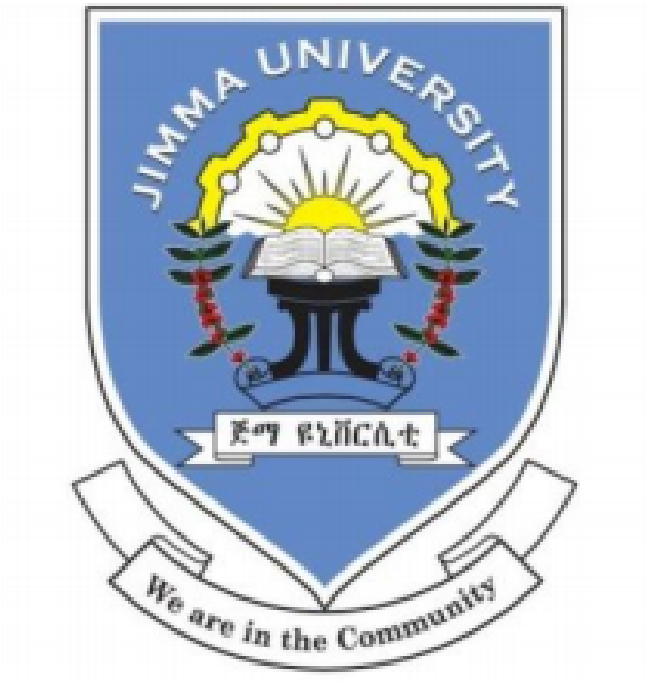

STRUCTURAL AND ELECTRONIC PROPERTIES OF FeO USING DENSITY FUNCTIONAL THEORY(DFT) WITH HUBBARD CORRECTION

A Thesis Submitted to
Jimma University College of Natural science
Department of Physics

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE In PHYSICS(CONDENSED MATTER PHYSICS)

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DEPARTMENT OF PHYSICS

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Table of Contents

List of Figures

List of Tables

ABSTRACT

In this thesis, the first principle calculation based on density functional theory (DFT) with Hubbard correction was employed to investigate the electronic and structural properties of FeO 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 FeO per atom was calculated as a function of cutoff energy and k-points sampling. Secondly, the optimal lattice constants of bulk FeO was calculated for a series possible parameters using the results obtained from energy convergence test (i.e 80 Ry and $10 \times 10 \times 10$ k-points). Moreover the band structure and density of states with Hubbard correction of FeO have been calculated based on the frame work of density functional theory. The results of calculations show that the total minimum energy of FeO 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 was 8.2 Bohr or 4.338 Angstrom. The band structure and the density of states of FeO is determined.

Acknowledgment

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Chapter 1

Introduction

1.1 Back ground of the study

Iron oxides are chemical compounds composed of iron and oxygen. It is the most important transition metal oxides due to its occurrence in different phases[1]. Among these pure phases of iron oxide, FeO, which is known as wüstite. It has its potential applications in magnetic devices such as magnetic tunnel junctions [1].

Being the member of transition metal (TM) monoxides, FeO has strongly correlated electron systems. In the narrow 3d bands of transition metals, interaction between delocalized and localized effects results different electronic structure of FeO [2]. Large number of experimental and theoretical studies has been carried out to investigate properties of transition metal monoxides but only few reports are present about wüstite. Wüstite has been less investigated due to its non-stoichiometric existence at room temperature. Cubic wüstite, (Fe_{1-x} O), can only be synthesized at ambient pressure with variation of x in the range of $0.05 < \mathrm{X} < 0.15$. While, meta-stable wüstite gives mixture of two phases of iron oxide: one is hematite while second is magnetite [2].

To use and apply this transition metal, electronic structural property is the beating heart of scientific discovery rational design in molecular and material science. Control and rational design of materials and molecular properties is obtained through a fundamental understanding of electronic structure across multiple length and time scales[3]. The state of motion of particles cannot be solved analytically for systems in which three or more distinct masses interact. To solve this problem, the density functional theory was appeared in different principles or approaches. After five decades of formulation of density functional theory (DFT) [7], it is still in use as a basic computational tool to investigate various calculations on electronic structures of complex systems. Density functional theory was used due to simplicity and high efficiency with providing possibility to represent ground state energies in terms of electronic charge density

[6]. Various approximations are needed to be used in actual calculations by DFT to give exact expression of the total energy functional. Among these approximations, local density approximation (LDA) and generalized gradient approximations (GGA) are widely used [6]. However, Underestimation of band gap for insulators and semiconductors is the main problem with both these functional. This underestimation is due to the deficiency of self- interaction cancellation and inappropriate description of and correlation exchange in comparison to changes. In case of materials having transition metals, with d shells, this problem exceeds and may give wrong prediction of electronic structure of that material. In order to improve this underestimation of GGA and LDA for materials having transition metal, Hubbard potential can be added. This leads to the GGA+U and LDA+U methods.
The focus of this thesis is, determining electronic and structural properties of FeO with the help of density functional theory with Hubbard correction.

1.2 Statement of the problem

It is clear that many body problems are complicated and difficult to solve. That is, the state of motion cannot be solved analytically for systems in which three or more distinct electrons interact. To solve this many body problems, the density functional theory is preferred as an accurate and reliable tool. However, it usually fails for strongly correlated materials. Hubbard correction to treat strong correlated electronic state. In order to solve strong correlated materials of money body problem by using DFT+U. The basic purpose of DFT is that any property of the interacting systems can be viewed as a functional of the ground state density n_o(r); that is one scalar function of position n_o(r) , in principle determines all the information in the many body wave functions for the ground state. Iron oxides are add pigment to cosmetics and skincare, but they also have the added benefit of protecting the skin from visible and blue light. The electronic structure of FeO was studied by different scholars analytically. However the electronic and structural properties of FeO is not well studied computationally. So the aim of this research is to study electronic and structural properties of FeO and potential based on density functional theory using quantum espresso package for the exchange-correlation energy.

1.3 Research questions

The research questions of this study are;

- What is the total minimum energy of FeO convergence test with respect to cutoff energy?
- what is the total minimum energy of FeO per atom with respect to K-point sampling ?
- How to determine the equilibrium lattice constant of FeO ?
- How to determine the band structure of FeO ?
- How to calculate the total density of states of FeO ?

1.4 Objective of the study

1.4.1 General objective

- The main objective of the study is to investigate the structure and electronic properties of iron monoxide(FeO) using density functional theory with Hubbard correction.

1.4.2 Specific objective

- To carry out total minimum energy of FeO convergence test with respect to cutoff energy.
- To calculate the total minimum energy of FeO per atom with respect to k-points sampling.
- To determine the lattice constant of FeO.
- To determine the band structure of FeO.
- To calculate the total density of states of FeO.

1.5 Significance of the study

Understanding the electronic and structural properties of many electron system (in particular FeO) helps to know about the system in detail. Moreover it helps to develop computational skills for solving many body problems.

1.6 Scope of the study

The scope of this study is the calculations of electronic and structural properties of FeO. However FeO has rocksalt structures. The total minimum energy and the equilibrium lattice constants of FeO were calculated with respect to cut-off energy and k-point samplings, while the band gap and density of states of FeO were calculated based on density functional theory (DFT) with Hubbard correction.

1.7 Limitation of the study

The research study was not free from limitation. There were some issues which has hindered the attainment of the study objectives stated under the objectives of the study. Some limitations that the writer were face are:

- Shortage of time
- Lack of internet access
- Shortage of recreance material

Chapter 2

Literature Review

2.1 Introduction

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

2.2 Structural and Electronic Properties Calculations

Interaction of electrons with atomic cores affects both the physical and chemical properties of a system. The treatment of electron-electron interactions is the major source of difficulty in the interpretation of these properties since the interactions are inseparable or treated without approximation. Schrödinger equations well solved for a specific system can be differentiated from one to other forms of modeling approaches since they are majorly ab-initio in nature. The solution of Schrödinger equations remains a difficult task. Exact solutions of the equation, in general, can only be solved if time is scaling exponentially with system size. This scaling precludes exact calculations for all but the smallest and simplest of systems e.g., the hydrogen atom. The degree of accuracy and the predictive power can be lost by the introduction of approximations which may be used to reduce the equations to a form that can be solved.
The density functional theory (DFT) and computer simulation methods involved in various solving of the Schrödinger equations have become more successful in calculations involving electronic structure properties and other material properties applicable to several systems.

2.3 Electronic structure of the problem

The foundation of the theory of electronic structure of matter is the non relativistic Shrödinger equation for the multi-electron wave function ψ. So our major goal in this electronic and structural calculation of Iron Oxide.

2.3.1 Born Oppenhimer approximation

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

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

So we can consider the electrons as moving in the field of fixed nuclei. This first step of the BO approximation is therefore often refereed to as the clamped nuclei approximation. The nuclear kinetic energy is zero and their potential is marly a constant.

2.4 Electronic structure of FeO

FeO is a very interesting compound for geophysics as it has Earth's lower mantle and outer core. The phase transitions undergo at high pressure over a wide range of temperatures. It was found that an important transition from the cubic rock salt structure to a rhombohedrally distorted phase occurs at room temperature at about 16 GPa in correspondence to the onset of the AFM order from the paramagnetic (PM) state. In fact the Neél temperature, which is 198 K at ambient pressure condition is found to increase with pressure and reaches the room value at about 16 GPa. Another structural phase transition is found to occur at 70 GPa when this compound transforms from B1 (cubic or rhombohedrally distorted) to B2 (hexagonal) phase while becoming metallic [6].

A stable, cation-deficient phase written as Fe_{1x} O (with 1-x ranging from 0.83 to 0.95) exists at 0.1 MPa pressure and temperatures greater than 567^0C. This phased is proportionates to Fe metal and Fe_3O_4 when cooled slowly to temperatures lower than 567^0C. At this temperature, the equilibrium curves of $Fe/Fe_{1+x}O$ and $Fe_{1+x}O/Fe_3O_4$ intersect. If, however, $Fe_{1+x}O$ is rapidly quenched from the equilibrium region, the non-stoichiometric form can be obtained as

a meta stable phase at room temperature.

2.5 The structural properties of FeO

Wüstite ($Fe_{1-x}O$) takes the cubic rock salt structure, with Fe^{2+} cations in octahedral sites. In the different direction, the material is made up of alternating planes of fcc O anions and metal cations. In practice, this compound is always defective, with (1-x)-values ranging from 0.83 to 0.95. The defects are known to be Fe^{3+} cations on tetrahedral sites linked to four Fe_{oct} vacancies (so-called Koch-Cohen defects), which further agglomerate into clusters of four interstitial s linked to 13 Fe_{oct} vacancies. Exactly how the clusters join together is still debated. It is interesting to note that a similar motif underlies the SCV reconstruction at the Fe_3O_4 surface. The most common occurrences of this compound are in the Earth's lower mantle, but it also forms as an intermediate in the reduction of Fe_3O_4 and Fe_2O_3 to Fe. Fe_{1-x}O can be stable above 840 K in reducing conditions, but dis proportionate into Fe and Fe_3O_4 if cooled slowly below 840 K. If the material is quenched rapidly from 840 K, Fe_{1-x}O can exist as a meta stable phase. There is an ongoing debate if FeO forms in the non-equilibrium low-temperature reduction of iron oxides. Fe_{1-x}O exhibits anti ferromagnetism below the Néel temperature of 200 K, with the Fe^{2+} magnetic moments aligned parallel to the close packed planes, but in opposite directions from one plane to the next.

2.6 Application of iron oxide

Some of the applications of FeO are mentioned as follows.

- **Iron Steel Feed stock** Ferric iron is the main source of iron for the entire steel industry. Steel itself is an alloy made of iron, carbon, and several other elements, but iron is the base metal and makes up over 95 of the atomic structure of steel. As construction and building continue to rebound, use of iron oxides to manufacture structural components for use within the industries is expected to grow significantly.

- **Pigment Production** Because of its striking red color, iron (III) oxide is considered a valuable pigment for use in a wide variety of manufacturing processes. Some iron oxide pigments have been approved by the FDA for use within cosmetics manufacturing; other pigments are primarily used within the construction industry for coatings, paints, and other industrial finishes. Transparent iron oxide pigments are also sold commercially as staining products, such as wood stain for decking.

- **Magnetic Tape Manufacturing** Magnetic tape energizes an electromagnet to affect a recording medium.In practice, the magnetic medium readily "picks up" the polarity transferred onto it but does not easily lose that polarity after the fact. These tapes have applications in video recording, data recording, and particularly within auto recording, as well as on the back of credit cards.Iron (III) oxide is the most common magnetic particle used for making magnetic storage tape; it was once the most commonly used medium for computer data storage but has been overtaken by cobalt alloys and other thinner, higher-storage solutions.

2.7 Density Functional Theory (DFT)

Density functional theory (DFT) is a computational quantum mechanical modeling method which is widely applied in all areas of Physics and chemistry, wherever properties of systems need to be calculated [10,11,12],. Using this theory, a many electron system can be determined by using functional i.e functions of another function, which in this case is the spatially dependent electron density. It provides a framework to obtain the total energy, total minimum energy, cut-off energy, k-points, crystal structural properties and etc. The DFT has its roots in Thomas-Fermi model for the electron structure of materials. It was first put on a firm theoretical footing by Walter-Kohn Pierre Hohenberg in the framework of the Hohenberg- Kohn theorems (H-K) which states that (i) all ground –state properties of a system, including the total energy are some functional of the ground-state charge density and (ii) the correct ground state charge density minimizes the energy functional i.e,

$$E[n] = T[n] + U[n] + \int V(r)n(r\delta 3r) \tag{2.1}$$

where n is the charge density, T is the kinetic energy, V is the potential energy from the external field (typically due to positively charged nuclei of crystal),U is the electron-electron interaction energy and r is the position. The formulation is applied to any system of interacting particles in an external potential V ext(r). As mentioned above, DFT follows different approaches to attain its central target. Some of theories or approaches were encountered with some drawbacks. One of these is the Thomas-Fermi theory, which is the poor approximation of kinetic energy functional.DFT in principle, is an ab-initio method that it does not use any experimental results on chemical bonding. It works with the electrondensity only. There are significant advantages to a computational theory based on electron densities. The first is in relation to efficiency; the electron density depends on the three spatial variables in contrast to the 4N variables that wave functions depends on (three spatial and one spin per electron).therefore large system can be theoretically modeled .In addition, electron correlation is conceptually easier to include in DFT.

It has achieved a certain status as a standard first method. This the first principle calculations have gained great success in studying the equilibrium properties of matter, though there are still many challenges to DFT [13]. One of the big issues is how to solve the problems when encountering with electronic degeneracy. Such an issue usually does not pose a problem to the equilibrium conditions. It is well known that electronic degeneracy cannot exist in the ground state of a nonlinear atomic geometry. In DFT we only need to find the charge distribution throughout our system. We can describe only single electron 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 [13, 14]. The major problem in DFT is that the exact functional for exchange and correlation are not known, except for the free electron gas. However approximations exist which permit the calculation of certain physical quantities quite accurately. In physics the most widely used approximation is the local density approximation (LDA), where the functional depends only on the density at coordinate where the functional is evaluated [15, 16, 17].However in this work the generalized gradient approximation (GGA) was used because of its better approximate nature.

2.8 Many electron system

The ultimate goal of most approaches in solid state physics, quantum chemistry and in this electronic structural calculation of FeO is the solution of the time independent, non relativistic Schrödinger equation [18,19]. The electronic Schrödinger equation of a system of N electrons reads,

$H\psi(r_1, ...r_N) = E\psi(r_1, ...r_n)$

Where H is Hamiltonian of the system, E is energy, $r_N$is coordinate of the electron with index N and $\psi(r_1, ..., r_N)$ is the many particles wave function.

$$H = T_e + V_{ne} + V_{ee} + T_n + V_{nn} \tag{2.2}$$

$$T_e = \sum^{N} -\frac{1}{2}\nabla_i^2 \tag{2.3}$$

$$V_{ne} = \sum_{a}^{N}\sum_{1}^{Ne} \frac{za}{[Ra - ri]}\nabla_i \tag{2.4}$$

$$V_{ee} = \sum_{i}^{Ne}\sum_{j>1}^{Ne} \frac{1}{|r_i - r_j|} \tag{2.5}$$

$$T_n = \sum_{a}^{N} -\frac{1}{2}\nabla_i^2 \tag{2.6}$$

$$V_{nn} = \sum_{a}^{N} \sum_{b>a}^{Ne} \frac{ZaZb}{|Ra - Rb|} \tag{2.7}$$

The first to terms represent the kinetic energy of the electrons and nucleons, $T_e$and T_n. The third term represents the electrostatic repulsion between the electrons,V_{ee}. The fourth term represents the electrostatic attraction between the electrons and nuclei, V_{ne} , and the last term between the nuclei,V_{nn} . m_e is the mass of the electrons, and M_I the mass of the cores. Z_I is the number of protons in each core.

2.9 The Thomas Fermi theory

The Thomas Fermi theory is the simple example of a DFT. It emerges when we ignore the exchange energy and make the simplest possible approximation for the kinetic energy [20]. For a solely varying density function the kinetic energy density will only depend on the number of density at the same position. Taking the specific function from the Fermi gas, we arrive at the kinetic energy functional.

$$T[n(r)] = \int \frac{3}{10}\frac{(3\pi^2)^{2/3}}{M} n(r)^{5/3} d^3r \tag{2.8}$$

And the sum of the K,E and potential energy terms will give us the total energy within the Thomas Fermi approximations

$$E[n(r)] = \int \frac{3}{10}\frac{(3\pi^2)^{2/3}}{M} n(r)^{5/3} d^3r + \frac{e^2}{2}\int \frac{n(r)n(r')}{|r - r'|} d^3r' d^3 + \int n(r) V_N(r) d^3r \tag{2.9}$$

Where the first term is kinetic energy of the electrons, the second term is the potential energy of the electrons due to their mutual electric repulsion and the third term is the potential energy of an atom ' s electrons, due to the electric attraction of positively charged nucleus. Note that the expression only depends on density n(r). Unfortunately, this theory has limited validity due to its poor approximation of kinetic energy functional.

2.10 Hartree-Fock method

In this section we will introduce the Hartree-Fock (HF) approximation. The HF ap- proximation is the corner stone of almost all conventional, i.e., wave function based Quantum mechanical methods, it is also of great conceptual importance. An under- standing of the physics behind this approximation will thus be of great help in our later analysis of density functional theory. In the Hartree-Fock scheme the simplest, yet physically sound approximation to the complicated

many-electron wave function is utilized. In its general formulation the approximation consists of approximating the N-electron wave function by an antisymmetrized product of N one-electron wave functions $\psi_i(x_i)$ [23]. This product is usually referred to as a Slater determinant.
To discus the property of an interacting system, such as electrons in a molecule or solid, it is natural to consider the many-electron wave function,$\psi(r_1, r_2, ...r_N)$, where the r i denotes the particle coordinates and spins. In 1928 Hartree made the most widely used of all approximations forψ. In his contribution, Hartree approx- imated the many-electron wave function as a product of single-particle functions termed as Hartree product [24], i.e.

$$\Psi(r_1, r_2, ...r_N) = \psi_1(r_1 1)...\psi_N(r_N). \tag{2.10}$$

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

$$[\frac{-\hbar^2}{2m}\nabla^2 + V_{ext} + \Phi]\psi_i(r) = \epsilon_i\psi_i(r) \tag{2.11}$$

Where the Coulomb potential Φ_i because of all the other N-1 electrons, is given by Poisson's equation,

$$\nabla^2\Phi_i = 4\pi e^2 \sum_{j=1, i\neq j}^{N} |\psi_j|^2 \tag{2.12}$$

And V_{ext} is the potential due to the nuclei. After expressing the electronic wave function as a single Slater determinant, the HF procedure will solve for those orbital which minimize the electronic energy based on variational method.
Generally this HF (self consistent field calculation) approximation, assumes that each electron interacts only with the average charge cloud (charge density) of the other electrons.[21]

$$\delta\langle\Psi^{(N)}|H|\Psi^{(N)}\rangle = 0 \tag{2.13}$$

2.11 Hohenberg-Kohn theorem

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 ground state density. The H-K theorem implies that the ground- state for any system can be determined by varying the charge density until the global minimum in the energy functional is found.

2.11.1 The First theorem of Hohenberg-Kohn

The ground state energy of many body system is a unique functional of the particle density. In principle all properties of the ground state can be expressed as functional of the ground state

spin density matrix ρ_0. Therefore, the ground state wave function ψ (which can be determined by the density function theory) minimizing the energy functional [22].

$$E[\Psi] = \langle \Psi | H | \Psi \rangle \tag{2.14}$$

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

$$\langle \hat{O} \rangle [\rho_o] = \langle \psi_o[\rho_o] o | \psi[\rho_o] \rangle \tag{2.15}$$

Where Ô is an arbitrary operator.This is in particular true for the ground state energy E[ρ_o] or the expectation value of the kinetic energy $T[\rho_o]$ or for the interaction energy of the electrons $U[\rho_o]$.

2.11.2 Second theorem of Hohenberg- kohn

A universal functional for the energy E[n] in terms of the density n(r) can be defined, valid for any external potential V_{ext} (r). for any particular V_{ext} (r), the exact ground state energy of the system is the global minimum value of this functional, and the density that minimize the functional is the exact ground state density n_o (r) [22].
The total energy can be written as,

$$E[n] = T[n] + V_{Ne}[n] + V_{ee}[n] = F_{HK}[n] + V_{Ne}[n] \tag{2.16}$$

Where ; $F_{HK}[n] = T[n] + V_{ee}$[n] which is universal functional.

2.12 The kohn-sham approach

Density functional theory is based on two pivotal theorems due to Hohenberg and Khon [22]. So practical implementation of DFT require an explicit construction of the HK free energy functional, F_{HK} [ρ] [22]. As discussed in the HK theorem above, and from the Schrödinger equation, we see that the energy functional contain three terms. The kinetic energy, the interaction with the external potential, and the electron-electron interaction. The challenge of DFT lies in the HK universal functional of the density $F_{HK}[\rho]$. Which is expressed as a sum of kinetic and electron-electron functional are unknown. The possibility of finding a good approximation to these functional is the subject of much of current research to day. Since it makes the minimization of the energy would be possible.
Kohn and Sham proposed the following approach to approximating the kinetic and electron-electron functionals. The approach does not exclusively work in terms of the particle or charge density, but brings a special kind of wave functions (single-particle orbital) back in to the game.

Generally mapping of an interacting many electron system ($V_{ee} \neq 0$) in to a system with independent particles moving into an effective potential (non-interacting system,$V_{ee} = 0$) is made. As a consequence DFT then looks like an effective single-particle theory, although many-body effects are still-included via the so called exchange-correlation functional [16]. We will now see how this is done.

2.13 The Khon-Sham equation

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

If F $[\rho]$ where a known and sufficiently simple functional of ρ, the problem of determining the GS energy and density in a given external potential would be rather easy. Since it requires merely the minimization of a functional of the three dimensional density function. The major part of the complexities of the many electron problems are associated with the determination of the universal functional F $[\rho]$.

The KS exact energy functional is written as,

$$E[\rho] = T_s[\rho] + V_{ext}[\rho] + V_H[\rho] + E_{xc}[\rho] \tag{2.17}$$

In this equation,

$$T_s[\rho] = -\frac{1}{2}\sum^{N}\langle\phi_i|\nabla^2|\phi_i\rangle = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\int d^3r\phi^*(r)\nabla^2\phi_i(r) \tag{2.18}$$

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

$$\rho(r) = \sum_{i=1}^{N}|\phi_i|^2 \tag{2.19}$$

The functional,

$$V_{ext}[\rho] = \int \rho(r)V(r)dr \tag{2.20}$$

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

$$V_H[\rho] = \frac{1}{2}\int \frac{\rho(r_1)\rho(r_2)}{|r_1 - r_2}dr_1dr_2 \tag{2.21}$$

is the electron-electron interaction considered as a classical coulomb interaction or Hartree energy. The last term, $E_{xc}[\rho]$, incorporates everything else and is called the exchange correlation energy. It is the only term that is unknown. In a way, the KS method packs all the complexity of the total energy function in the exchange- correlation functional.
Writing the energy functional explicitly in terms of density built from non-interacting orbital's, and applying the variational theorem, we find that the orbital's which minimize the energy satisfy the following set of equations,

$$[\frac{-1}{2}\nabla^2 + V_{ext}(r) + \int \frac{\rho(r')}{|r-r'|}dr' + V_{xc}(r)]\phi_i(r) = \varepsilon_i\phi_i(r) \tag{2.22}$$

where,

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho]}{\delta\rho} \tag{2.23}$$

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

2.14 The exchange-correlation energy

The exchange-correlation energy E_{xc} of a many electron system is the key quantity of DFT.In the context of Kohn-Sham theory, E_{xc} is defined as a functional of the electron density ρ. In Kohn- Sham expression the total electronic energy $E[\rho]$ is given by;

$$E[\rho] = T_s[\rho] + V[\rho] + W_H[\rho] + E_{xc} \tag{2.24}$$

Where T_s - is the kinetic energy of a non-interacting particle system with densityρ, V is the energy of electron-nuclear attraction, W_H is the coulomb or Hartree energy and E_{xc} is the exchange-correlation energy.

$$E_{xc}[\rho] = E_x[\rho] + E_c[\rho] \tag{2.25}$$

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

2.14.1 The Local Density Approximation (LDA)

The first family of exchange correlation functional is the LDA functional [22]. The idea of this functional is the first look at the case of a homogeneous electron gas. In such a system, one considers the electron moving in uniform external potential. In DFT, the electron density

rather than the wave function is the basic variable.

$$E_{xc}^{LDA}[n] = \int n(r)E_{xc}[n(r)]dr \tag{2.26}$$

In LDA, there is no known formula to calculate the total energy of many electrons moving in an external potential using the density. Hohnberg and Kohn proved that there exist a universal functional of the density called, G $[\rho]$ such that:

$$E[\rho_r] = \int V(r)\rho d^3r + \frac{1}{2}\int \frac{\rho_r\rho_{r'}}{|r-r'|}d^3rd^3r' + G[\rho] \tag{2.27}$$

Where the first term on the right hand side is the energy due to external potential while the second term is the classical coulomb energy of the electron system. The main deficiency of the LDA was the strong over binding with bond energies in error by about 1ev. On the one hand this renders LDA useless for most applications in condensed matter physics. On other hand, the problem was hardly visible in solid state physics where bonds are rarely broken, rearranged so that the errors canceled.

2.14.2 The generalized gradient approximation (GGA)

This functional (GGA) depends on the local electron density as the spatial variation of the electron density that is represented by density gradient. The idea behind this functional was to improve the approximation of LDA by considering not only the electron density, but also the local gradient of that density [23,24].

The GGA functional can be written as;

$$E_{xc}^{GGA}[n] = \int n(r)E_{xc}[n(r)\nabla_a]dr \tag{2.28}$$

The $E_{xc}^{GGA}[n]$ is the exchange correlation energy per particle of an electron gas. The GGA gives better total energies. When a bond between two atoms is broken, the surface is increased. In GGA, this bond-breaking process is more favorable than in LDA and hence bond is weakened. Thus the GGA cures the over binding error of the LDA. These gradient corrections greatly improved the bond energies and made density functional theory useful also for chemists. The most widely distributed GGA functional is the Perdew Burke-Ernzerhof (PBE) functional [25].

2.14.3 Meta-GGA (mGGA)

The next step in the development of gradient approximations is to incorporate the kinetic energy density or/and the Laplacian of the density. Such functionals are generally referred to as meta-GGA functionals.

The form of the functional is typically:

$$E_{xc}^{mGGA} = \int n(r)\varepsilon_{xc}(n, |\nabla|, \nabla^2, \tau)dr \tag{2.29}$$

where the kinetic energy density τ is;

$$\tau = \frac{1}{2}\sum|\nabla\phi_i|^2 \tag{2.30}$$

Still higher accuracy (of course, at a higher cost) can be obtained by using the so-called hybrid schemes.

2.14.4 Hybrid Schemes

These fourth generation functionals add "exact exchange" calculated from the HF- like functional to some conventional treatment of DFT exchange and correlation:

$$E_{xc}^{hbrid} = \alpha E_x^{HF} + E_c \tag{2.31}$$

where α can be chosen to satisfy particular criteria. The functional which is widely used in the quantum community, is an example. Here three adjustable parameters (a_{1-3}) are used to fit calculated values to a molecular data base.
As mentioned earlier, the functionals currently used in density functional simulations form a natural hierarchy. Although, it cannot be claimed that there is a systematic approach to the exact functional, it is clear that improvements are being made in the underlying functional form and that the description of ground state properties is improving. The most notable recent advances being those in which the non-local nature of the exchange potential is introduced in one form or another. The current hierarchy with expected accuracy decreasing as we go down the table. This hierarchical classification is what is often referred to as the Jacob's ladder.

2.15 Plane wave basis sets and Pseudo potentials

2.15.1 Plane wave basis set

In calculations of solid states or condensed matter, the DFT will be applied with plane wave basis sets [26]. When dealing with a crystal which has atoms periodically arranged, the electrons are in a periodic potential U(r),where u(r+R)=u(r) and R is the Bravais lattice. As the Bloch theorem states below that, a discrete plane- wave basis sets are used to expand the electronic wave function at each K-points. In principle, an infinite plane wave basis sets is required to expand the electronic wave function. However, the coefficients $C_i|K+G|^2$ plane waves with small kinetic energy,$\frac{h}{2m}|K+G|^2$are typically more important than those with large kinetic energy. Thus, plane-wave basis sets can be truncated to include only plane wave that have kinetic energy less than some particular cut-off energy.

2.15.2 The pseudo-potential

Pseudo potentials have been introduced to avoid describing the core elements explicitly and to avoid the rapid oscillation of the wave function near the nucleus, which normally require either complicated or large base sets. Due to this, the fundamental idea of pseudo- potential is the replacement of one problem with another. Its primary application in electronic structure is to replace the strong coulomb potential of the nucleus and the effects of tightly bound core electrons by an effective ionic potential acting on the valence electron [28] . The pseudo potential approximation is motivated by the fact that the behavior of valence electrons in the bonding region primarily determines the electronic structure and the structural properties of many materials. In a pseudo-potential formulation, the effect of the core electrons and that of nuclear potential are combined to form an effective ionic pseudo-potential. The pseudo-potentials are commonly constructed, so that outside of a core region the valence pseudo wave functions match the corresponding states derived from all electron calculation, inside the region they are smooth functional. This formulation makes pseudo-potential calculations quite efficient, since the core orbital do not need to be recomputed. The relaxation correction takes in to account the relaxation of the electron system up on the excitation of an electron.

The orthogonalized plane waves (OPW) $\phi_n$is defined by $\phi_k = e^{ik.r}\sum_c b_c\psi_k^c(r)$ where $\psi_k(r)$is the core wave function the sum is over all core levels with Bloch wave vector k , and we require that ψ_k are orthogonal to every core level.

$\int dr\psi_k^c(r)\phi_k(r)$=0

The starting point for pseudo potential calculations and analysis is the application of nearly free electron (NFE) theory to find the valence levels Φ_{kv}. The pseudo potential is the sum of the actual periodic potential and VR

$Where; V^R = \sum_c(E_k^v - E)(dr\psi_k^c)\psi_k^c$

$$H + V^R = \frac{-\hbar^2}{2m} + U + V^R \tag{2.32}$$

where; $U + V^R = V^{spendo}$

U- is negative near ion cores while V^R - is always positive.

Moreover pseudo potentials have been introduced to avoid the rapid oscillations of the wave function near the nucleus, which normally require either complicated or large basis sets and to avoid describing the core electrons explicitly. Hamann, Schluter and Chiang showed in 1979 how pseudo potentials can be constructed in such a way that their scattering properties are identical to that of an atom to first order in energy. These first principles pseudo potentials relieved the calculation from the restrictions of empirical parameters. Highly accurate calculations have become possible especially for semiconductors and simple metals. An approach by Zunger and Cohen towards first principles pseudo potentials precedes other approaches.[27]

2.16 Periodic super cells

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

2.16.1 Bloch theorem

A Bloch function is the generalization of a plane wave for an electron in periodic potential.Bloch-theorem states that in a periodic solid each electronic wave function can be written as the product of cell periodic and wave like part.

$$\psi_k(r) = e^{iG.r} UK(r) \tag{2.33}$$

Where $U_k(r)$ is the periodic potential in space with the same periodicity as the supper cell. That is

$$U_k(r + n_1a_1 + n_2a_2 + n_3a_3) = U_k(r) \tag{2.34}$$

for any integers n_1, n_2, n_3 This theorem is 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,

$$U_k(r) = \sum_G C_i, Ge^{iG\cdot r} \tag{2.35}$$

where C_i ,G are expansion coefficients, the reciprocal lattice vectors G are defined by;

$$G + \vec{a} = 2\pi n \tag{2.36}$$

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,

$$\Psi_k(r) = \sum_G C_{i,k} + Ge^{i(k+G)} \cdot r \tag{2.37}$$

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 or limited. The number of plane waves can be restricted by placing an upper boundary to the kinetic energy of the plane waves. This boundary is called energy cut-off (E_{cut})

2.16.2 Cut-offs energy

Energy cut-offs limit the number of plane wave components. The minimum length scale depends on the elements in the system. 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

$$\psi_k(r) = e^{ik\cdot r}U_k(r) \tag{2.38}$$

where $UK(r)$s periodic in space with the same periodicity as the supper 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.

$$U_k(r)\sum C_{iG}e^{[}i(K+G)\cdot r] \tag{2.39}$$

Where the summation is over all vectors defined by;

$$G = n_1b_1 + n_2b_2 + n_3b_3 \tag{2.40}$$

With integer values n_i. The set of vectors defined by G in reciprocal space are defined. So that for any real space lattice vector, combining the two equations above give

$$\psi_k(r) = \sum_G C^{iK\cdot Ge}(iK+G) \tag{2.41}$$

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. hey are solutions with kinetic energy.

$$E = \frac{\hbar^2}{2m}|K+G|^2 \tag{2.42}$$

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 the infinite sum above to include only solutions with kinetic energies less than some value;
The infinite sum then reduces to

$$\psi_k(r)\sum_{G+K} CG + Ke^{i(K+G)r} \tag{2.43}$$

This expression includes slightly different numbers of terms for different values of k the discussion above has introduced one more printer that must be defined whenever a DFT calculation is performed the cutoff energy (E_{cut}).

2.16.3 K-points sampling

The solution that is used most widely was developed by monk-horst pack in 1976. 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-points can be significantly reduced by using the k-point total energy method [29,30].

2.16.4 Hubbard model

The Hubbard model is a useful approximation for particles in a periodic potential at sufficiently low temperatures, where all the particles may be assumed to be in the lowest Bloch band, and long-range interactions between the particles can be ignored. Hubbard's focused on electron correlations in narrow energy bands of transition metals. If interactions between particles at different sites of the lattice are included, the model is often referred to as the "extended Hubbard model". In particular, the Hubbard term, most commonly denoted by U, is applied in first principles based simulations using Density Functional Theory, DFT. The inclusion of the Hubbard term in DFT simulations is important as this improves the prediction of electron localization.[32]

The Hubbard model introduces short-range interactions between electrons to the tight-binding model, which only includes kinetic energy (a "hopping" term) and interactions with the atoms of the lattice (an "atomic" potential). When the interaction between electrons is strong, the behavior of the Hubbard model can be qualitatively different from a tight-binding model. For example, the Hubbard model correctly predicts the existence of Mott insulators: materials that are insulating due to the strong repulsion between electrons, even though they satisfy the usual criteria for conductors, such as having an odd number of electrons per unit cell.

The Hubbard model is based on the tight-binding approximation from solid-state physics, which describes particles moving in a periodic potential, sometimes referred to as a lattice.

Hubbard correction is a computational tool that can be applied widely not only to crystals but also to the strongly correlated metals attached to other non correlated systems.

2.17 Practical implementations of the Hubbard correction

DFT+U is applicable for all open shell orbitals, such as d and f orbitals for transition metal elements with localized orbitals existing in extended states, as in the case of many strongly correlated materials and perovskites, where localized 3d or 4f orbitals are embedded in elongated s-p states. A complicated many-electron problem is made of electrons living in these localized orbitals, where they experience strong correlations among each other and with a subtle coupling with the extended states. Isolating a few degrees of freedom relevant to the correlation is the idea in the Hubbard model, where screened or re normalized Coulomb interaction (U) is kept among the localized orbitals' electrons [33]. In other word, the localized orbitals in the band gap, which are present as localized states (d- and f-states), are too close to the Fermi energy. From that aspect, the U value should be used to push theses states away from the Fermi level, such as that provided by the GGA+U theory, which adds to the Hamiltonian a term that increases the total energy preventing the unwanted de localization of the d- or f-electrons, when two d- or f-electrons are located on the same cation [34]. It is worth mentioning that using too large values of U will over-localize the states and lead to an un physical flattening of the appropriate bands, which unlike fitting to many other properties, will make the it worse. Also, the increase in the U value can cause an overestimation of the lattice constants as well as a wrong estimation of the ground state energy due to the electronic interaction error. Therefore, applying Hubbard correction to solve the band gap problem is necessary for predicting the properties of transition metal oxides.

Chapter 3

3.1 Methodology

The DFT calculations were performed with the generalized gradient approximations with Hubbard correction(GGA+U) exchange correlation functional, Vanderbilt ultra soft pseudo potential and the plane wave basis sets were implemented in the Quantum ESPRESSO program package. This Quantum ESPRESSO program package is an integrated module of computer codes for electronic and structural calculations and materials modeling depending on the frame work of DFT, plane wave basis sets (PW) and pseudo potentials to represent the electron-ion interaction.

The practical usefulness of ground-state DFT depends entirely on using the exchange correlation energy functional s, that includes all many body principle effects, which are at the same time sufficiently simple and accurate. Considering a right exchange correlation energy functional is used, we can calculate the exact exchange correlation potential. The next step would be solving the single particle Schrödinger equation defined by Kohn-Sham equations. All the solution must be determines in a self-consistent method. Self-consistency means that, if we insert the solutions φ_i , in electron density equation, the calculated density is used to determine the corresponding total potential in equation and solve the Schrödinger equation, then we find the same function φ_i from which we started.

To solve the Kohn-Sham equations, we first specify the nuclear coordinates in order to obtain the nuclear potential $V_n(r)$. Now an assumed value for electron density is used to determine approximate Hartree and exchange and correlation potentials. By solving the khon-sham equations we obtain the new wave function, which can be used to construct a better estimate of density and the total potential.This interaction continues the new density matches the old density with in an acceptable tolerance.Once, we calculate the electron density in ground state n(r),it is possible to calculate the total energy of the system,as it is functional ground state electron density(equation (2.21)). Self-consistent method is illustrated in figure 3.1, it illustrate clear computational procedure for calculation.

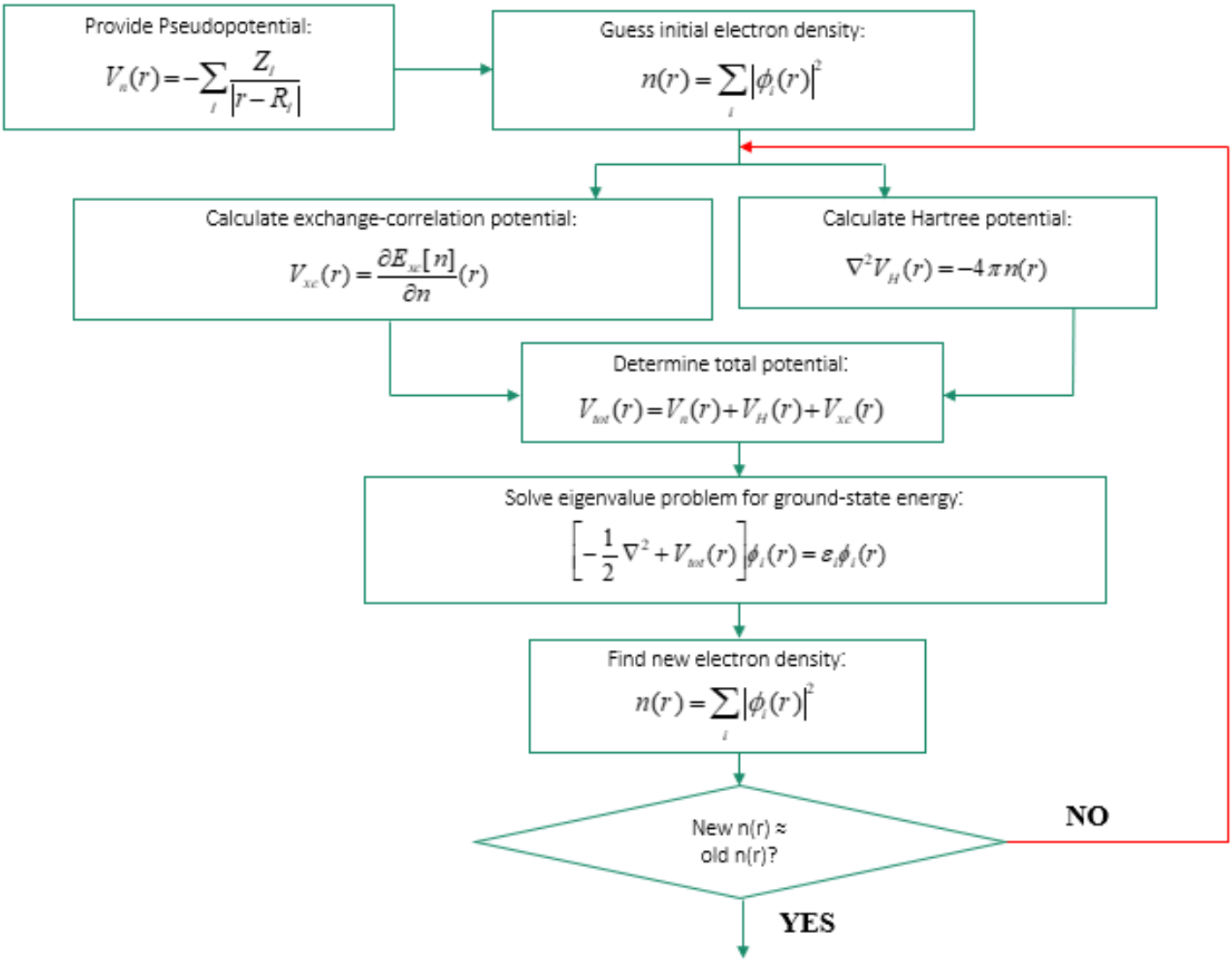

Figure 3.1: Diagram for finding the self -consistent solutions for Kohn-Sham equations

Chapter 4

Results and Discussion

Introduction

In this thesis first principle calculation was employed to calculate the electronic and structural properties of FeO using Quantum espresso package. The plane wave self-consistent field (PWscf) code is implemented as our first principle energy code which uses ultra-soft pseudo potentials (US-PP) within density functional theory. The main features of pseudoscience process is to eliminate the effects of rapid oscillations of the core electrons near the nuclei or to replace the strong coulomb potential with the weaker one. Thus the ultra-soft pseudo potentials with the generalized gradient approximation with Hubbard Correction (GGA+U) exchange correlation functional were employed to calculate the electronic and structural properties of FeO. The convergence issue was checked in two ways. Firstly by varying cutoff energy from 30 Ry to 150 Ry for fixed Monk-Pack mesh grid (K-points) and lattice constants. Secondly, by varying K-point samplings (2 to 16) keeping cutoff energy and lattice parameters constant. The equilibrium lattice constant was calculated by fixing cutoff energy at 80 Ry and K-point at $10 \times 10 \times 10$. Finally the band structure and density of states of FeO have been investigated based on DFT with Hubbard correction.

4.1 Total minimum energy of FeO with respect to energy cutoff

In this part of the calculation the total energy of Iron Oxide is performed as a function of cutoff energy.The total minimum energy of FeO with respect to cutoff energy was calculated for fixed values of K-Points and lattice constant. In this research we have considered the cubic structure of FeO for total energy calculation,the k-points are $2 \times 2 \times 2$.The calculation was done using different energy cutoff values from 30 Ry to 150 Ry.

Energy cutoffs(Ry)	Total energy(Ry)
30	-735.06706739
40	-735.60403255
50	-735.72120192
60	-735.70198281
70	-735.73607420
80	-735.74164169
90	-735.74332946
100	-735.74351091
110	-735.74383398
120	-735.74435499
130	-735.74472118
140	-735.74486324
150	-735.74490567

Table 4.1: The computed results of total minimum energy with respect to energy cutoff

4.1.1 Convergence test of total minimum energy of FeO per atom with respect to cutoff energy

The convergence test of the total minimum energy of FeO 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 converged at 80 Ry plane wave cutoff energy and the total ground state energy had its minimum at -735.74332946. The calculated results show that 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. We can realize that when the number of basis functions approaches infinity, energy is close to the ground state energy.

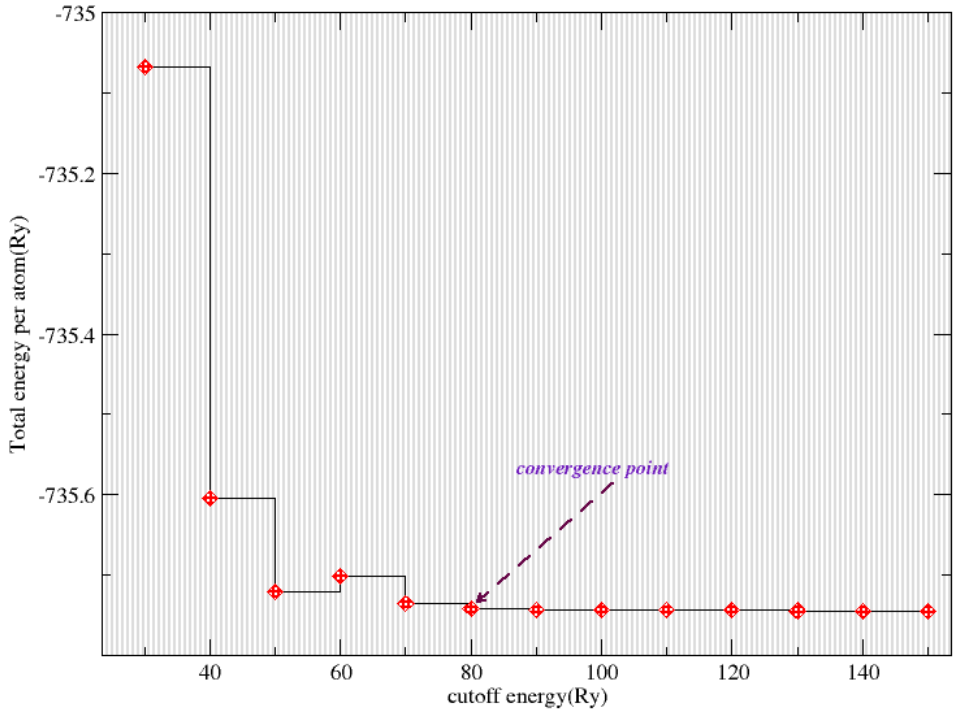

Figure 4.1: Total minimum energy of FeO per atom with respect to energy cutoff

4.2 Total minimum energy of FeO with respect to K-point grids

In this case, the calculation was done using different k- point grids from 2 × 2 × 2 to 16 × 16 × 16 mesh grids. Here the other variables such as lattice constant and energy cutoff were kept fixed. The result is described in Table 4.2.

k-points grid	Total energy(Ry)
2x2x2	-734.98480020
4x4x4	-735.06504508
6x6x6	-735.06706739
8x8x8	-735.06714893
10x10x10	-735.06845862
12x12x12	-735.06861815
16x16x16	-735.06845258

Table 4.2: The results of the total minimum energy of FeO per atom with respect to K-points sampling

4.2.1 Convergence test of total minimum energy of FeO per atom with respect to K-points sampling

A convergence test of total energy for k-point sampling was performed on FeO. The total energy of FeO atom was calculated using various sets of k-points ranging from 2×2×2 to 16×16×16. In each of these cases the plane wave kinetic energy cutoff of 30 Ry was used. The total minimum energy of FeO 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 × 10 × 10 Monkhorst-Pack mesh grid. The total ground state energy has its minimum at -735.06845862 Ry as given in Fig.4.2.

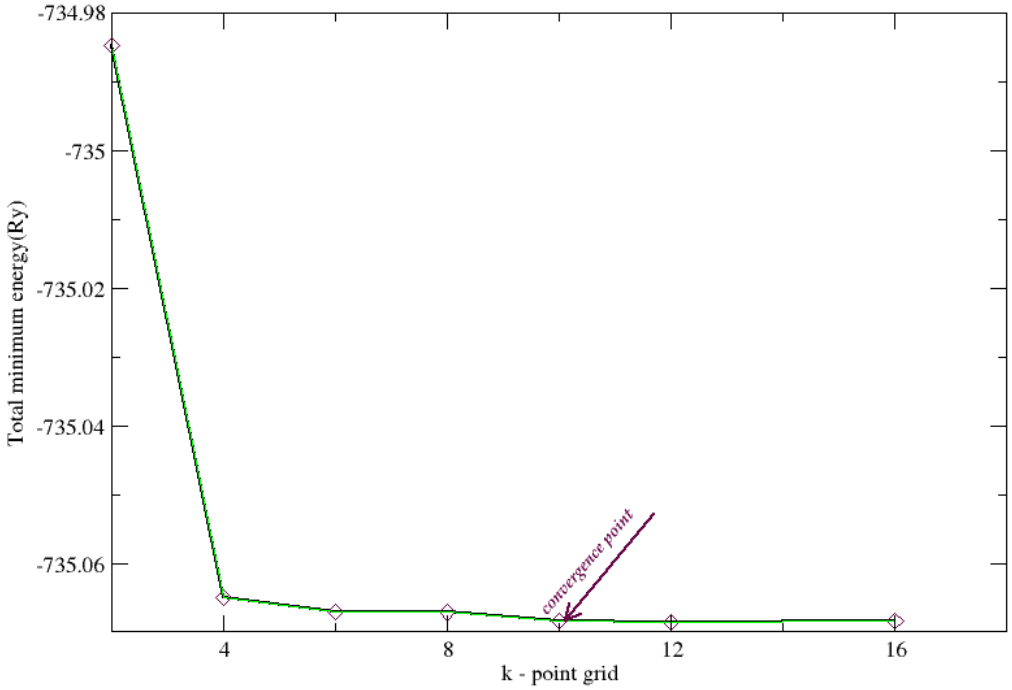

Figure 4.2: Total minimum energy of per atom with respect to k-point grid size

4.3 The equilibrium lattice constant of FeO with respect to total energy

The crystal structures of a material are defined by its lattice constants. While these lattice constants are the most common properties of a crystal system, they play an important role in the electronic properties of the materials.

The total energy of a structure is parabolic as a function of the lattice constant. This parabolic curve has a single minimum total energy. The structure with the least possible total energy is the most stable structure of that certain material. The corresponding lattice constants of this most stable system are automatically the equilibrium lattice parameters of the material. The procedure to calculate equilibrium lattice constant of FeO was computing lattice constant between 7.60 Bohr to 8.50 Bohr, in steps of 0.1 Bohr.

Lattice constant(Bohr)	Total energy(Ry)
7.60	-735.64184975
7.70	-735.67390497
7.80	-735.69835425
7.90	-735.71610842
8.00	-735.72787019
8.10	-735.73433232
8.20	-735.73603464
8.30	-735.73356945
8.40	-735.72743828
8.50	-735.71799395

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

4.3.1 Convergence test of total energy of FeO with versus lattice constant

To find the equilibrium lattice constant of FeO we perform total energy calculation for a series of plausible parameters. In this calculation the energy cutoff and the k.point sampling are made fixed (80Ry,10 × 10 × 10 k.point) using the cutoff and k.point grid criteria for energy convergence. The numerical calculation shows that the equilibrium lattice constant is 8.2 Bohr(4.3392 Angstrom).

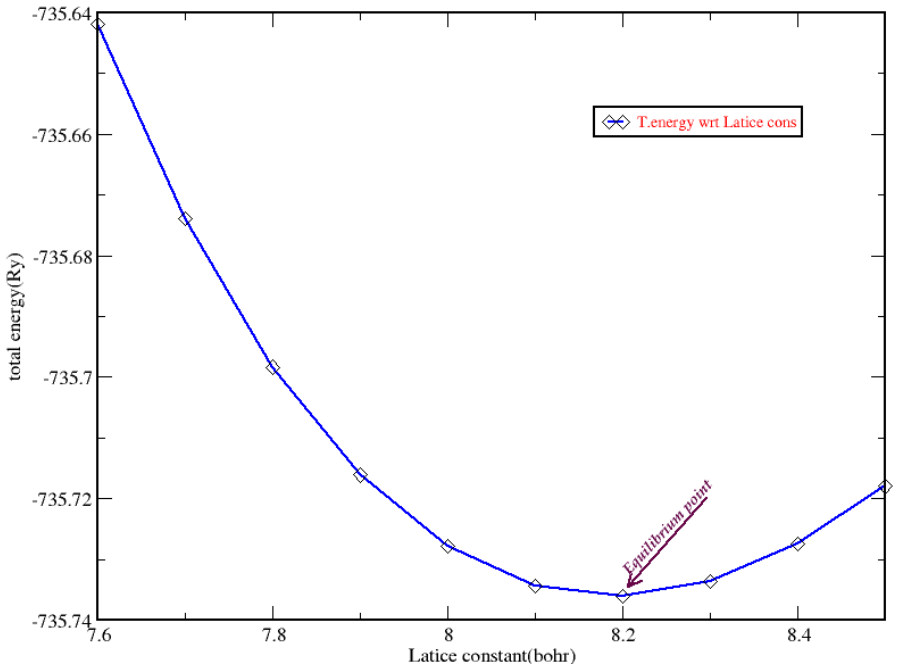

Figure 4.3: Total minimum energy of FeO per atom with respect to lattice constant

From the figure (4.3) we can see that the using GGA+U exchange-correlation functional with the Hubbard correction of the lattice parameter is 4.339 Å(8.2 Bhor) and the energy value at that point is -735.73603464 eV. When compared to the experimental value of the lattice parameter 4.288 Å(8.19 Bhor) [3] the lattice parameter calculated using GGA+U functional is 0.12 percent,this result is in good agreement with compared experimental values. The exchange-correlation functionals used and the errors of these margins are very likely accepted while computing crystal structure properties. Table 4.4 the comparison of the lattice parameter values calculated using exchange-correlation functionals in this experiment with the experimental values and the percentage of the experimental value is also shown.

Table 4.4: Comparison of calculated lattice parameters with experimental value .

Methods	Lattice Parameter in (Å)	Percentage
Our work (GGA+U)	4.3392	0.12
Experimental value [3]	4.288	-
PBE/GGA	-	-

4.4 Band structure of FeO

Band structures are a representation of the allowed electronic energy levels of solid materials and are used to better inform their electrical properties.Band It describes the range of energy levels that electrons may have within it, as well as the ranges of energy that they may not have (called band gaps or forbidden bands).

The band gap has been calculated as the difference between the energies for the minimum of the conduction band and the maximum of the valence band. Band gaps are categorized either as direct band gaps or indirect band gaps.For similar k-vectors then this becomes a direct band gap. The momentum of electrons and holes are similar in both the conduction band and the valence band that is an electron can emit a photon directly. Any differences in k-vector then an indirect band gap is formed and this means that a photon cannot be emitted.

Energy gap between occupied and un occupied energy levels is among the ways that we can determine the difference between electrical properties of metals, semiconductors and insulators. To determine the band structure the k-points are generated along high symmetry points using k-point path with the help of xcrysden software. The energy band structure of FeO is presented in figure 4.4.

The calculated band gap energy of FeO (wüstite) was 2.45 eV. As the result of calculation shows that FeO has indirect band gap which makes it an interesting material for application in pigment production.

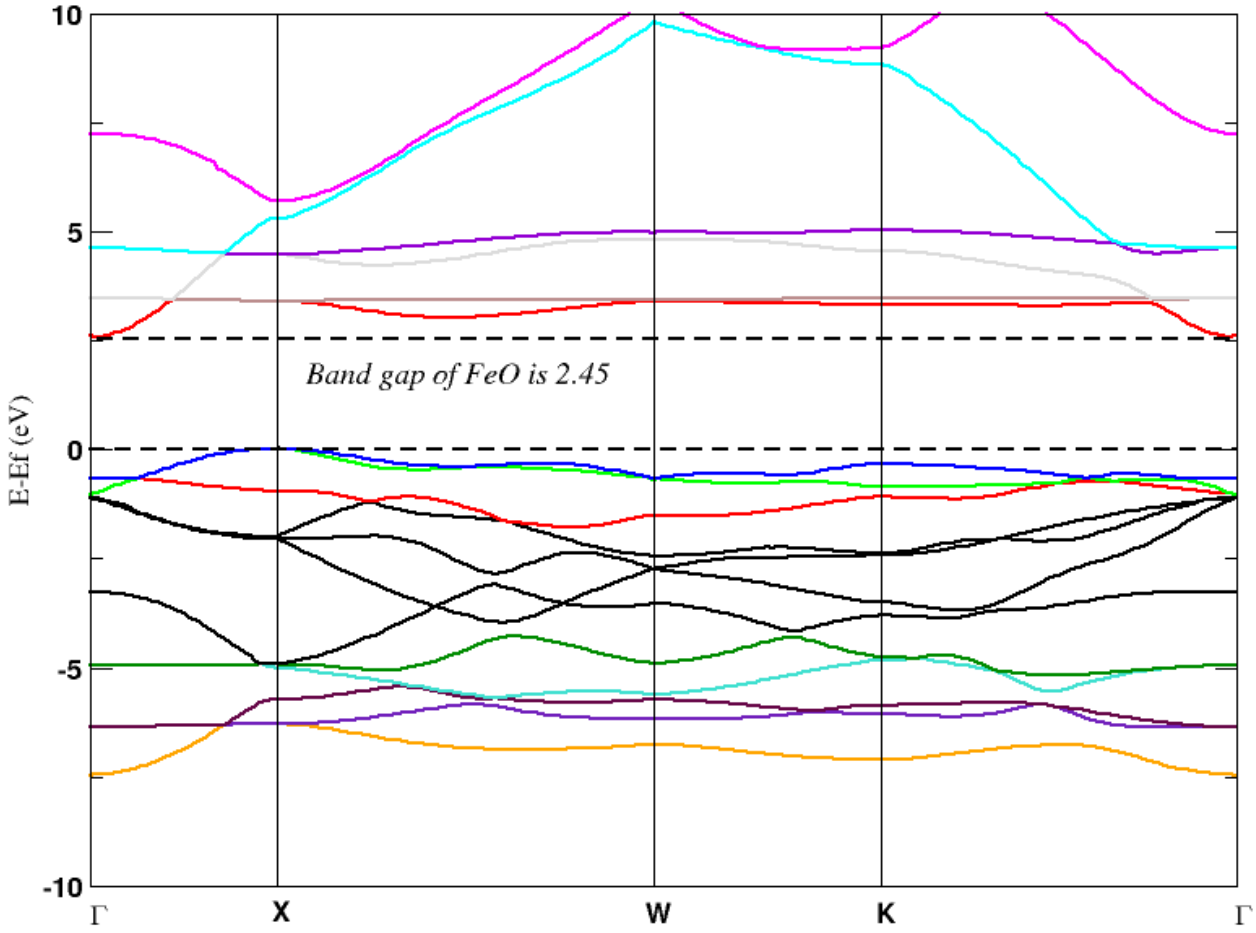

Figure 4.4: Band structure of FeO

From the figure (4.4) we can see that the using generalized gradient approximation with Hubbard correction (GGA+U) exchange-correlation functional the calculated band gap values of FeO is 2.45 eV. This result is good agreement with the reported experimental values,i.e. 2.4 eV[3]. The error of these margins are very likely accepted. Table 4.5 the comparison of the band gap of FeO values calculated using exchange-correlation functionals in this experiment with the reported experimental values is shown.

Table 4.5: Comparison of calculated band gap by using GGA+U(U=5.2 eV) with experimental value.

Methods Used	Band gaps(eV)	Percentage
Our work (GGA+U)	2.45	2.08
Experimental value [3]	2.4	-
PBE/GGA	-	-

4.5 Density of states of FeO

The density of states function describes the number of states that are available in a system and is essential for determining the carrier concentrations and energy distributions of carriers within a semiconductor.

Density of states of materials can be best defined as the number of states divided by the energy interval for every single energy level that electrons available can occupy. It is an average of space occupied by the system over time domains.

The main issue we can see from calculating the density of states (DOS) of FeO (wustite) is the investigation of its electronic transport properties. In the figure 4.5, we see that before the Fermi level enters the conduction band, there is an semiconductor region. The Fermi level (E_f) was referenced at 0 eV. The calculated values of density of state of FeO was 2.42 eV.

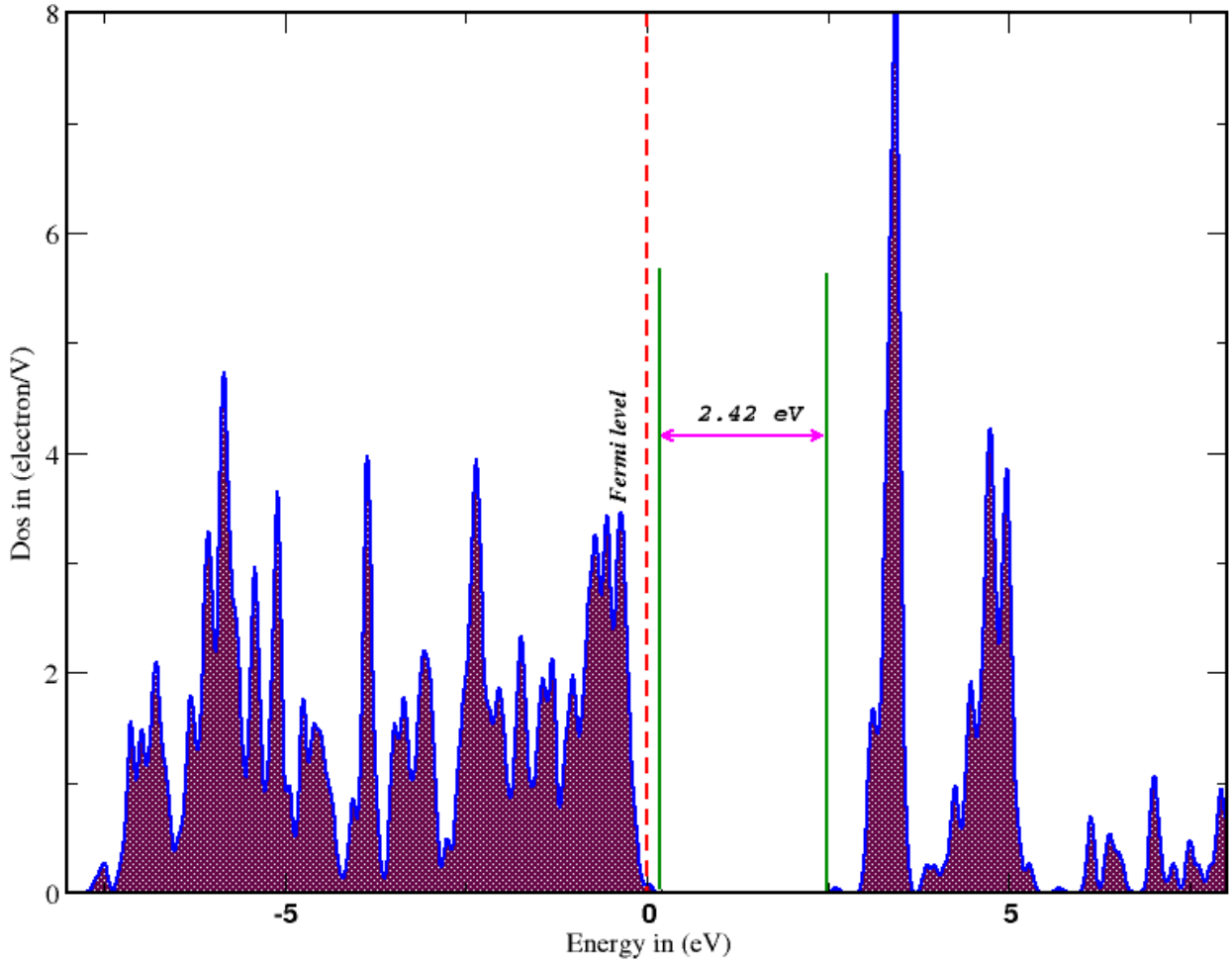

Figure 4.5: Density of states (DOS) of FeO

Chapter 5

Conclusion

In this thesis first principle calculation (DFT) was used to investigate the electronic and structural properties of FeO. The plane wave self-consistent field (PWSCF), ultra-soft pseudo potentials and the exchange correlation potential was approximated with generalized gradient approximation and Hubbard Correction. All calculations have been carried out using Quantum Espresso package. The total minimum energy calculation was performed as a function of cutoff energy and k-point samplings. The total energy convergence test was achieved at the energy cutoff 80 Ry and at 10 $\times$ 10 $\times$ 10 k-point grid size. The total minimum energy of FeO per atom is -735.74164169 Ry with respect to energy cutoff and -735.06845862 Ry with respect to k-point grid size. The computational 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. The optimal lattice constant of FeO was calculated using the above total energy convergence test by varying lattice parameter of 'a'. Our numerical calculation shows that the equilibrium lattice constant is (a = 8.2 and c = 8.5) Bohr. The obtained result is overestimated as compared to the experimental result due to the approximate nature of the applied DFT .The band structure was determined by generating k-points along high symmetry points using K-point path with the help of xcrysden software. The computed values of band structure and density of states of FeO was 2.45 eV and 2.42 eV respectively.In general the results of calculation show that FeO is a wide band gap semiconductor material which can be applied in pigment production.

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Course Code	Course Title	Cr. hr	Number grade	Rank **	Remark
Phys 799	Graduation Thesis	6	–	–	–

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