INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF COBALT OXIDE (CoO) USING DENSITY FUNCTIONAL THEORY WITH HUBBARD CORRECTION

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF JIMMA UNIVERSITY, DEPARTMENT OF PHYSICS IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN PHYSICS

BY

REDUWAN BEDRU ADEM

PHYSICS DEPARTMENT

JIMMA, ETHIOPIA

JUNE, 2014 E.C

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A Thesis Submitted to Center of Jimma University Physics Department in Partial Fulfillment of the Requirements for the degree of Master of Science in Physics

By Reduwan Bedru Adem

Approved by Board of Examiners

Menberu Mengesha(Dr)   ....
Advisor   Signature   Date

Mr. Edobus Mosisa   ....
Co-advisor   Signature   Date

Tolu Biressa(Dr)   ....
Internal Examiner   Signature   Date

Sintayehu Mekonnen(Dr)   ....
External Examiner   Signature   Date

Declaration

I hereby declare that the work which is being presented in this thesis entitled "INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF COBALT OXIDE (CoO) USING DENSITY FUNCTIONAL THEORY WITH HUBBARD CORRECTION" is original work of my own and all the resource materials used for this thesis have been duly acknowledged.

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Reduwan Bedru (Candidate)   Date

Submission date: June 15, 2014 E.C

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List of Abbreviations

eV	Electron volt
TMO	Transition metal oxide
TMMO	Transition metal mono-oxide
DFT	Density functional theory
U	Hubbard correction
PBE	Perdew-Burke-Ernzerhof
CBM	Conduction band minimum
VBM	Valence band maximum
LDA	Local density approximation
GGA	Generalized gradient approximation
Ecutwfc	Kinetic energy cut-off wave functions
Ecutrho	Kinetic energy cut-off density
Ry	Rydberg
SCF	Self consistent field
DOS	Density of states
PDOS	Projected density of states
CoO	Cobalt mono-Oxide
Co_3O_4	Cobalt Oxide nano-particles
xc	Exchange-correlation
a.u	Atomic unit
SOC	Spin orbit coupling
SIC	Self interaction correction
cF	Cubic face
AF-II	Antiferromagnetic type-2
ccp	Cubic-closed packed
hcp	Hexagonal closed packed
NaCl	Sodium Chloride
H-K	Hohenberg-Kohn
PWSCF	Plane wave self consistent field

Abstract

Cobalt oxide (CoO) has been widely studied due to its many advantages, such as starting material for the manufacture of other chemicals and catalysts, in pigments such as color reagents and in ceramics, a ground-coat frit, promotes the adherence of enamel to steel and also used as a blue coloring agent for pottery, enamel and glass. In this thesis the structural and electronic properties of Cobalt mono-Oxide (CoO) were investigated using density functional theory with Hubbard correction (DFT+U) using Quantum Espresso package. Our study is based on DFT+U with the Perdew-Burke-Ernzerhof (PBE)+U exchange-correlation functional, Vanderbilt (ultra soft) pseudo-potentials and the plane wave basis set implemented in the Quantum-ESPRESSO package. The calculation of the total minimum energy were calculated as a function of cutoff energy and K-points sampling. The total minimum energy per cell is monotonically decreasing with increasing cutoff energy due to variational principle. However, this trend can not be predicted from increasing the k-points sampling. Moreover, the equilibrium lattice constant is calculated using results obtained from energy convergence test (i.e; 40 Ry and $5 \times 5 \times 5$). The computational value of the equilibrium lattice constant is $4.24\text{\AA}$. This result is in good agreement with experimental value which is $4.27\text{\AA}$. Finally, discussing band structure (with calculated band-gap=2.45 eV) and density of state of CoO, the electrical property of CoO is determined based on energy band gap.

Keywords: Cobalt mono-Oxide, Density Functional Theory, Hubbard correction, Electronic properties and structural properties.

Acknowledgements

First of all, I would like to thank my Almighty God. Secondly I would like to express my deep gratitude to my advisor Dr. Menberu Mengesha for his valuable, intellectual, constructive and meaningful suggestions and valuable encouragement. Starting from the planning up to the development of this research work his outstanding advice, extreme supporting for his effortful and consistent advice were remembered ever. I thank him a lot for his guidance to the right research direction. Lastly, Many thanks go to my families for their great support and encouragement in all aspects from start to end of this research work.

1 Introduction

1.1 General Background

Cobalt (Co) is found with minerals containing a possible variety of elements (Ni, As, S, Fe, Cr, Cu, Pb, and Mn) as the oxide, sulfide or arsenide but is not found naturally occurring as the metal. Co is not mined directly but is produced as a byproduct (mostly from Ni and Cu mining) of mining operations in Africa, the former Soviet Union and North America. Cobalt is an element that is low to moderately abundant in the Earth's crust. Its abundance is roughly that equal to scandium. Cobalt and scandium are the less abundant of the first row transition elements, making them both candidates as internal standard (IS) elements [1]. In recent years, transition metal cobalt (Co) and cobalt oxide are known as promising materials due to their extensive applications in lithium-ion batteries, electronic gas-sensing, data storage, catalysis and electro-chromic devices [2,3]. Cobalt has two oxides that are more commonly encountered in conventional sample preparation schemes, namely CoO and Co_3O_4[1]. CoO is a metallic coloring oxide that produces blue in glazes at all temperatures (unless in very high percentages where it will be black). Black Cobalt Oxide (Co_3O_4) is a key source of CoO used in glazes, glass, and enamels. Cobalt is the most powerful ceramic colorant and it is stable in most systems, it appears in many recipes at 1% or lower. It melts very actively in oxidation. If it is mixed into a fluid frit base in high enough a percentage, it will completely crystallize during cooling. Cobalt is also useful as a body and slip stain. However, cobalt materials are very expensive, this severely limits its practical use in many things[4].

CoO, which is inorganic compound, grey green, can be obtained by heating the sample to temperatures in excess of 1000 °C. This temperature is generally considered unnecessarily high in sample dry ashing preparations. CoO has been reported in several structural forms, such as rock salt, wurtzite and zinc blende. The rock-salt cubic structure (space group Fm3hm) with octahedral Co^{2+} atoms is the most stable phase of CoO[5]. Cobalt(II) oxide has for centuries used as a coloring agent on kiln fired pottery. The additive provides a deep shade of blue named cobalt blue. The band gap (CoO) is around 2.4 eV. It also is used in cobalt blue glass[6].

Historically, DFT+U was introduced to accurately describe the d- and f-type electrons of transition-metal(TM) and rare-earth compounds, as it was thought that the U parameter would correct these strongly correlated, localized states (i.e., d- and f-type states). Density-functional theory (DFT)

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with approximate exchange-correlation (xc) functionals e.g., local-density approximation (LDA) or generalized-gradient approximation (GGA) has been remarkably successful in predicting ground-state properties of a large variety of systems, such as crystal structure and thermodynamic stability. However, these DFT calculations have known limitations, including the underestimation of the band gap (on the order of $\sim 40\%$ in semiconductors and insulators) due to self-interaction errors (SIE) inherent to approximate xc functionals. Various xc functionals and methods were developed to alleviate this problem. A very popular extension of DFT is the DFT+U approach, in which the Hubbard U correction acts selectively on a subset of states in the system (typically, of d or f character) by imposing the piecewise linearity in the energy functional as a function of the occupations of this subset. DFT+U is only marginally more expensive than DFT within LDA or GGA, while significantly improving various properties of materials such as transition-metal compounds [7].

The scope of DFT and DFT+U is limited to ground-state properties, including electronic band gaps but excluding optical band gaps. The optical band gap of a material is the minimal energy required for absorbing an incident photon (corresponding to a neutral excitation), whereas the electronic band gap is the difference between the occupied and unoccupied states (corresponding to charged excitations). In most inorganic semiconductors, the electronic band gap and the optical band gap are approximately equal, but for organic semiconductors, the difference between these two energies (the exciton binding energy) may be substantial. It is thus expected that DFT+U would be more accurate at predicting optical band gaps for inorganic semiconductors than for organic semiconductors. To improve the precision of the computed electronic band gaps, DFT+U incorporates a corrective U term designed to restore piecewise linearity of the total energy with respect to the occupations of the orbitals within the Hubbard manifold, which acts to approximate derivative discontinuities. Often the U parameter is chosen semi-empirically by fitting it to reproduce experimental band gaps, experimental oxidation enthalpies, or other properties. However, fitting U to reproduce a subset of experimental data is not a predictive approach, especially in cases when no prior data is available [7].

1.2   Statement of the Problem

It is obvious that many body problems are complicated and a bit challenging to solve. Because of this the state of motion cannot be solved analytically for

systems in which three or more masses are interact. To solve this many body problems, the density functional theory(DFT) collaborated with Hubbard potential(U) or DFT+U is preferred as an accurate and reliable tool. The material, Cobalt Mono-Oxide (CoO) or Cobalt(II) oxide has for centuries used as a coloring agent on kiln fired pottery. The additive provides a deep shade of blue named cobalt blue. It is used extensively in the ceramics industry as an additive to create blue colored glazes and enamels as well as in the chemical industry for producing cobalt(II) salts. It also is used in cobalt blue glass. But its electronic and structural properties are not well studied. This material was studied before in DFT and reported as it is conductor[46] and semi-conductor[45]. Since, DFT underestimate the bandgap of highly correlated materials (CoO), it is aimed to investigate this material in order to improve the electronic and structural properties of CoO using DFT+U with the help of Quantum Espresso Package.

1.3 Research questions

1. What is the ground state energy of CoO per atom?
2. What is the equilibrium lattice constant of CoO?
3. What is the magnitude and nature of the band structure of CoO?
4. What is the density of state of CoO?

1.4 Objectives

1.4.1 General Objective

The general objective of this study is to investigate the electronic and structural properties of Cobalt Oxide by using DFT+U with the help of Quantum Espresso Package.

1.4.2 Specific Objectives

The specific objectives of this study are:
• To carryout total minimum energy convergence test with respect to cut-off energy and K-point sampling
• To calculate the lattice constant of CoO
• To calculate the band structure of CoO
• To describe the total and partial density of states of CoO

1.5 Scope of the Research

Due to the shortage of time and budget constraint the scope of the study is limited to determining the convergence of total minimum energy with respect to cutoff-energy and K-points sampling, the theoretical lattice constant, band structure, density of states and projected density of states.

1.6 Significance of the study

The significance of this study is to understand the electronic and structural properties of CoO (many electron system) using computational technique. Understanding the electronic and structural properties of many electron system (in this thesis CoO) helps to know about the system in detail; and significantly improving properties of materials such as transition-metal compounds (CoO). Moreover, this study can be used as preliminary base for future research works related to computational modeling of materials for different applications.

1.7 Organization of the study

The thesis is organized and separated to five chapters. Chapter one is introduction part which discusses background of the study, problem statement, objectives of the study, its significance and the scope. Chapter two reviews related literature on the subject such as previous studies and findings. Chapter three discusses research methodology. Chapter four discusses the results of the study and includes, explains the results and discusses the findings of the study. Chapter five concludes the results of the study and recommends for action and directs future research directions.

2 Literature Review

2.1 Cystal Structures

Transition metal monoxide (TMMO) CoO adopt two simple crystal structures; cubic close packed (ccp) and hexagonal close packed (hcp). **In ccp structure** cations occupy the octahedral sites of the ccp array of anions, stable form for most metal monoxide[13]. **In hcp structure** cations are located at tetrahedral sites of the hcp array of anions, is thermodynamically unstable relative to ccp[13]. Hence, we study the most stable (ccp structure).

   Rock Salt(NaCl): It is well-known that the cubic rock salt structure is the most stable CoO phase. It consists two interpenetrating face centred cubic (fcc) sub-lattices of Co^{2+} and O^{2-} with Lattice constant a=4.26$\mathring{A}$[13]. Periclase (Rock salt) monoxide ($c - CoO, Fm\bar{3}m$) (225)[13].

2.2 Structural Properties

Cobalt(II) oxide is an inorganic compound that has been described as an olive-green or gray solid. It is used extensively in the ceramics industry as an additive to create blue colored glazes and enamels as well as in the chemical industry for producing cobalt(II) salts. Cobalt Oxide (CoO) crystals adopt the periclase (rock-salt) structure with a lattice constant of 4.2615$\mathring{A}$, is antiferromagnetic below 16 °C. It has Molar mass of 74.9326 g/mol and it is odorless. it's appearance is olive or gray powder (colour varies from olive-green (CoO) to red, depending on particle size), have density 6.45g/cm^3, melting point 1,933 °C(3,511 °F; 2,206K). It is Cubic, $cF8$ crystal structure with space group of $Fm\bar{3}m$, No. 225, and is insoluble in water. It has magnetic susceptibility of χ +4900E-6cm3/mol[9]. Cobalt is a moderately reactive metal. In air or oxygen environment, it is oxidized, forming a thin layer of cobalt oxide on the surface of the metal. This layer serves as a protection or passivation layer that prevents further oxidation or corrosion. Practically insoluble in water, ethanol and ammonium hydroxide; rather soluble in acids (hydrochloric, sulfuric, nitric). CoO Compound is stable in its Co^{2+} oxidation state[12].

2.3 Electronic Properties

DFT commonly underestimates the band gap of materials where the valence electrons are highly localized, such as Co oxides. Here, we therefore adopt

the DFT+U method to describe correctly the electronic and geometric properties of CoO. DFT+U is a correction of the pure DFT method, where the U parameter is a Hubbard-like potential added to the Kohn-Sham DFT Hamiltonian. DFT+U usually provides accurate results for 3d transition metal oxides, hence the use of this method in our investigation. We have considered several U parameters, ranging from 0 to 5 eV, in order to calculate the lattice parameters, the band gaps, and the bulk moduli of the materials, following the procedure used in previous works [11].

Metal monoxides such as CoO have a rock-salt NaCl crystal structure and the most stable magnetic ordering below its Néel temperature is the antiferromagnetic type II(AF-II). In the solid state calculations, this magnetic ordering can not be represented as there is a geometrical frustration in the CoO crystal structure. Thus, to investigate the AF-II structure, we have considered a rhombohedral four-atom unit cell, which is equivalent to the geometry used in previous theoretical studies where the authors investigated the electronic and magnetic structures of CoO[11].

A U value of $\sim 3.0eV$ describes adequately the band gap of CoO[11]. As we will consider a system containing pure Co and its oxides in future investigations, we need to determine one U value. We will therefore ensure that the formation energies of the cobalt oxide phases are in good agreement with experiment results. Thus, an effective increment of the on-site Coulomb repulsion in the Co d electrons by 3 eV is a fair compromise to investigate the physical and chemical properties of Co, and its oxides. According to the study of [Africa-UK Partnership for the Computer aided Development of Sustainable Catalysts Research Article] They have adopted U = 3 eV to describe and discuss in more detail the electronic structure, elastic constants, and mechanical properties of CoO. They have determined the inter-atomic distances for the materials and found CoO bulk, determined a Co-O distance of 2.142Å[11].

The electronic configuration of CoO can be written as Co 3d O 2p. In the ground state, the O 2p band is completely occupied whereas the Co 3d band is only partly occupied[33]. According to the band theory, one expects metallic properties of CoO since the valence band is only partly occupied. A metallic nature of CoO is also predicted by the density functional theory (DFT) which is the most successful tool for describing the electronic properties of solids [33]. However, experiments have revealed that CoO is an insulator with a band gap of 2.5 eV[33]. This discrepancy has been attributed to the strong electron-electron interaction in the 3d-band which strongly affects the

electronic structure of CoO. Therefore, the one electron approach of the band model as well as the DFT approach fails since the electrons strongly interact during its motion. The band gap increases with the Hubbard (U) parameter. Kurmaev found a value of 2.60 eV using synchrotron-excited oxygen X-ray K-emission spectroscopy[31].

2.4   Applications

Recently, Cobalt oxide (CoO) has been widely studied due to its many advantages, such as starting material for the manufacture of other chemicals and catalysts, in pigments such as color reagents and in ceramics, a ground-coat frit, promotes the adherence of enamel to steel and also used as a blue coloring agent for pottery, enamel and glass. It is used in ceramics and enamels as a colorizer and decolorizer[12,47].

2.5   Many electron system

The ultimate goal of most approaches in solid state physics, quantum chemistry and in this electronic structural calculation of CoO is the solution of the time independent, non relativistic Schrödinger equation. The state of motion can not be solved analytically for systems in which three or more distinct masses interact. To solve this problem we can use approximations[15].

2.5.1   Ab Initio Methods

Ab Initio, meaning "from first principles", methods solve the Schrödinger equation and does not rely on empirical or experimental data. Beginning with fundamental and physical properties, calculate how electrons and nuclei interact. For complex systems, Ab Initio methods make assumptions to obtain approximate solutions to the Schrödinger equations and solve it numerically. "Computational Cost" of calculations increases with the accuracy of the calculation and size of the system[37].

• **Born-Oppenheimer Approximation:** Nuclei are heavier than electrons and can be considered stationary with respect to electrons. Also know as "clamped nuclei" approximations and leads to idea of potential surface[37].

The time-independent Schrödinger equation of a system reads:

$$H\psi(r_1, ..., r_N) = E\psi(r_1, ..., r_N) \tag{1}$$

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.

For many electron system:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|r_i - r_j|} - \sum\frac{\hbar^2}{2M_I}\nabla_I^2 + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|R_I - R_J|} \tag{2}$$

Where, M_I-is mass of the nuclei
m_e-is mass of the electron
Since nuclei are much heavier than electrons, the nuclei appear fixed or stationary. Hence $M_I >> m_e$ the kinetic energy (K.E) of the nuclei become:
$\frac{\hbar^2}{2M_I}\nabla_I^2 \approx 0$.

Then;

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_{i,I}\frac{Z_I e^2}{|r_i - R_I|} + \frac{1}{2}\sum_{i \neq j}\frac{e^2}{|r_i - r_j|} + \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J e^2}{|R_I - R_J|} \tag{3}$$

In atomic unit $(e = 1, \hbar = 1, me = 1)$.

- The Kinetic energy; $\hat{T} = -\frac{1}{2}\sum_i \nabla_i^2$ due to electron(e^-)

- External potential; $\hat{V}_{ext} = \sum_{i,I} V_i(|r_i - R_I|)$ due to electron and nuclei

- The interaction potential; $\hat{V}_{int} = \frac{1}{2}\sum_{i \neq j}\frac{1}{|r_i - r_j|}$ due to $e^- e^-$ interaction

- The Nuclear potential; $\hat{V}_{IJ} = \frac{1}{2}\sum_{I \neq J}\frac{Z_I Z_J}{|R_I - R_J|}$ due to interaction of nuclei.

Therefore the total energy for interacting Hamiltonian is:

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 + \hat{V}_{ext} + \hat{V}_{int(e-e)} + \hat{V}_{IJ} \tag{4}$$

The wave function $\psi(R, r)$ of the many electron molecule is a function of nuclear(R) and electronic(r) coordinates. Born-Oppenheimer Approximation: Separate electronic and nuclear motion:

$$\psi(R, r) = \psi_e(r; R)\psi_n(R) \tag{5}$$

Solve electronic(r_i) part of Schrodinger equation

$$\hat{H}_{ri}\psi_{ri}(r; R) = E_{ri}\psi_{ri}(r; R) \tag{6}$$

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Born-Oppenheimer(BO) approximations leads to the concept of potential energy surface.

$$V(R) = E_{ri} + V_{R_I R_J} \qquad (7)$$

The electronic potential is a function of nuclear coordinates. Due to their masses the nuclei move much slower than the electrons. We can consider the electrons as moving in the field of fixed nuclei. We can ignore the nuclear kinetic energy and their potential energy is merely constant. Thus, the electronic Hamiltonian reduced to:

$$\hat{H} = \hat{T}_e + \hat{V}_{ext(e-N)} + \hat{V}_{int(e-e)} \qquad (8)$$

The total energy is then:

$$E_T = E_{rirj(elec)} + E_{RIRJ(nuc)} \qquad (9)$$

Where $E_{RIRJ(nuc)} = \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|R_I - R_J|}$

- **Slater Determinants:** Expand the many electron wave function in terms of Slater determinants.

- **Basis Sets:** Represent Slater determinants by molecular orbitals, which are linear combination of atomic-like-orbital functions. (i.e. basis sets).

2.6   The Variational Principle for the Ground State

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

$$E[\psi] = \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} \qquad (10)$$

Where, $\langle \psi | \hat{H} | \psi \rangle = \int \psi^* | \psi dx$

The variational principle states that the energy computed from a guessed ψ is an upper bound to the ground-state energy E_0. Full minimization of the functional $E[\psi]$ with respect to all allowed N-electrons wave functions will give the true ground state ψ and energy $E[\psi_0] = E_0$. For a system of N electrons and given nuclear potential V_{ext}, the variational principle defines a procedure to determine the ground-state wave function ψ_0, the ground-state energy $E_0[N, V_{ext}]$, and other properties of interest. In other words, the ground state energy is a functional of the number of the electrons N and the nuclear potential V_{ext}[36].

$$E_0 = E[N, V_{ext}] \qquad (11)$$

2.7   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. 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.[15]

$$T[n(\vec{r})] = \int \frac{3}{10} \frac{(3\pi^2)^{2/3}}{m} n(r)^{5/3} d^3 r \tag{12}$$

If E[n] is energy per particle of homogeneous electron gas of density [n] and n(r) local density given total energy

$$E[n] = \int E(n) n(r) dn \tag{13}$$

In electrostatic screening in region where there is no electrostatic contribution to chemical potential

$$E_F = \frac{\hbar^2}{2m} (3\pi^2)^{3/2} n^{2/3}(r) \tag{14}$$

$$E[n] = \frac{1}{2} (3\pi^2)^{3/2} n^{2/3}(r) \tag{15}$$

$$\hat{T} = \int E(n) n(r) dr = \frac{1}{2} (3\pi^2)^{3/2} (\frac{3}{5}) \int n^{5/3}(r) dr = \frac{3}{10} (3\pi^2)^{3/2} \int n^{5/3}(r) dr \tag{16}$$

Potential Energy (Coulomb interaction) (e-e interaction)

$$E_c = \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr' \tag{17}$$

Potential Energy (Electron-nuclear interaction)

$$E_{ext} = \int n(r) V_{ext}(r) dr \tag{18}$$

And the sum of the K,E and potential energy terms will give us the total energy within the Thomas Fermi approximations. That is the energy of an atom is finally obtained using the classical expression for the nuclear nuclear potential and the electron-electron potential:

$$E[n] = T[n] + E_c[n] + E_{ext}[n] \tag{19}$$

$$E[n] = \frac{3}{10} (3\pi^2)^{3/2} \int n^{5/3}(r) dr + \int n(r) V_{ext}(r) dr + \frac{1}{2} \int \frac{n(r)n(r')}{|r - r'|} dr dr' \tag{20}$$

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 [15].

"Fermi level" is the term used to describe the top of the collection of electron energy levels at absolute zero temperature. This concept comes from Fermi-Dirac statistics. Electrons are fermions and by the Pauli exclusion principle cannot exist in identical energy states. So at absolute zero they pack into the lowest available energy states and build up a "Fermi sea" of electron energy states. The Fermi level is the surface of that sea at absolute zero where no electrons will have enough energy to rise above the surface. The concept of the Fermi energy is a crucially important concept for the understanding of the electrical and thermal properties of solids. Both ordinary electrical and thermal processes involve energies of a small fraction of an electron volt[38].

In solid materials, electron energy levels form bands of allowed energies, separated by forbidden bands. **Valence band** is outermost (highest) band filled with electrons (all states occupied). **Conduction band** is next highest band to valence band (empty or partly filled). **Gap** is energy difference between valence and conduction bands, is width of the forbidden band. Electrons in a completely filled band cannot move, since all states occupied (Pauli principle)[38].

The Fermi function f(E) gives the probability that a given available electron energy state will be occupied at a given temperature[38]. The Fermi function comes from Fermi-Dirac statistics and has the form

$$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1} \tag{21}$$

The basic nature of this function dictates that at ordinary temperatures, most of the levels up to the Fermi level E_F are filled, and relatively few electrons have energies above the Fermi level. The Fermi level is on the order of electron volts, where as the thermal energy kT is only about 0.026 eV at 300K. The band theory of solids gives the picture that there is a sizable gap between the Fermi level and the conduction band of the semiconductor. At higher temperatures, a larger fraction of the electrons can bridge this gap and participate in electrical conduction[38].

2.8   Hartree- Fock theory

Hartree theory is designed to solve many electron problem from fundamental physical principles. He proposed method by solving first scrodinger equation for individual electron in states $a_1, a_2, a_3, ..., a_n$ with individual solutions; $\psi_{a1}(r_1), \psi_{a2}(r_2), \psi_{a3}(r_3), ..., \psi_{an}(r_n)$. Each $\psi_{ai}(r_i)$ is solution to scrodinger equation, their product should satisfy the solution of many electron problem. This method of combining the wave function of individual electrons is called Hartree product.

HF theory is the Variational theory obtained by the expectation value of the Hamiltonian, allowing all wave functions that can be represented as Slater determinants. This theory was developed by two individuals, Hartree and Fock. Fock applied the slater determinant to the Hartee method and proposed the Hartree- Fock method and involves antisymmetric natures of waves, spin orbital (slater determinant), orthogonality and angular momentum [15]. One of the strategies of HF is, the self-consistent solutions are obtained by employing variational principle, which is given by;

$$\delta \langle \psi^{(N)} | H | \psi^{(N)} \rangle = 0 \tag{22}$$

Hartree-Fock Scrodinger equation (HFSE) is:

$$[-\tfrac{1}{2}\nabla^2 + V_{ext}(r) + \sum_{j,\sigma j} \int dr' \psi_j^{\sigma*}(r') \psi_j^{\sigma j}(r') \tfrac{1}{|r-r'|}] \psi_i^\sigma(r)$$

$$- \sum_j \int dr' \psi_j^{\sigma*}(r') \psi_i^\sigma(r') \frac{1}{|r-r'|} \psi_j^\sigma(r) = E_i^\sigma \psi_i^\sigma(r) \tag{23}$$

The Hamiltonian can be written if the exchange term in this equation is modified it can be written as analogous to SE of non interacting electron, except the effective Hamiltonian depends on the state

$$\hat{H}_{eff}^i \psi_i^\sigma(r) = [-\frac{\hbar^2}{2}\nabla^2 + V_{eff}^{i,\sigma}(r)] \psi_i^\sigma(r) = E_i^\sigma \psi_i^\sigma(r) \tag{24}$$

For $\hat{V}_{eff}$

$$\hat{V}_{eff}(r) = V_{ext}(r) + V_{Hartree}(r) + V_x^{i,\sigma}(r) \tag{25}$$

and The Exchange term is:

$$\hat{V}_x^{i,\sigma}(r) = - \sum_j \int dr' \psi_j^{\sigma*}(r') \psi_i^\sigma(r') \frac{1}{|r-r'|} \frac{\psi_j^\sigma(r)}{\psi_i^\sigma(r)} \tag{26}$$

Wave-function is written as a single determinant

$$\psi = det(\phi_1, \phi_2, ...\phi_N) \tag{27}$$

The electronic Hamiltonian can be written as:

$$\hat{H} = \sum_i^N h(r_i) + \sum_{i \neq j} V_{int}(r_{i,j}) \tag{28}$$

For $h(r_i)$-is single electron Hamiltonian of ith particle and $V_{int}(r_{i,j})$-interaction between particle i and j.

$$h(r_i) = -\frac{\hbar^2}{2m}\nabla_i^2 - \frac{Ze^2}{r_i} = -\frac{1}{2}\nabla_i^2 - \frac{Z_I}{r_{i,I}} \tag{29}$$

Because the electronic Hamiltonian (in atomic units, $\hbar, m_e, 4\pi\epsilon_0, e = 1$).

$$V_{int}(r_{i,j}) = \frac{1}{|r_i - r_j|} \tag{30}$$

The electronic energy of the system is given by:

$$E = \langle \psi | \hat{H} | \psi \rangle \tag{31}$$

The resulting HF equations from minimization of energy by applying of variational theorem:

$$\hat{f}(x_1)\phi_i(x_1) = \varepsilon_i \phi_i(x_1) \tag{32}$$

where ε_i is the energy of orbital X_i and the Fock operator f, is defined as:

$$\hat{f}(x_1) = \hat{h}(x_1) + \sum_j [\hat{J}_j(x_1) - \hat{K}_j(x_1)] \tag{33}$$

$\hat{J}_j \Longrightarrow$ Coulomb operator $\Longrightarrow$ average potential at x due to charge distribution from electron in orbital ϕ_i defined as:

$$\hat{J}_j(x_1)\phi_i(x_1) = [\int \frac{\phi_j^*(x_2)\phi_j(x_2)}{r_{12}}dx_2]\phi_i(x_1) \tag{34}$$

$\hat{K}_j \Longrightarrow$ Exchange operator $\Longrightarrow$ Energy associated with exchange of electrons $\Longrightarrow$ No classical interpretation for this term.

$$\hat{K}_j(x_1)\phi_i(x_1) = [\int \frac{\phi_j^*(x_2)\phi_i(x_2)}{r_{12}}dx_2]\phi_j(x_1) \tag{35}$$

The Hartree-Fock equation are solved numerically or in a space spanned by a set of basis functions (Hartree-Fock-Roothan equations):

$$\phi_i = \sum_{\mu=1}^{K} C_{\mu i} \bar{\phi}_\mu \tag{36}$$

$$S_{\mu v} = \int dx_1 \bar{\phi}_\mu^*(x_1) \bar{\phi}_v(x_1) \tag{37}$$

$$\sum_v F_{\mu v} C_{vi} = \varepsilon_i \sum_v S_{\mu v} C_{vi} \tag{38}$$

$$F_{\mu v} = \int dx_1 \bar{\phi}_\mu^*(x_1) \hat{f}(x_1) \bar{\phi}_v(x_1) \tag{39}$$

$$FC = SC\varepsilon \tag{40}$$

The Hartree-Fock-Roothan equation is a pseudo-eigenvalue equation. C's are the expansion coefficients for each orbital expressed as a linear combination of the basis function. Note: C depends on F which depends on C $\longrightarrow$ need to solve self-consistently. Starting with an initial guess orbitals, the HF equations are solved iteratively or self consistently (Hence HF procedure is also known as self-consistent field or SCF approach) obtaining the best possible orbitals that minimize the energy[39].

Basis Sets: Represent Slater determinants by molecular orbitals, which are linear combination of atomic-like-orbital functions i.e. basis sets.

In order to calculate electronic wave function and energy

$$E_e = \frac{\langle \psi_e | \hat{H}_e | \psi_e \rangle}{\langle \psi_e | \psi_e \rangle} \tag{41}$$

The total electronic wave function is written as a Slater Determinant of the one electron functions, i.e. molecular orbitals, MO's

$$\psi_e = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(1) & \phi_2(1) & ... & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & ... & \phi_N(2) \\ ... & ... & ... & ... \\ \phi_1(N) & \phi_2(N) & ... & \phi_N(N) \end{vmatrix} \tag{42}$$

Molecular Orbitals(MO's) are written as a linear combination of one electron atomic functions or atomic orbitals (AO's).

$$\phi_i = \sum_{\mu=1}^{N} C_{\mu i} X_\mu \tag{43}$$

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$C_{\mu i} \Longrightarrow$ MO coefficients $X_\mu \Longrightarrow$ atomic basis functions.

Obtain coefficients by minimizing the energy via Variational Theorem. Variational Theorem is Expectation value of the energy of a trial wave-function is always greater than or equal to the true energy[39].

$$E_e = \langle \psi_e | \hat{H}_e | \psi_e \rangle \geq \varepsilon_0 \qquad (44)$$

Increasing $N \Longrightarrow$ Higher quality of wave-function $\Longrightarrow$ Higher computational cost

2.8.1 Major problems of HF method

1) HF equation can only be solved directly only in special cases such as spherically symmetric coordinates and homogeneous electron gas.
2) In HF method the gap between the addition and removal of energies electrons greatly overestimated because of neglecting relaxation of orbitals and other effects of correlation.

2.9 Post Hartree-Fock Methods

Methods that improve the Hartree-Fock results by accounting for the correlation energy are known as Post Hartree-Fock methods. The starting point for most Post HF methods is the Slater Determinant obtain from Hartree-Fock Methods[39].
Configuration Interaction (CI) methods- Express the wave-function as a linear combination of Slater Determinants with the coefficients obtained variationally

$$|\psi\rangle = \sum_i C_i |\psi_i\rangle \qquad (45)$$

Many Body Perturbation Theory- Treat the HF determinant as the zeroth order solution with the correlation energy as a perturbation to the HF equation.

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}' \qquad (46)$$

$$\varepsilon_i = E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + ... \qquad (47)$$

$$|\psi_i\rangle = |\psi_i^{(0)}\rangle + \lambda|\psi_i^{(1)}\rangle + \lambda^2|\psi_i^{(2)}\rangle... \qquad (48)$$

Coupled Cluster Theory-The wave-function is written as an exponential ansatz

$$|\psi\rangle = e^{\hat{T}}|\psi\rangle_0 \qquad (49)$$

where $|\psi\rangle_0$ is a Slater determinant obtained from HF calculations and $\hat{T}$ is an excitation operator which when acting on $|\psi\rangle_0$ produces a linear combination of excited Slater determinants.

2.10   Density Functional Theory(DFT)

Density functional Theory by Hohenberg, 1964 and Kohn, 1965, together with the Generalized Gradient Approximation[44] have been widely used to study the structural and electronic properties of solids. However, the study of FeO and transition metal monoxides (TMMO) MO (M=Mn, Co, Fe, Ni) within the DFT-GGA methods is a special challenge. For these systems, LDA and GGA introduce errors in the self interaction terms of the strongly correlated electrons, which result in a de-localization of the electrons and a reduction of band gaps in the case of MnO and NiO. As it will be seen in this work, FeO and CoO are described as metallic compounds in the GGA picture[8]. In this context, the LDA+U[43] method becomes a candidate as a first approximation to the solution of the problem. In this method, the strongly correlated electrons are separated from the DFT picture and treated within a Hartree-Fock-like method by introducing parameter U for the coulombian interaction and J for the electronic exchange. In an original work by Anisimov[19] it is pointed out that spin-orbit coupling (SOC) should be taken into account to completely break the degeneracy of the d orbitals at the Fermi level. More recently, in works, Hybrid functional have been shown to reproduce electronic properties more accurately on FeO and TMMO in general[8]. However, in this work we reproduce experimental results for band gaps using the picture of GGA+U.

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. 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, cutoff 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 two Hohenberg-Kohn theorems.

$$E[n] = T[n] + U[n] + \int V(r)n(r)\delta^3 r \qquad (50)$$

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

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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 electron density 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. 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[40].

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 Schrodinger 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. 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].

2.10.1 The 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[40].

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 n_0. Therefore, the ground state wave function ψ (which can be determined by the density function theory) minimizing the energy functional [40].

$$E[\psi] = \langle \psi | \hat{H} | \psi \rangle \tag{51}$$

Using $\psi_0[n_0]$ one can determine all properties by calculating;

$$\langle \hat{o} \rangle [n_0] = \langle \psi_0[n_0] | \hat{o} | \psi_0[n_0] \rangle \tag{52}$$

Where, $\hat{o}$ is an arbitrary operator.

Second theorem of Hohenberg- kohn

A universal functional for the energy E[n] interms 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 $n_0(r)$ [15]. The total energy can be written as,

$$E[n] = T[n] + V_{Ne}[n] + V_{ee}[n] = F_{HK}[n] + V_{Ne}[n] \tag{53}$$

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

2.11 The kohn-sham theory

Kohn and Sham (KS) proposed to put wave mechanics in to the kinetic energy functional, but retain the density variable n(r) elsewhere. Their theory was tightly linked to HF Slater approximation of many body fermions theory. The weakest part of the Thomas Fermi theory was the treatment of the kinetic energy functional in this theory. Kohn-sham considered the exchange and

correlation energies and supposed to calculate the exact kinetic energy of a non interacting reference system with the same density as the real interacting system[15].

$$E_{KS}[\psi_1, ..., \psi_n] = \sum_a^N \frac{\hbar^2}{2m} \int d^3r \nabla\psi_a^* \cdot \nabla\psi_a + \frac{1}{2} \int d^3r \frac{e^2}{|r-r'|} n(r)n(r')+$$

$$E_{xc}[n] + \sum_a \int d^3r V_{ext}(r)|\psi_a|^2$$

(54)

Which is used together with the definition,

$$n(r) = \sum_a^N |\psi_a(r)|^2 \tag{55}$$

Accurate values of the exchange and correlation energies obtained for chemically interacting systems are essential for analysis of the effect of electron correlation with in Kohn-sham (KS) theory. Two of the earliest density functional are the local density approximation (LDA) and generalized gradient approximation (GGA)[15].

2.12   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 n. In Kohn-Sham expression the total electronic energy $E[n]$ is given by;

$$E[n] = T_S[n] + V[n] + W_H[n] + E_{xc} \tag{56}$$

Where T_S-is the kinetic energy of a non-interacting particle system with density n, V is the energy of electron-nuclear attraction, W_H is the coulomb or Hartree energy and E_{XC} is the exchange-correlation energy. An accurate values of the exchange and correlation energies obtained for chemically interacting systems are essential for analysis 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))[15].

2.12.1   The Local Density Approximation (LDA)

The first family of exchange correlation functional is the LDA functional [15]. 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.

$$E_{xc}^{LDA}[n] = \int n(r)E_{xc}[n(r)]d\vec{r} \tag{57}$$

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

$$E[n_r] = \int V(r)nd^3r + \frac{1}{2}\int \frac{n_r n_r'}{|r-r'|}d^3rd^3r' + G[n] \tag{58}$$

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 1 ev. 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.

2.12.2 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 [15]. The GGA functional can be written as;

$$E_{xc}^{GGA}[n] = \int n(r)E_{xc}[n(r)\nabla_n]d\vec{r} \tag{59}$$

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 [15].

2.13 Plane wave basis sets and Pseudo potentials

2.13.1 Plane wave basis set

In calculations of solid states or condensed matter, the DFT will be applied with plane wave basis sets. 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 $C_i, K + G$ for the plane waves with small kinetic energy, $\frac{\hbar}{2m}|K + G|^2$ 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 [16].

2.13.2 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 [16]. 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.

The potential inside some core radius r_c is replaced by a pseudo-potential describing the nucleus and core radius. Outside r_c the wave functions for all-electron (ψ_{AE}) and wave functions for pseudo-potentials (ψ_{pseudo}) are the same and much smaller realistic basis sets can be used.

A plane wave cutoff, which is the highest kinetic energy of all basis functions and specifies the number of basis functions, specifies the size of the basis group. The basis set for convergence can be managed systematically by growing the cutoff on the plane wave.[16]

$$E_{cut} = \frac{\hbar^2}{2m}|G_{max}|^2 \tag{60}$$
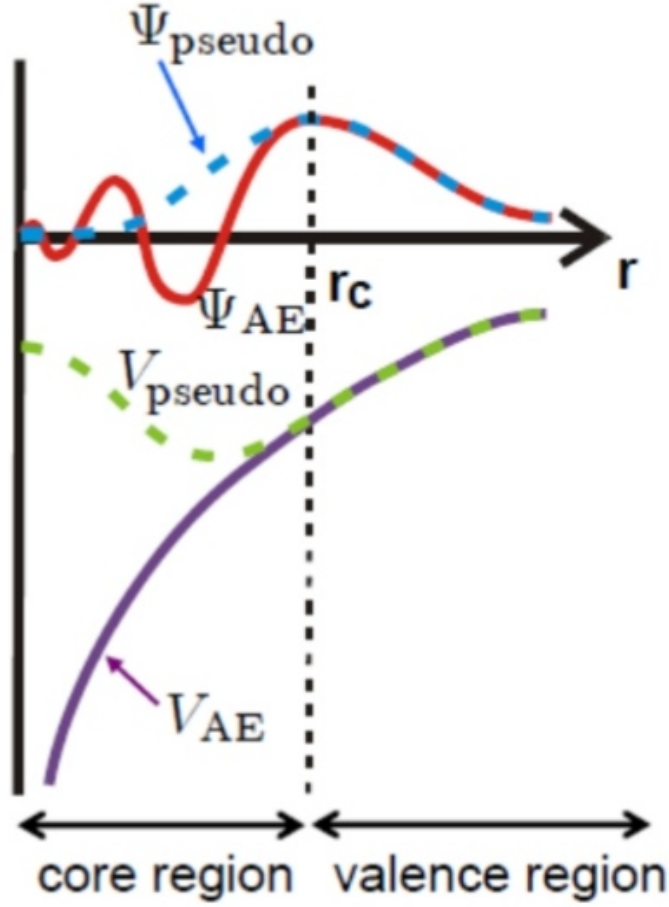
Figure 1: Approximations of Pseudo-potentials

2.14 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.

$$\psi_k(\vec{r}) = e^{iG\cdot\vec{r}} U_k(\vec{r}) \tag{61}$$

Where, $U_K(\vec{r})$ is the periodic potential in space with the same periodicity as the supper cell. That is;

$$U_k(\vec{r} + n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3) = U_k(\vec{r}) \tag{62}$$

for any integers n_1, n_2 & n_3

2.15 The DFT+U Approach

The present implementation of DFT+U stems from the early contributions by Anisimov and others,[18-22] who proposed to correct the failures of the LDA functional in dealing with the strongly localized d or f electrons of transition metal ions. An on-site correction was thus constructed to account for strong electronic correlations poorly described within the local-density or generalized-gradient approximations and formulated as follows:

$$E_{DFT+U}[n(r)] = E_{DFT}[n(r)] + E_U[n_{mm'}^{I\sigma}] = E_{DFT}[n(r)] + E_{HUB}[n_{mm'}^{I\sigma}] - E_{DC}[n^{I\sigma}] \tag{63}$$

where $n(r)$ is the electronic density, $n_{mm'}^{I\sigma}$ are generalized atomic orbital occupations with spin σ associated to the I atom, and $n^{I\sigma}$ is the sum of the occupations corresponding to all eigen-states, $\sum_m n_{mm'}^{I\sigma}$. $E_{DFT}[n(r)]$ is the standard LDA or GGA energy functional, and $E_{HUB}[n_{mm'}^{I\sigma}]$ represents the "correct" on-site correlation energy. Since $E_{DFT}[n(r)]$ already contains an approximate correlation contribution, a term intended to model such a contribution, $E_{DC}[n^I\sigma]$, must be subtracted to avoid double counting.

In this work, we resort to the rotationally invariant formulation of DFT+U introduced by Liechtenstein et al.[18] and later simplified by Dudarev and his co-workers[18], in which the non-sphericity of the electronic interactions and the differences among the interactions in like-spin and unlike-spin channels are neglected. With these assumptions, the correction to the energy functional can be written

$$E_U[n_{mm'}^{I\sigma}] = \frac{U}{2} \sum_I \sum_{m,\sigma} [n_{mm}^{I\sigma} - \sum_{m'} n_{mm'}^{I\sigma} \cdot n_{m'm}^{I\sigma}] = \frac{U}{2} \sum_{I\sigma} Tr[n^{I\sigma}(1 - n^{I\sigma})] \tag{64}$$

where U is the Hubbard parameter describing on-site correlations. In principle, different definitions for the occupation matrix are possible, which in turn will determine different values for U. In this case we define

$$n_{mm'}^{I\sigma} = \sum_v f_v \langle \psi_v^\sigma | \phi_m^I \rangle \langle \phi_{m'}^I | \psi_v^\sigma \rangle \tag{65}$$

with f_v being the weight of the electronic state v, ϕ_m^I the valence atomic orbital $|lm\rangle$ of atom I, and ψ_v^σ the one-electron wave function corresponding to the state v with spin σ. The diagonalization of the occupation matrices leads to the following expression for the energy correction:

$$E_U[n_{mm'}^{I\sigma}] = \frac{U}{2} \sum_{I,\sigma} \sum_i \lambda_i^{I\sigma}(1 - \lambda_i^{I\sigma}) \tag{66}$$

Equation above clearly reflects the nature of the correction, which imposes a penalty (mediated by U) for fractional occupations, thus favoring either fully occupied or empty orbitals ($\lambda \approx 1$ and $\lambda \approx 0$, respectively). We note that, under this definition, U corresponds to the difference U-J, as utilized by Anisimov and other researchers.[20-22] For example, the adoption of U = 4 eV in the present calculations is comparable to a U value of 5eV in combination with a J value of 1 eV in the work of Rollmann.[23] Whereas in recent applications U is considered a fitting parameter,[23,24] here we obtain it from the spurious curvature of the DFT energy as a function of the occupations. As shown by Cococcioni and de Gironcoli,[25] the value of U can be estimated as the difference between the screened and bare second derivative of the energy with respect to the occupations:

$$U = \frac{\partial^2 E_{DFT}}{\partial (n^I)^2} - \frac{\partial^2 E_{DFT}^o}{\partial (n^I)^2} \tag{67}$$

In particular, we are interested in the self-consistent U, which we will call U_{sc}, originating from the curvature of the $DFT + U$ ground state. To compute U_{sc}, a few linear-response calculations must be performed at a finite U_{in} value, each one yielding a corresponding U_{out} value. It can be shown that there is a linear dependence between U_{in} and U_{out}, from which U_{sc} can be extrapolated[26]:

$$U_{out} = \frac{\partial^2 E_{quad}}{\partial (n^I)^2} = U_{sc} - \frac{U_{in}}{m} \tag{68}$$

E_{quad} groups all electronic terms within the $DFT + U$ functional that have quadratic dependence on the occupations, whereas m can be interpreted as an effective degeneracy of the orbitals whose population is perturbed. This procedure, which allowed us to attain an improved description of the multi-plet splittings and bonding is the one adopted here to calculate a self-consistent U parameter. Another criterion has also been explored, requesting that a linear-response calculation at a finite U value returns this same value of U at the output, for example, $U_{in} = U_{out}$. The parameter fulfilling this criterion will be hereafter denoted U_{sc}. This second criterion is not as appealing as the first one, since U_{sc} seems to be the "right definition" for self consistency.

2.15.1   Hubbard model

According to the conventional band theories, strongly correlated materials are predicted to be conductive, while they show insulating behavior when experimentally measured. This serious flaw of the band theory was pointed out by Sir Nevil Mott, who emphasized that inter-electron forces cannot be neglected, which lead to the existence of the band-gap in these falsely predicted

conductors (Mott insulators) [27]. In these "metal-insulators," the band-gap exists between bands of like character i.e., between sub-orbitals of the same orbitals, such as 3d character, which originates from crystal field splitting or Hund's rule. The insulating character of the ground state stems from the strong Coulomb repulsion between electrons that forces them to localize in atomic like orbitals (Mott localization). This Coulomb potential, responsible for localization, is described by the term "U," and when electrons are strongly localized, they cannot move freely between atoms and rather jump from one atom to another by a "hopping" mechanism between neighbor atoms, with an amplitude t that is proportional to the dispersion (the bandwidth) of the valence electronic states[28].

Since the problem is rooted down to the band model of the systems, alternative models have been formulated to describe the correlated systems. One of the simplest models is the "Hubbard" model [36,37]. The Hubbard model is able to include the so-called "on-site repulsion," which stems from the Coulomb repulsion between electrons at the same atomic orbitals, and can therefore explain the transition between the conducting and insulating behavior of these systems. Based on this model, new Hamiltonian can be formulated with an additive Hubbard term that explicitly describes electronic interactions. The additive Hubbard Hamiltonian can be written in its simplest form as follows [28]:

$$H_{Hub} = t \sum_{\langle i,j \rangle \sigma} (c^{\dagger}_{i,\sigma} c_{j,\sigma} + h \cdot c) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} \tag{69}$$

As predicted, the Hubbard Hamiltonian should be dependent on the two terms t and U, with $\langle i,j \rangle$ denoting nearest-neighbor atomic sites and $c^{\dagger}_i, c_j$, and n_i are electronic creation, annihilation, and number operators for electrons of spin on site i, respectively. The hopping amplitude t is proportional to the bandwidth (dispersion) of the valence electrons, while the on-site Coulomb repulsion term U is proportional to the product of the occupation numbers of atomic states on the same site [28]. The system's insulating character develops when electrons do not have sufficient energy to overcome the repulsion potential of other electrons on neighbor sites, i.e., when $t << U$. The ability of the DFT scheme to predict electronic properties is fairly accurate when $t >> U$, while for large U values, DFT significantly fails the HF method, which describes the electronic ground state with a variationally optimized single determinant, that cannot capture the physics of Mott insulators.

2.15.2 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 [28]. 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 [28]. It is worth mentioning that using too large values of U will over-localize the states and lead to an unphysical flattening of the appropriate bands, which unlike fitting to many other properties, will make the fit 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[28]. The value U=3.7 eV is the most suitable and adequate value for CoO and NiO[42].

2.15.3 Optimizing the U value

From the literature of this chapter, one can intuitively conclude that corrective functional LDA+U is particularly dependent on the numerical value of the effective potential U_{eff}, which is generally referred to in literature as U for simplicity. However, the U value is not known and practically is often tuned semi-empirically to make a good agreement with experimental or higher level computational results. However, the semi-empirical way of evaluating the U parameter fails to capture its dependence on the volume, structure, or the magnetic phase of the crystal, and also does not permit the capturing of changes in the on-site electronic interaction under changing physical conditions, such as chemical reactions. In order to get full advantage of this method, different procedures have been addressed to determine the Hubbard

U from first principles [28]. In these procedures, the U parameter can generally be calculated using a self-consistent and basis set in an independent way. These different ab initio approaches for calculating U have been applied to different material systems, where the U value is calculated for individual atoms. For each atom, the U value is found to be dependent on the material specific parameters, including its position in the lattice and the structural and magnetic properties of the crystal, and also dependent on the localized basis set employed to describe the on-site occupation in the Hubbard functional. Therefore, the value of effective interactions should be re-computed for each type of material and each type of LDA+U implementation (e.g., based on augmented plane waves, Gaussian functions, etc.). Most programs these days use the method presented by Cococcioni[25]; Where the values of U can be determined through a linear response method [28], in which the response of the occupation of localized states to a small perturbation of the local potential is calculated. The U is self-consistently determined, which is fully consistent with the definition of the DFT+U Hamiltonian, making this approach for the potential calculations fully ab initio. The value of U implemented by Cococcioni, is $U_{eff} = U\text{-}J$, where J is indirectly assumed to be zero in order to obtain a simplified expression[28]. Nonetheless, J can add some additional flexibility to the DFT+U calculations, but it may yield surprising results including reversing the trends previously obtained in the implemented DFT+U calculations [28].

3 Research Methodology

3.1 Materials

Soft-wares like Quantum ESPRESSO, Fortran programming, X-cry-S-den, X-m-grace, Gnu-plot and Latex(Tex-studio) and computers are essential instruments, which will be used to accomplish this study. The study is purely theoretical. The books, articles, journals, published thesis and dissertations carried out based on the thesis title are to be sources of information.

3.2 Computational Details

QUANTUM ESPRESSO is an open source implementation made available under the GNU General Public License of the DFT techniques and related codes. The central component of QE is the PWscf module, which carries out the self-consistent calculations that require most of the rest of QE to work. Calculations were carried out on a Linux 64-bit operating system. The calculations were performed using QUANTUM ESPRESSO. Such calculations are Total energy Vs Ecutwfc convergence, Total energy Vs Ecutrho convergence, Total energy Vs K-mesh convergence, Total energy Vs Lattice constant convergence, band structure and state density.

The physical (structural) and Electronic properties of CoO will be calculated using Quantum-Espresso code in the frame work of the density functional theory and Hubbard Correction. The DFT+U calculations will be performed with the generalized gradient approximations and Hubbard correction of Perdew-Burke-Ernzerhof ($GGA + U$ - $PBE + U$) exchange correlation functional, Vanderbilt ultra-soft pseudo-potential and the plane-wave basis sets will be 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 $DFT + U$, plane-wave basis sets (PW) and pseudo-potentials to represent the electron-ion interaction[40].

Flow Chart for Kohn-Sham calculations:-Schematic representation of the self-consistent loop for solution of the Kohn-Sham equations. In general one may iterate two such loops simultaneously for the two spins, with the potential for each spin depending upon the density of both spins.

$n(r)$ - initial guess

Calculate effective potential:
$$V_{KS}[n] = V_{ext}[n] + V_{Hartree}[n] + V_{XC}[n]$$

Solve Kohn-Sham equation:
$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{KS}(r)\right)\psi_i(r) = \varepsilon_i\psi_i(r)$$

Calculate the density:
$$n(r) = \sum_{i=1}^{N}|\psi_i(r)|^2$$

NO — Self Consistent?

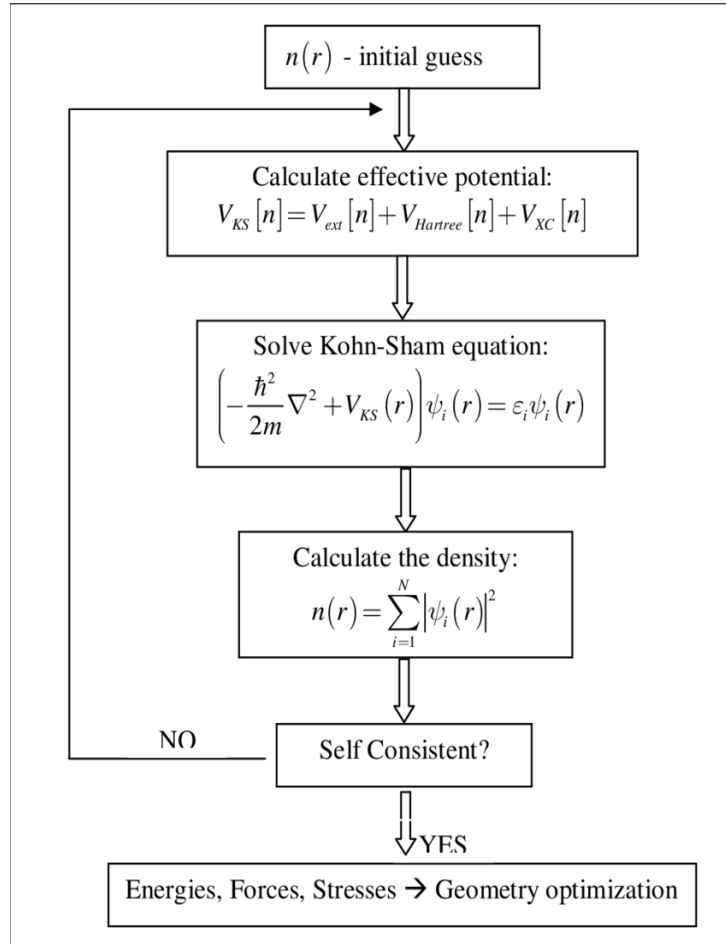↓ YES

Energies, Forces, Stresses → Geometry optimization

Figure 2: A general self-consistent scheme to solve the Kohn-Sham equation

3.3 Data Collections

Total minimum energy convergence test with respect to cut-off energy, K-point sampling and lattice constants for CoO calculations data were collected as below respectively. The first point of delta ($\triangle$)where the difference of two consecutive data become $\leq 10^{-3}$ or $\leq 10^{-4}$ were used as a point of starting for convergence.

Table 1: Data collected for convergence test of total energy Vs ecutwfc for which K-points sampling used is $3 \times 3 \times 3$

ecutwfc (Ry)	Etot(Ry)	$\triangle$	Selected point
10	-594.98202497	-78.5818546	
20	-673.56387957	-4.76008413	
30	-678.32396370	-0.19318305	
40	-678.51714675	-0.00721805	$\sqrt{}$
50	-678.52436480	-0.00170385	
60	-678.52606865	-0.00209905	
70	-678.52816770	-0.00167912	
80	-678.52984682	-0.00027523	
90	-678.53012205	-0.00011188	
100	-678.53023393	-0.00046644	
110	-678.53070037	-0.00028752	
120	-678.53098789	-0.00007880	
130	-678.53106669	-0.00026431	
140	-678.53133100	-0.00062141	
150	-678.53195241	0.00000000	

Table 2: Data collected for convergence test of total energy Vs K-Points sampling for which ecutwfc = 40 Ry, ecutrho = 320 Ry

k-Points	Etot(Ry)	$\triangle$	Selected point
$1 \times 1 \times 1$	-678.06715359	-0.46099535	
$3 \times 3 \times 3$	-678.52814894	-0.00376409	
$5 \times 5 \times 5$	-678.53191303	-0.00001713	$\sqrt{}$
$7 \times 7 \times 7$	-678.53193016	0.00010828	

k-Points	Etot(Ry)	Δ	Selected point
$9 \times 9 \times 9$	-678.53182188	0.00003151	
$11 \times 11 \times 11$	-678.53179037	0.00000916	
$13 \times 13 \times 13$	-678.53178121	0.00000137	
$15 \times 15 \times 15$	-678.53177984	-0.00000200	
$17 \times 17 \times 17$	-678.53178184	-0.00000071	
$19 \times 19 \times 19$	-678.53178255	0.00000000	

Table 3: Data collected for convergence test of total energy Vs Lattice parameter (alat) for which K-points sampling used is $5 \times 5 \times 5$, ecutwfc = 40 Ry and ecutrho = 320 Ry

alat (a.m.u)	Etot(Ry)	Δ	Selected point
7.6	-678.48301323	-0.02230699	
7.7	-678.50532022	-0.01439789	
7.8	-678.51971811	-0.00930362	
7.9	-678.52902173	-0.00393582	
8.0	-678.53295755	0.00082304	√
8.1	-678.53213451	0.00501667	
8.2	-678.52711784	0.00871173	
8.3	-678.51840611	0.01193863	
8.4	-678.50646748	0.01478669	
8.5	-678.49168079	0.00000000	

Table 1, 2 and 3 are taken with a precision of $10^{-3}, 10^{-5}$ and 10^{-4} respectively.

4 Results and Discussions

4.1 Introduction

In this chapter, the structural and electronic properties of Cobalt monoxide (CoO) is calculated within the frame work of the density functional theory with Hubbard correction. The important aspects studied in this research are the total minimum energy convergence with K-point sampling and kinetic energy cut-off wave functions (ecutwfc), lattice constant, band structure and density of states. Results are mainly presented in figures. The first results are the total minimum energy per cell with respect to ecutwfc as well as K-points sampling. Then comes the results for the equilibrium lattice constants, band structure and density of states. Graphs were plotted to obtain the optimized parameters for CoO structure with in the Perdew-Burke-Ernzerhof (PBE+U) exchange-correlation functional, Vanderbilt (ultra soft) pseudo-potentials and the plane wave basis set.

4.2 Geometrical Structure of CoO

CoO (cobalt monoxide) with rock-salt structure (NaCl structure) consists of two interpenetrating fcc sub-lattices of Co^{2+} and O^{2-}. These two sub-lattices are shifted along the body diagonal by half of its length. Thus each ion has six of the other ions as its nearest neighbors as shown in Figure below. Each cubic unit cell (not the primitive unit cell) has four Co^{2+} and four O^{2-} ions. The lattice constant of CoO is 4.24 Å. Each ion has 6 of the other kind of ions in a distance of $(\frac{1}{2})a_0 = 2.12$ Å as its nearest neighbors, 12 ions of the same kind in a distance $(\sqrt{2}/2)a_0$ as its second nearest neighbors and again 8 ions of the other kind in a distance of $(\sqrt{3}/2)a_0$ as its third nearest neighbors.
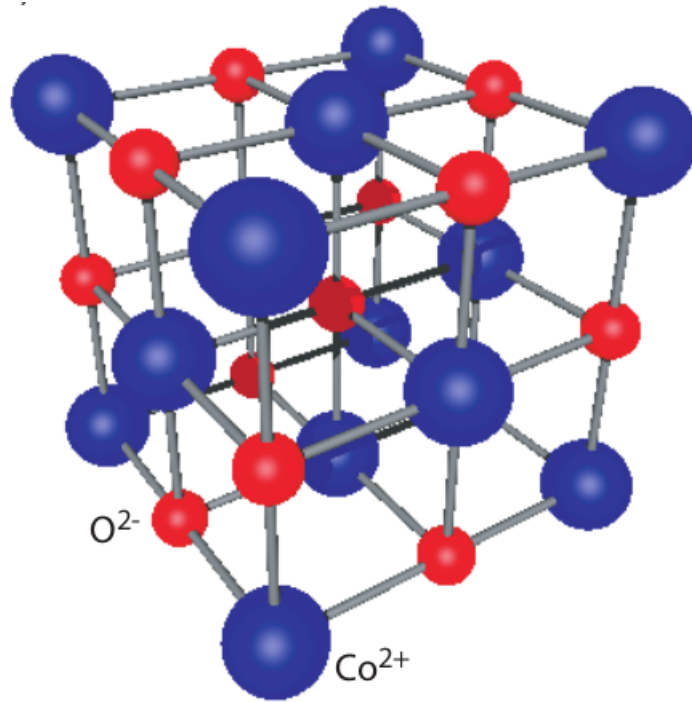

Figure 3: Unit cell of CoO, which consists of two O and Co fcc sub-lattice lattices

4.3 Convergence test of total minimum energy of CoO with respect to energy cutoff

The total minimum energy of CoO is calculated as a function of energy cutoff (ecutwfc) (i.e, The kinetic energy cut off convergence is checked by changing the cut off energy). In this case the input code used were $3 \times 3 \times 3$ K-points mesh and lattice constant of 8.0 a.m.u or 4.23 $\mathring{A}$. The calculation was done using different ecutwfc values, that range from (10-150) Ry. An increment of energy cutoff for wave function is made until the convergence is achieved (i.e., the place where the energy becomes nearly constant). To take both Ecutwfc and Ecutrho in SCF calculations, ecutrho = $8\times$ ecutwfc is used. As we can see from the graph below, the total minimum energy start to converge at 40 Ry plane wave cutoff energy, 320 Ry ecutrho and the total ground state energy had its minimum at -678.52 Ry. Moreover, the total minimum energy is monotonically decreasing with increasing energy cutoffs for wave function. Finally, the total energy against kinetic energy cut-off were plotted in graph below.
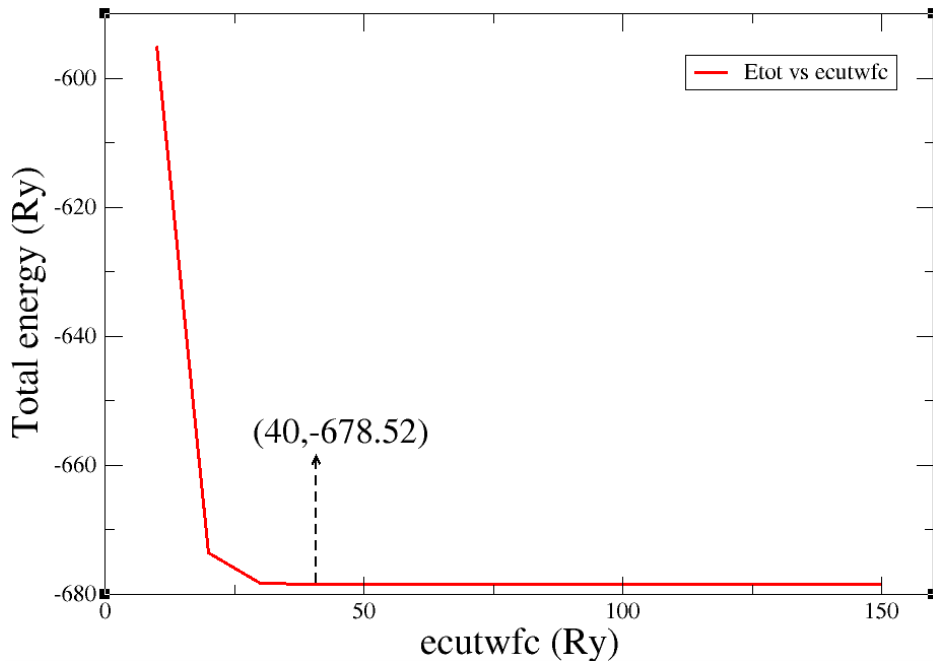
Figure 4: Total minimum energy versus Kinetic energy cut-off

4.4 Convergence test of total minimum energy of CoO with respect to K-point-sampling

For performing convergence test for K-points, SCF calculations were done using different 10 k-points values that range from $(1 \times 1 \times 1)$-to-$(19 \times 19 \times 19)$ K-points. The other variables such as lattice constant, energy cutoff, are kept fixed. The total minimum energy is calculated as a function of K- points sampling size using PWSCF code. The total energy versus K-points sample size is shown in graph below. It can be observed that the total minimum energy of CoO converged at $(5 \times 5 \times 5)$ K-points sample and the total ground state energy has its minimum at -678.53 Ry. Finally, the total energy against K-points mesh were plotted in graph below.
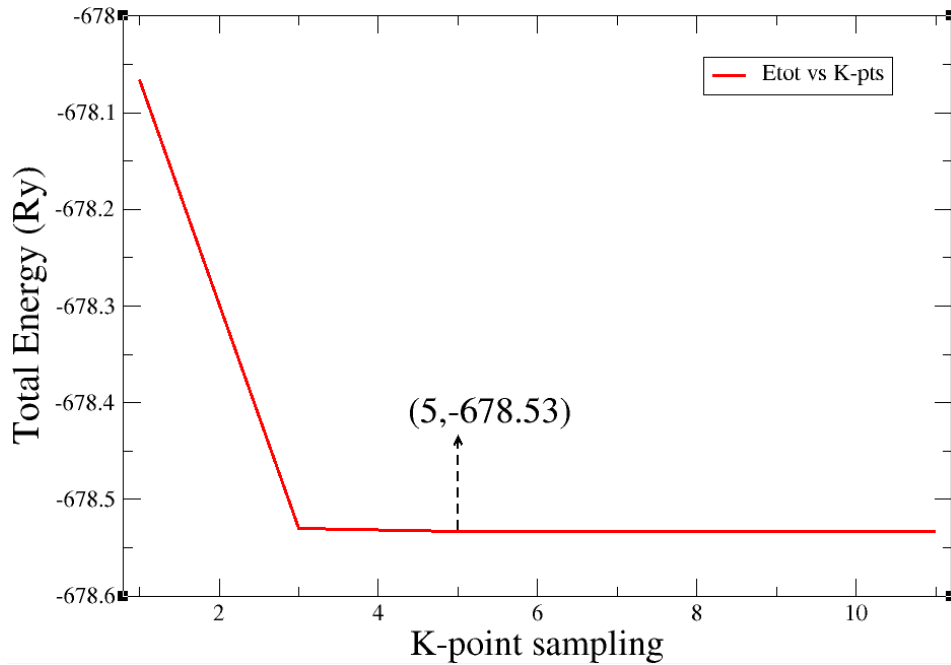
Figure 5: Total minimum energy versus K-points sampling

4.5   Lattice parameter convergence

The converged values of K-Point ($5 \times 5 \times 5$), Kinetic energy cut off (ecutwfc = 40 Ry) and charge density (ecutrho = 320 Ry) is used to perform convergence test for lattice parameter. Lattice constant ranging from $(7.6 - 8.5)$ Bohr with difference of 0.1 is taken and the lattice constant convergence reached at 8.011 Bohr ($4.24\mathring{A}$) which is the value for which we get minimum total energy and this value is used for further calculations. Finally, the total energy plotted against that lattice constant ($4.24\mathring{A}$) shown in graph below.

Table 4: Calculated and experimental values of Lattice constant

This work (Å)	Theory (Å)	Experiments (Å)
4.24	4.260[13] 4.2615[49] 4.29[45]	4.27[50]

Figure 6: Total Energy versus lattice parameter

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4.6 Band Structure Calculations

Table 5: Calculated values of Band-gap for which K-points = 5 that contain 201 points

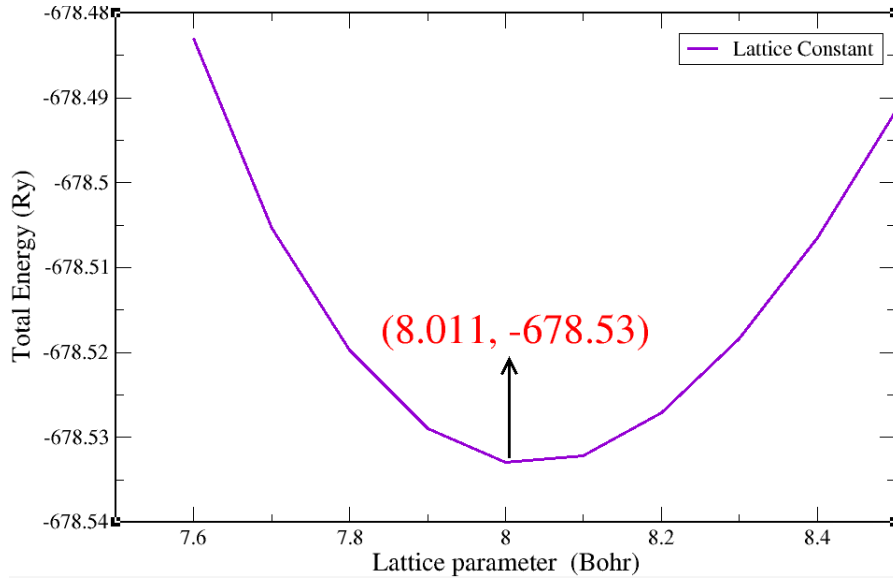| Sources	Methods	Band-gap/eV
This work	DFT+U (PBE+U)	**2.45**
Theoretical values	DFT+U (PBE+U)	**2.4**[6]
	DFT+U (PBE+U)	**2.5**[33]
	DFT+U (PBE+U)	**2.3**[42]
	DFT (PBE)	**1.55**[45]
Experiments	X-ray K-emission spectroscopy	**2.6**[31]

The band structure is a good way to visualize the wave vector-dependence of the energy states, the band-gap, and the possible electronic transitions. As shown in figure below, the maximum of valence band at X coincides with minimum of conduction band at X in left part of the plot shown by arrow. Therefore, CoO is a direct band gap with band gap shown in the table below. The minimum of the conduction band and the maximum of the valence band occur at the same momentum. The energy E of a particle is always associated with a wave-vector k (or momentum), which implies that, for any transition between bands, both energy and momentum must be conserved. When an electron absorbs enough energy to exceed the energy gap Eg, the electron can jump from the valence band into the conduction band. The source of the energy could be photons, phonon, or electric field.

At T = 0K, occupancy is "digital": No occupation of states above E_F and complete occupation of states below E_F and at T > 0K, occupation probability is reduced with increasing energy. The crystal behaves as an insulator because the allowed energy bands are all empty, for then no electrons can move in an electric field. At higher temperatures, higher energy states can be occupied, leaving more lower energy states unoccupied[35]. Know that the value of Hubbard parameter U=3.7 eV is the most suitable one in order to study electronic and structural properties of CoO[42]. As we saw from the table 5, we calculated Band-gap of CoO for Hubbard parameter (U = 3.7 eV) and we get 2.45 eV. Experimentally studied band-gap of CoO using synchrotron-excited oxygen X-ray K-emission spectroscopy, and founded value of 2.60 eV[31]. Our calculated result (2.45 eV) is close to experimental value (2.60 eV) with 5.8% error. Band-gap value of DFT shows About 37% under-estimation when we compare with our calculated DFT+U value.
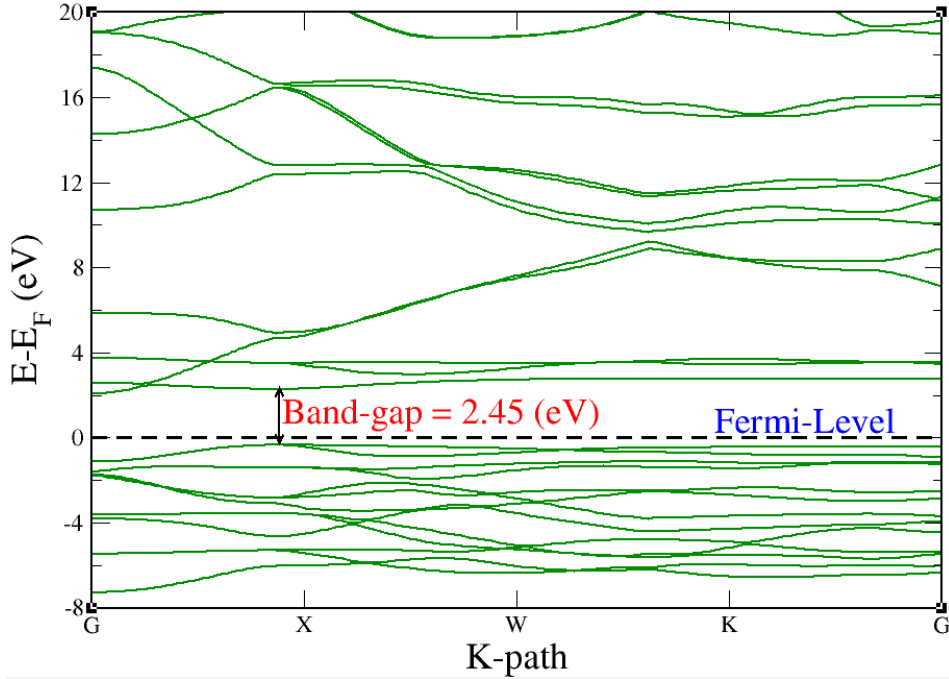
Figure 7: Band structure plot (Fermi level is indicated at 0 eV). PBE + U calculation employed.

4.7 Density of States

The band structure is a good way to visualize the wave vector-dependence of the energy states, the band-gap, and the possible electronic transitions. The actual transition probability depends on how many states are available in both the initial and final energies. The band structure is not a reliable guide here, since it only tells about the bands along high symmetry directions. What we need is the full density of states across the whole Brillouin zone, not just the special directions. We have to sample the Brillouin zone evenly, just as we do for the calculation of the ground state. The density of states (DOS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, i.e. the number of electron states per unit volume per unit energy.

The result of the number of states in a band is useful for predicting the conduction properties. If the Fermi level lies in an occupied band gap between the highest occupied state and the lowest empty state, the material will be an insulator or semiconductor. The main issue we can see from calculating the DOS of CoO is the investigation of electronic transport properties

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of CoO. The calculated energy gap of CoO is between the occupied and un-occupied energy levels is 2.35 eV. CoO show clear insulating properties and antiferromagnetic (AFM) ordering below the Neel temperature T_N.
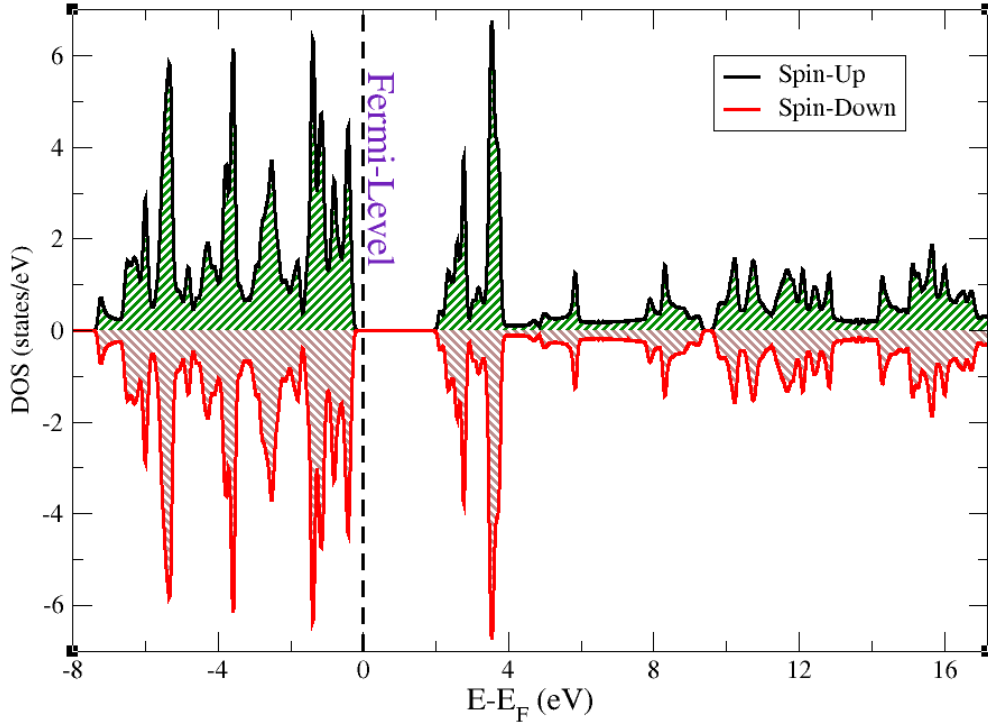
Figure 8: Density of states plot (Fermi level is indicated at 0 eV). PBE + U calculation employed.

The vertical line at $\pm(5.3,6)$ eV, $\pm(3.5,6.2)$ eV, $\pm(1.4,6.5)$ eV indicates highest occupied level from the valence band, shows the highest density of states exist there. The vertical line at $\pm(3.5,6.7)$ eV indicates highest occupied level from the Conduction band, shows the highest density of states exist there. The density of states becomes zero between -0.2 and 2.15 eV.

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4.8   Projected density of states (PDOS)

The projected density of states (PDOS) is mainly show the relative contribution of a particular atom/orbital to the total DOS. The PDOS plots also show which specific states have the highest density of states (DOS) near the valence band maximum (VBM) and conduction band minimum (CBM) in semiconductors and insulators. The Projected density of states (PDOS) of CoO originate from Co-d and O-p states. The valence band, located from $\pm$(-8 - 0) eV and states O-2p is mainly dominant state in top of valence band. The conduction band, located from (0 - 14) eV and Co-d is mainly a dominant state in the bottom of conduction band.

The output SCF calculation of spin polarized CoO shows total magnetization = 0.00 Bohr mag/cell which indicates it is Anti-ferromagnetic. The other evidence is the spin up and spin down DOS is symmetrical. In Anti-ferromagnetic, some spins go up and some down in opposite direction, that canceling each other out. Thus magnetization should be zero. From SCF calculations we get 2.75 magnetic moment/μ and the experimental value is 2.74[42] magnetic moment/μ. Our values have an error of 0.36 %.
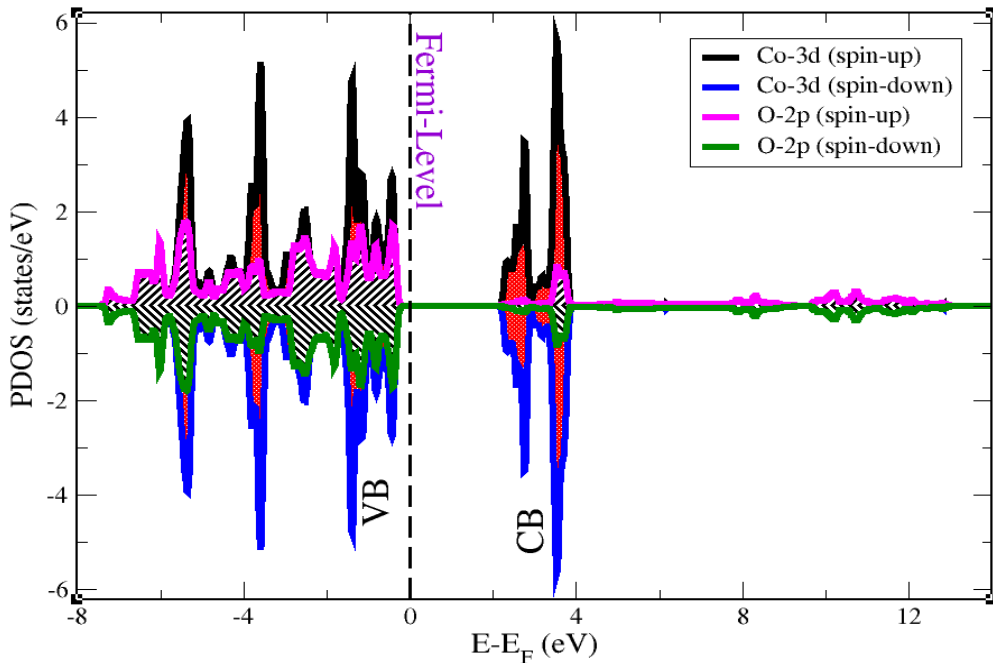

Figure 9: Projected density of states (Fermi level is indicated at 0 eV). PBE + U calculation employed.

5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this thesis, we investigated structural and electronic properties of CoO using DFT+U. The electronic and structural properties of this material were investigated within the framework of the density functional theory with Hubbard corrections (DFT+U) with the Perdew Burke-Ernzerhof and Hubbard (PBE+U) exchange-correlation functional, Vanderbilt (ultra soft) pseudo-potentials and the plane wave basis set implemented in the Quantum-ESPRESSO program package. All calculations have been carried out with Quantum Espresso package. The total minimum energy calculation is performed as a function of cutoff energy and Monk-horst pack-grid size (K-points sampling), respectively fixing the other parameters constant. The total energy convergence test is achieved, at the energy cutoff 40 Ry for the energy cutoff case and at $5 \times 5 \times 5$ k-point grid size for the K-point sampling case. The total minimum energy is -678.52 Ry for the first case and -678.53 Ry for the second case. The numerical calculation shows that the equilibrium lattice constant is 4.24 Å. This value is in good agreement with existing experimental value 4.27 Å with an error of 0.7 %. Band-gap investigation shows direct band gap of CoO is 2.45 eV. Comparing our calculated band-gap value with experimental value (2.6 eV) shows about 5.8 % error. This amount error shows as our value is somewhat in good agreement. Generally, CoO is **Mott-Hubbard insulator** under normal pressure. However, it makes an **insulator-metal** transition at high pressure.

5.2 Recommendation

In this thesis we investigate the electronic and structural properties of CoO. From those electronic calculations outstanding results are obtained. But due to shortage of time, optical properties, checking efficiency and performance in applications are not performed. So we recommend continuing with those parameters to fully tell the efficiency theoretically.

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JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
PERFORMANCE CERTIFICATE FOR MASTER'S DEGREE

Name of Student: Reduwan Bedru
Graduate Program: MSc Regular
ID No.   RM 0665/13-0
1. Course Work Performance Excellent, Very Good, Good, Satisfactory, Fail.

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

Thesis Title
INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROP-
ERTIES OF COBALT OXIDE (CoO) USING DENSITY FUNC-
TIONAL THEORY WITH HUBBARD CORRECTION (DFT+U)
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Reduwan Bedru Adem   ....
Graduate student   **Signature**   **Date**

 Email address   **redchance59@gmail.com**

 Phone   **+251 945 050 959**

Menberu Mengesha(Dr):   ....
Advisor   **Signature**   **Date**

INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF COBALT OXIDE (CoO) USING DENSITY FUNCTIONAL THEORY WITH HUBBARD CORRECTION (DFT+U)

 Degree Awarded: MSc

 College of Natural science, Jimma University