conjunction with the Fermi-Dirac distribution, the smearing factor actually takes on a physical meaning, namely to directly reflect the electronic temperature of the system, and thus describes the occupational probability of the electronic state. An increment of smearing for different functions is made until the convergence is achieved. The total minimum energy converges very fast using Marzari-Vanderbilt or Methfessel-Paxton smearing relative to Gaussian or Fermi-Dirac smearing for the given values of degauss. An increment of the smearing is necessary to obtain fully converged total minimum energy of Ni. The convergence in cold smearing is very

fast than Fermi-Dirac smearing. To describe total minimum energy of nickel versus smearing for different functions, four different colors are used as shown in the Fig.4.5.

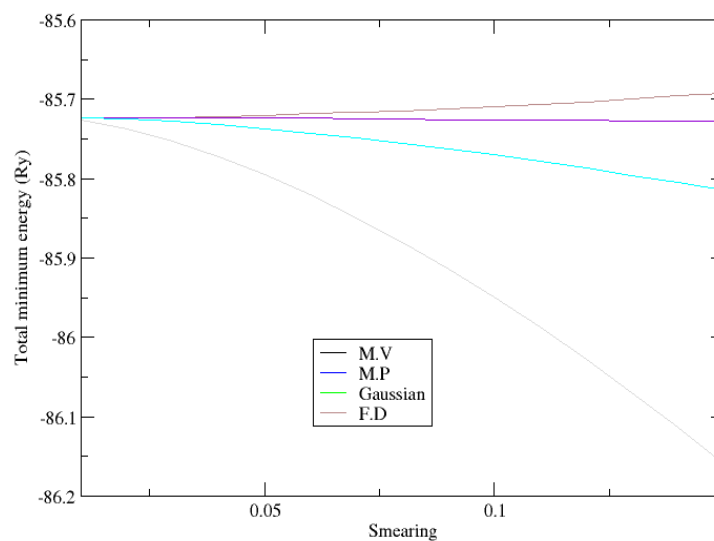


Figure 4.5: the total minimum energy of Ni with respect to smearing for different smearing functions

Chapter 5

Conclusion

The electronic and structural properties of Ni was investigated within the frame work of the DFT , plane wave basis sets , and pseudopotentials (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, Monkhorst pack-grid size, lattice constant and smearing for different occupational function respectively fixing the other parameters constant. The total energy convergence test was achieved, at the energy cutoff 100 Ry and at $10 \times 10 \times 10$ k-point grid size. The total minimum energy is -85.72415624 Ry with respect to energy cutoff and -85.72240765 Ry with respect to k-point grid size. The results show that the total minimum energy per atom is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-point sampling. Our numerical calculation shows that the equilibrium lattice constant is 6.47 Bohr . This result is in good agreement with experimental value. The total magnetization calculation was performed as a function of smearing (Marzari-Vanderbilt). The total magnetization convergence test was achieved, at smearing/degauss=0.11. Furthermore, the negative magnetization observed in low fields has been ascribed to

two oppositely ordered ferromagnetic super exchange interactions. Finally, for Ni metallic systems, the choice of smearing function is also a major consideration to minimizing the electronic energy in a DFT calculation. First Brillouin zone integration in metallic nickel (system) have been performed by smearing techniques, such as the Fermi-Dirac (F-D), Gaussian, Methfessel-Paxton (M-P), and Marzari-Vanderbilt (M-V) cold smearing. The results show that the convergence in cold smearing is very fast than Fermi-Dirac smearing.

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Graduate Program: **Regular, MSc.**

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|-----------------|--------------------------|----------|--------------|------------------|--------|
| Phys 799 | Graduation Thesis | 6 | 78.6 | Very Good | |

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