INVESTIGATION OF STRUCTURAL AND ELECTRONIC PROPERTIES OF CUPROUS OXIDE USING DENSITY FUNCTIONAL THEORY

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This is to certify that the Thesis prepared by **Jewar Teyib** Graduate Studies entitled "**Investigation of Structural and Electronic properties of Cuprous oxide using density functional theory**" in partial fulfillment of the requirements for the degree of **Master of Science** in physics complies with the regulations of the University and meets the accepted standards with respect to originality and quality. .

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Signature of Author

To my Family!

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Abstract

In this thesis the Structural and electronic properties of Cuprous Oxide (Cu_2O) is investigated with density functional theory (DFT) using Quantum Espresso package. Our study is based on Density Functional Theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set implemented in the Quantum-ESPRESSO package. The total minimum energy and the total minimum force of Cu_2O is calculated as a function of cutoff energy and K-points sampling. The total minimum energy per cell is monotonically decreased with increased 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., 50 Ry and $7 \times 7 \times 7$). The computational value of the equilibrium lattice constant is 4.32 Å. This result is in good agreement with experimental value which is 4.27 Å. Finally, discussing band structure and density of state of three dimensional Cu_2O, the electrical property of three dimensional Cu_2O is determined based on energy band gap.

Keywords: Density Functional Theory, Cuprous oxide, Structural and electronic properties.

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Chapter 1

Background of the Study

1.1 Introduction

Copper (I) Oxide or Cuprous Oxide is the inorganic compound with the formula Cu_2O. It is one of the principal oxides of copper, the other being CuO or cupric oxide. Cu_2O is composed of two Cu and an Oxygen atoms which has $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ or $[Ar]3d^{10}4s^1$ and $1s^2 2s^2 2p^4$ or $[He]2s^2 2p^4$ electron configurations respectively. It found as the reddish mineral cuprite. This red colored solid is a component of some antifouling paints. The compound can appear either yellow or red, depending on the size of the particles [1]. Copper (I) Oxide may be produced by several methods [2]. Most straight forwardly, it arises via the oxidation of copper metal. The solid of Cu_2O is diamagnetic. In terms of their coordination spheres, copper centers are 2-coordinated and the oxides are tetrahedral. It dissolves in HCl to give solution of $Cucl_2$. Cu_2O degrades to copper (II) Oxide in moist air. It crystallizes in a cubic structure with a lattice constant $a_1 = 4.2696\text{Å}$ [3].

Cu_2O is one of the most studied materials, and many experimental semiconductor applications have been demonstrated first in semiconductor, semiconductor diodes

[4] and Phonoritons [5]. The lowest exciton in Cu_2O are extremely long lived; absorption line shaped have been demonstrated with nano eV line widths, which is the narrowest bulk exciton resonance over observed [6]. It is important and useful material for many technological applications, from gas sensors to nano-electronics and nano-catalysis [7]. Cu_2O is a well examined binary oxide of copper, especially for harvesting solar energy. Schottky junctions, homo junctions and heterojunctions up to nano-composite structures based on Cu_2O have all been studied extensively during the last two decades. Density functional theory (DFT) is one of the most convenient computational tools for the prediction of the properties of different classes of materials. Based on this we studied the structural and electronic properties of Cu_2O using density functional theory implementing Quantum Espresso open source code.

1.2 Statement of the Problem

It is known that the schrödinger equation of many body problems are difficult to solve analytically. Cu_2O is a system with many electrons. Today first principle calculation which is based on solving the fundamental equations of quantum mechanics have become ubiquitous in science and condensed matter physics. So the purpose of this study was to investigate the structural and electronic property of Cu_2O using density functional theory with the help of Quantum Espresso packages.

1.3 Research Questions

- What is the total minimum energy of Cu_2O per cell with respect to cutoff energy ?
- What is the total minimum energy of Cu_2O per cell with respect to K-points sampling ?
- What is the minimum force of Cu_2O per cell with respect to cutoff energy ?
- What is the minimum force of Cu_2O per cell with respect to K-points sampling ?
- What is the lattice constant of Cu_2O ?
- What is the band structure Cu_2O ?
- What is the density state of Cu_2O ?

1.4 Objectives of the Study

1.4.1 General Objectives

The general objective of this study is to predict the electronic and structural properties of Cu_2O using density functional theory .

1.4.2 Specific Objectives

▶ To calculate the total minimum energy of Cu_2O per cell with respect to cutoff energy;

▶ To calculate the total minimum energy of Cu_2O per cell with respect to K-points sampling;

▶ To calculate the total minimum force of Cu_2O per cell with respect to cutoff energy;

▶ To calculate the total minimum force of Cu_2O per cell with respect to K-points sampling;

▶ To calculate the lattice constant of Cu_2O;

▶ To calculate band structure and density state of Cu_2O.

1.5 Significance of the Study

This study will serve as a guide for interested learners on structure and electronic properties of many body electron system of Cu_2O using new computational technique known as ab initio technique. Moreover it helps to give additional data on the electrical property of three dimensional Cu_2O. It also helps to compare the experimental results with respect to our calculation. It will give additional data on the electronic properties. It can be used as a reference material for any one who is interested to do research in this area.

1.6 Scope of the Research

Due to time and budget constraint, the study is limited to determine the total minimum energy, force, theoretical lattice constant, band structure and density state of Cu_2O using density functional theory.

Chapter 2

Review of Related Literatures

2.1 Introduction

The Schrödinger equation including time, is covered any problem in the electronic structure of matter. In most cases however, one is concerned with atoms and molecules without time-dependent interaction, so we may focus on the time-independent Schrödinger equation [8]. Solving the Schrödinger equation to obtain energies and forces, require only the number of atomic constituents as input, and should describe the chemical properties of the system with high accuracy.

2.2 Schrödinger Equation

The ultimate goal of most approaches in solid state physics and quantum chemistry is the solution of the time-independent, non-relativistic Schrödinger equation.

$$\hat{H}\Psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1\vec{R}_2, ..., \vec{R}_M) = E_i\psi_i(\vec{x}_1, \vec{x}_2, ..., \vec{x}_N, \vec{R}_1, \vec{R}_2, ..., \vec{R}_M) \qquad (2.2.1)$$

$\hat{H}$ is the Hamiltonian for a system consisting of M nuclie and N electrons.

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \frac{1}{2}\sum_{A=1}^{M}\frac{1}{M_A}\nabla_A^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}} + \sum_{A=1}^{M}\sum_{B>A}^{M}\frac{Z_A Z_B}{R_{AB}} \quad (2.2.2)$$

A separable solution of time independent Schrödinger equation has the property that every measurement of the total energy is certain to return the value E. Here, atomic units are used, $m_e = e = \hbar = 4\pi\varepsilon_0 = 1$. A and B run over the M nuclei while i and j denote the N electrons in the system. The first two terms describe the kinetic energy of the electrons and nuclei. The other three terms represent the attractive electrostatic interaction between the nuclei and the electrons and repulsive potential [9] due to the electron-electron and nucleus-nucleus interactions.

2.3 The Variational Principle for the Ground State

For a system in the state Ψ, the expectation value of the energy is given by:

$$E[\Psi] = \frac{\langle \Psi \mid \hat{H} \mid \Psi \rangle}{\langle \Psi \mid \Psi \rangle} \tag{2.3.1}$$

where, $\langle \Psi \mid \hat{H} \mid \Psi \rangle = \int \Psi^* \hat{H} \Psi d\vec{x}$

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 $E[\psi_0] = E_0$.

$$E_0 = min_{\Psi \to N} E[\Psi] = min_{\Psi \to N} \langle \Psi \mid \vec{T} + \vec{V}_{Ne} + \vec{V}_{ee} \mid \Psi \rangle \tag{2.3.2}$$

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 [10]. In other words, the ground state energy is a functional of the number of the electrons N and the nuclear potential V_{ext}:

$$E_0 = E[N, V_{ext}] \tag{2.3.3}$$

2.4 Quantum Many-Body Theory

The dynamics of a quantum system is governed by the Hamiltonian $\hat{H}$. particularly the ground state of the system, are obtained as solutions of the eigenvalue equation

$$\hat{H} \mid \Psi\rangle = E \mid \Psi\rangle, \tag{2.4.1}$$

$\langle\Psi \mid \Psi\rangle = 1$

Alternatively they are obtained as stationary solutions of the variational problem

$$\frac{\langle\Psi \mid \hat{H} \mid \Psi\rangle}{\langle\Psi \mid \Psi\rangle} \tag{2.4.2}$$

The variation (with respect to $\mid \Psi\rangle$) of the numerator on the left-hand side with the denominator kept fixed equal to unity leads immediately to eq. (2.4.1), the energy, E, thereby appearing as a Lagrange multiplier corresponding to the latter constraint. We are interested in systems of N electrons moving in a given external field and interacting with each other with pair forces. The Hamiltonian for this case consists of the kinetic energy operator $\hat{T}$, the potential operator $\hat{U}$ of the interaction of the particles with the external field, and the two-particle interaction operator $\hat{W}$:

$$\hat{H} = \hat{T} + \hat{U} + \hat{W} \tag{2.4.3}$$

The case $\hat{W} = 0$, of particles which do not interact with each other, i.e.

$$\hat{H}_0 = \hat{T} + \hat{U} \tag{2.4.4}$$

2.4.1 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation [9] plays a very important role in electronic structure calculations. The underling rationalization of this approximation is that the mass of nuclei are much heavier than electrons. Thus in most cases the nuclei move much more slowly than electrons. Hence, in many cases, one can consider the electrons are moving in a field produced by the fixed nuclei.This is the qualitative rationalization to separate the movement of electrons and nuclei.

Under this approximation the electronic Hamiltonian ($\hat{H}_{elec}$),

$$\hat{H}_{elec} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} \tag{2.4.5}$$

The solution to a Schrödinger equation involving the electronic Hamiltonian,

$$\hat{H}_{elec}\Psi_{elec} = E_{elec}\Psi_{elec} \tag{2.4.6}$$

is the electronic wave function,

$$\Psi_{elec} = \Psi_{elec}(r_i, R_A) \tag{2.4.7}$$

which describes the motion of the electrons and explicitly depends on the electronic coordinates (r_i) but parametrically on the nuclear coordinates (R_A). Furthermore, to completely specify an electron, it is necessary to assign the corresponding spin (ω), so together with the spatial coordinates, we denote these four coordinates collectively by x,

$$X = (r, \omega) \tag{2.4.8}$$

and the wave function for an N-electron system is written as

$\Psi(x1, x2, ..., xN)$. The total energy of fixed nuclei will also include the constant nuclear repulsion term leading to,

$$E_{tot} = E_{elec} + \sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} \tag{2.4.9}$$

where

$\sum_{A=1}^{M}\sum_{B>A}^{M} \frac{Z_A Z_B}{R_{AB}} = E_{nuc}$

2.5 The Hartree-Fock approximation

The Hartree-Fock(HF) method has a prominent status as it often paves the way toward more accurate calculations in modern quantum chemistry. At the same time, the HF method is also used extensively by itself to study various materials science problems, such as adsorption [11], defects in solids [12], and electronic structure of insulators [13].The Hartree-Fock method starts from using the single Slater determinant as an approximation of the wave function of the ground state of the N-electron system:

$$\mid \Psi\rangle = \mid x1, x2, ..., xa, xb, ..., xN\rangle \tag{2.5.1}$$

The HF energy expression,

$$\begin{aligned} E_{HF} = \langle \psi_{HF} \mid \hat{H} \mid \psi_{HF\rangle} = \sum_a \int x_a^\star(1)(-\frac{1}{2}\nabla^2 - \frac{Z_A}{r_{iA}})X_a(1)dx1 \\ +\frac{1}{2}\sum_{ab}\int X_a^\star(1)x_a(1)r_{12}^{-1}x_b^\star(2)x_b(2)dx1dx2 \\ -\frac{1}{2}\sum_{ab}\int X_a^\star(1)x_b(1)r_{12}^{-1}x_b^\star(2)x_a(2)dx1dx2 \end{aligned} \tag{2.5.2}$$

Each term at the right hand side in eq.(2.5.2)will be explained in the following. The first term,

$$\int x_a^\star(1)(-\frac{1}{2}\nabla^2 - \frac{ZA}{r_{iA}})x_a(1)dx1 = \langle x_a(1) \mid h \mid x_a(1)\rangle \tag{2.5.3}$$

$$h = -\frac{1}{2}\nabla^2 - \frac{Z_A}{r_{iA}}, \tag{2.5.4}$$

is the kinetic energy and potential energy for the attraction to the nuclei of a single electron. The last two terms in eq. (2.5.2) are involving two electrons, and the first one is the Coulomb term and the other one is the exchange term which arises from the antisymmetric nature of the Slater determinant. For the Coulomb term,it has the classical interpretation that it represents the Coulomb interactions between two electrons, It is convenient to define a Coulomb operator,

$$J_b(1) = \int \mid x - b(2) \mid^2 r_{12}^{-1} dx2 \tag{2.5.5}$$

Then the Coulomb term can be written as,

$$\int x_a^\star(1) x_a(1) r_{12}^{-1} x_b^\star(2) x_b(2) dx1dx2 = \langle x_a(1) | J_b(1) | x_a(1) \rangle \tag{2.5.6}$$

The exchange term, has no simple classical interpretation like the Coulomb term, but we can define an exchange operator by its effects when operating on $x_a(1)$:

$$K_b(1) x_a(1) = [\int X_b^\star(2) r_{12}^{-1} x_a(2) dx2] x_b(1) \tag{2.5.7}$$

$Kb(1)$ leads to an exchange of the variable in the two spin orbital. Furthermore, the exchange operator,$K_b(1)$ is said to be a nonlocal operator, as the results of $K_b(1)$ operating on the spin orbital x_a will depend on the value of x_a throughout all space. Then the exchange term can be written as,

$$\int X_a^\star(1) x_b(1) r_{12}^{-1} x_b^\star(2) x_a(2) dx1dx2 = \langle x_a(1) \mid K_b(1 \mid) x_a(1) \rangle \tag{2.5.8}$$

we can write the Hartree-Fock equation as an eigenvalue equation:

$$[h(1) + \sum_{b \neq a} J_b(1) - \sum_{b \neq a} K_b(1)] x_a(1) = E_a X_a(1) \tag{2.5.9}$$

The Fock operator is the sum of the operator $h(1)$ and an effective one-electron potential operator called the Hartree-Fock potential $v_{(1)}^{HF} = \sum_b J_b(1) - K_b(1)$.

So that the Hartree-Fock equation becomes:

$$f \mid x_a \rangle = E_a \mid x_a \rangle. \tag{2.5.10}$$

2.6 Density Functional Theory (DFT)

The density functional theory (DFT) is presently the most promising and also the most successful approach to compute the electronic structure of matter. Its applicability ranges from atoms, molecules and solids to nuclei and quantum and classical fluids. The DFT provides the ground state properties of a system, and the electron density plays a key role in original formulation. DFT differs from the wave function based methods by using the electron density $\rho(r)$ as the central quantity. The advantage of using the electron density over the wave function is the much reduced dimensionality. Regardless of how many electrons one has in the system, the density is always 3 dimensional. This enables DFT to be applied to much larger systems, hundreds or even thousands of atoms become possible. Partly for this reason, DFT has become the most widely used electronic structure approach today, particularly in the condensed matter physics community. Authoritative and comprehensive discussions of DFT can be found in a range of excellent review articles [14 , 15] and textbooks [16].

2.6.1 The electron density

The electron density is the central quantity in DFT. It is defined as the integral over the spin coordinates of all electrons and over all, but one of the spatial variables $(\vec{x} \equiv \vec{r}, s)$

$$\rho(\vec{r}) = N \int ... \int |\psi(\vec{x}1,\ \vec{x}2, ..., \vec{x}N)|^2 d\vec{x}1, d\vec{x}2 ... d\vec{x}N. \tag{2.6.1}$$

$\rho(\vec{r})$ determines the probability of finding any of the N electrons within volume element $d\vec{r}$.

2.6.2 The Thomas-Fermi Model

In this section, we briefly discuss the first density functional theory (1927) [17], its successes, and its limitations. In the Thomas-Fermi theory, Based on the uniform electron gas, they proposed the following functional for the kinetic energy:

$$T_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} \tag{2.6.2}$$

The energy of an atom is finally obtained using the classical expression for the nuclear nuclear potential and the electron-electron potential:

$$E_{TF}[\rho(\vec{r})] = \frac{3}{10}(3\pi^2)^{\frac{2}{3}} \int \rho^{\frac{5}{3}}(\vec{r})d\vec{r} - Z\int \frac{\rho(\vec{r})}{r}d\vec{r} + \frac{1}{2}\int\int \frac{\rho(\vec{r_1})\rho(\vec{r_2})}{r_{12}}d\vec{r_1}d\vec{r_2} \tag{2.6.3}$$

The energy is given completely in terms of the electron density. In order to determine the correct density to be included in Eq.(2.6.3), they employed a variational principle. They assumed that the ground state of the system is connected to the $\rho(\vec{r})$ for which the energy is minimized under the constraint of $\int \rho(\vec{r})d\vec{r} = N$.

F[n] is approximated by the local approximation for the (non-interacting) kinetic energy of a uniform gas, plus the Hartree energy

$$F^{TF}[n] = A_S \int d^3r n^{5/3}(r) + \frac{1}{2}\int d^3r \int d^3r' \frac{n(r)n(r')}{\mid r - r' \mid} \tag{2.6.4}$$

Several points need to be clarified.First, these expressions were developed for a spin unpolarized system, i.e., one with equal numbers of up and down spin electrons, in a spin independent external potential. Second, in the kinetic energy the power of n can be deduced by dimensional analysis, while the coefficient is chosen to agree with that of a uniform gas, yielding $A_S = (\frac{3}{10})(3\pi^2)^{2/3}$. Insertion of this approximate F into the Euler-Lagrange equation yields the Thomas-Fermi equation:

$$\frac{5}{3}A_S n^{2/3}(r) + \int d^3r' \frac{n(r')}{r - r'} + v_{ext}(r) = \mu \tag{2.6.5}$$

2.6.3 The Hohenberg-Kohn theorem

Modern density-functional theory was born in 1964 with the paper of Hohenberg and Kohn [18]. The Hohenberg-Kohn formalism of DFT is based on two theorems:

The first Hohenberg-Kohn Theorem:

The first Hohenberg-Kohn theorem demonstrates that the electron density uniquely determines the Hamiltonian operator and thus all the properties of the system. This first theorem states that the external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$.

Proof: let us assume that there were two external potential $V_{ext}(\vec{r})$ and $V'_{ext}(\vec{r})$ differing by more than a constant, each giving the same $\rho(\vec{r})$ for its ground state, we would have two Hamiltonians $\hat{H}$ and $\hat{H}'$ whose ground-state densities were the same although the normalized wave functions Ψ and Ψ' would be different. Taking Ψ' as a trial wave function for the $\hat{H}$ problem;

$$E_0 < \langle \Psi' \mid \hat{H} \mid \Psi' \rangle = \langle \Psi' \mid \hat{H}' \mid \Psi' \rangle + \langle \Psi' \mid \hat{H} - \hat{H}' \mid \Psi' \rangle = E'_0 + \int \rho(\vec{r})[V_{ext}(\vec{r}) - V'_{ext}(\vec{r})]d\vec{r}, \tag{2.6.6}$$

where E_0 and E'_0 are the ground-state energies for $\hat{H}$ and $\hat{H}'$, respectively. Similarly, taking Ψ as a trial function for the $\hat{H}'$ problem,

$$E'_0 < \langle \Psi \mid \hat{H}' \mid \Psi \rangle = \langle \Psi \mid \hat{H} \mid \Psi \rangle + \langle \Psi \mid \hat{H}' - \hat{H} \mid \Psi \rangle = E_0 + \int \rho(\vec{r})[V_{ext}(\vec{r}) - V'_{ext}(\vec{r})]d\vec{r}, \tag{2.6.7}$$

Adding Eq. (2.6.6) and Eq. (2.6.7), we would obtain $E_0 + E'_0 < E'_0 + E_0$, a contradiction, and so there cannot be two different $V_{ext}(\vec{r})$ that give the same $\rho(\vec{r})$ for their ground state. Thus, $\rho(\vec{r})$ determines N and $V_{ext}(\vec{r})$ and hence all the properties of the ground state, for example the kinetic energy $T[\rho]$, the potential energy $V[\rho]$, and the total energy $E[\rho]$. Now, we can write the total energy as

$$E[\rho] = E_{Ne}[\rho] + T[\rho] + E_{ee}[\rho] = \int \rho(\vec{r}) V_{Ne}(\vec{r}) d\vec{r} + F_{HK}[\rho], \tag{2.6.8}$$

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] \tag{2.6.9}$$

The first Hohenberg-Kohn theorem asserts that the density of any system determines all ground-state properties of the system, that is,

$$E = E[\rho] \tag{2.6.10}$$

where ρ is the ground-state density of the system. The First Hohenberg-Kohn theorem demonstrates that the density may be used in place of the potential as the basic function uniquely characterizing the system. It may be stated as: the ground-state density $n(r)$ uniquely determines the potential, up to an arbitrary constant. In the original Hohenberg-Kohn paper, this theorem is proven for densities with non-degenerate ground states. The proof is elementary, and by contradiction. Suppose there existed two potentials differing by more than a constant, yielding the same density. These would have two different ground-state wavefunctions, Ψ_1 and Ψ_2. Consider Ψ_2 as a trial wavefunction for potential $v_{ext,1}(r)$. Then, by the variational principle,

$$\langle \Psi_2 \mid \hat{T} + \hat{V}_{ext,1} \mid \Psi_2 \rangle \langle \Psi_1 \mid \hat{T} + \hat{V}_{ee} + \hat{V}_{ext,1} \mid \Psi_1 \rangle. \tag{2.6.11}$$

But since both wavefunctions have the same density, this implies

$$\langle \Psi_2 \mid \hat{T} + \hat{V}_{ee} \mid \Psi_2 \rangle \geq \langle \Psi_1 \mid \hat{T} + \hat{V}_{ee} \mid \Psi_1 \tag{2.6.12}$$

But we can always swap which wave function we call 1 and which we call 2, which reverses this inequality, leading to a contradiction, unless the total energies of the two wave functions are the same, which implies they are the same wave function by the variational principle and the assumption of non-degeneracy. An elegant constructive proof was found later by Levy [19], which automatically includes degenerate states. consider all wave fanctions Ψ which yield a certain density $n(r)$. Define the functional

$$F[n] = \min_{\Psi \rightarrow n} \langle \Psi \mid \hat{T} + \hat{V}_{ee} \mid \Psi \rangle \tag{2.6.13}$$

where the search is over all antisymmetric wave functions yielding n(r). Then, for any n(r), any wave function minimizing $\hat{T} + \hat{V}_{ee}$ is a ground-state wave function, since the ground-state energy is simply

$$E = \min_{n} \left(F[n] + \int d^3 r \upsilon_{ext}(r) n(r) \right), \tag{2.6.14}$$

from the variational principle, where the search is over all normalized positive densities. We denote the minimizing wavefunction in Eq. (2.6.13) by $\Psi[n]$. This gives us a verbal definition of the ground-state wavefunction. The exact ground-state wavefunction of density $n(r)$ is that wavefunction that yields $n(r)$ and has minimizes $T + V_{ee}$. We may also define the exact kinetic energy functional as

$$T[n] = \langle \Psi[n] \mid \hat{T} \mid \Psi[n] \rangle \tag{2.6.15}$$

and the exact electron-electron repulsion functional as

$$V_{ee}[n] = \langle \Psi[n] \mid \hat{V}_{ee} \mid \Psi[n] \rangle \tag{2.6.16}$$

.

The Second Hohenberg-Kohn Theorem:

The second Hohenberg-Kohn theorem states that $F_{HK}[\rho]$, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density. This is nothing but the variational principle:

$$E_0 \leq E[\tilde{\rho}] = T[\tilde{\rho}] + E_{Ne}[\tilde{\rho}] + E_{ee}[\tilde{\rho}] \tag{2.6.17}$$

In other words this means that for any trial density $\tilde{\rho}(\vec{r})$, which satisfies the necessary boundary conditions such as $\tilde{\rho}(\vec{r}) \geq 0$, $\int \tilde{\rho}(\vec{r}) d\vec{r} = N$, and which is associated with some $\tilde{V}_{ext}$, the energy obtained from the functional of Eq. (2.6.8) represents an upper bound to the true ground state energy E_0. E_0 results if and only if the exact ground state density is inserted in Eq. (2.6.2).

Proof: the proof of Eq. (2.6.17) makes use of the variational principle established for wave functions. We recall that any trial density $\tilde{\rho}$ defines its own Hamiltonian $\tilde{\hat{H}}$ and hence its own wave function $\tilde{\Psi}$. This wave function can now be taken as the trial wave function for the Hamiltonian generated from the true external potential V_{ext}. Thus,

$$\langle \tilde{\Psi} \mid \hat{H} \mid \tilde{\Psi} \rangle = T[\tilde{\rho}] + E_{ee}[\tilde{\rho}] + \int \tilde{\rho}(\vec{r}) V_{ext} d\vec{r} = E[\tilde{\rho}] \geq E_0[\rho] = \langle \tilde{\Psi}_0 \mid \hat{H} \mid \tilde{\Psi}_0 \rangle. \tag{2.6.18}$$

The second Hohenberg-Kohn theorem states that the functional F[n] is universal, i.e., it is the same functional for all electronic structure problems. This is evident from Eq. (2.6.13), which contains no mention of the external potential. The kinetic energy functional, $T[\phi] = \frac{1}{2} \int dx \mid \phi\prime(x) \mid^2$, is the same functional for all one-electron problems. When we evaluate the kinetic energy for a given trial orbital, it is the same for that orbital, regardless of the particular problem being solved.

second Hohenberg-Kohn theorem states that there is a single $F[n]$ which is exact for all electronic problems. The last part of the Hohenberg-Kohn theorem is the Euler-Lagrange equation for the energy. We wish to mininize $E[n]$ for a given $v_{ext}(r)$ keeping the particle number fixed. We therefore minimize $E[n] - \mu N$, and find the Euler-Lagrange equation:

$$\frac{\delta F}{\delta n(r)} + v_{ext}(r) = \mu \tag{2.6.19}$$

We can identify the constant μ as the chemical potential of the system, since $\mu = \frac{\partial E}{\partial N}$. The exact density is such that it makes the functional derivative of F exactly equal to the negative of the external potential (up to a constant). Note that it would be marvelous if we could find an adequate approximation to F for our purposes, so that we could solve Eq. (2.6.19) directly. It would yield a single integro differential equation to be solved, probably by a self-consistent procedure, for the density, which could then be normalized and inserted back into the functional $E[n]$, to recover the ground-state energy. Note also that insertion of $F^{HF}[n]$ will yield an equation for the density equivalent to the orbital HF equation.

2.6.4 The Kohn-Sham Equation

A major breakthrough in this area is provided by the Kohn-Sham construction of non-interacting electrons with the same density as the physical system, because solution of the Kohn-Sham equations produces the exact non-interacting kinetic energy, which includes almost all the true kinetic energy. We now have the theoretical tools to immediately write down these KS equations. The KS system is simply a fictitious system of non-interacting electrons [20], chosen to have the same density as the physical system. Then its orbitals are given by,

$$\left(-\frac{1}{2}\nabla^2 + V_s(r)\right)\phi_i(r) = \epsilon_i\phi_i(r), \tag{2.6.20}$$

$$V_s(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}} \tag{2.6.21}$$

and yield

$$n(r) = \sum_{i=1}^N \mid \phi_i(r) \mid^2 . \tag{2.6.22}$$

The subscript s denotes single-electron equations. But the Euler equation that is equivalent to these equations is

$$\frac{\delta T_S}{\delta n(r)} + V_S(r) = \mu, \tag{2.6.23}$$

where

$$T_S[n] = \min_{\phi \to n} \langle \Phi \mid \hat{T} \mid \Phi \rangle \tag{2.6.24}$$

is the kinetic energy of non-interacting electrons.The Kohn-Sham wavefunction of density $n(r)$ is that wave- function that yields $n(r)$ and has least kinetic energy. Obviously $T_S[n] = \langle \Phi[n] \mid \hat{T} \mid \Phi[n] \rangle$ which differs from $T[n]$.

2.7 Exchange-Correlation Energy Functional

Obviously to decompose the total xc-energy functional $E_{xc}[n]$ into an exchange part $Ex[n]$ and a correlation functional $E_c[n]$, in analogy to conventional many-body theory. the total energy E^{HF} and density n_{HF} of the Hartree-Fock (HF) approximation are reproduced if the correlation functional is completely neglected. The corresponding HF-only ground state energy functional $\tilde{E}[n]$,

$$E[n] = T_s[n] + E_{ext}[n] + E_H[n] + E_x[n], \tag{2.7.1}$$

is hence to be minimized by n_{HF},

$$E^{HF} = \tilde{E}[n_{HF}], \tag{2.7.2}$$

while for any other density one must have

$$E^{HF} < \tilde{E}[n], \tag{2.7.3}$$

$\forall n \neq n_{HF}$

2.7.1 The Local Density Approximation:

This is simplest approximation, and can be written as

$$E^{xc-LDA}[\rho(r)] = \int \rho(r)\varepsilon^{xc-unif}(\rho(r))d(r) \tag{2.7.4}$$

where $\varepsilon^{xc-unif}$ is the exchange-correlation energy per particle of the homogeneous electron gas of density ($\rho(r)$), i.e. the exchange-correlation energy density is taken to be that of a uniform electron gas of the same density. The exchange energy is known exactly and the correlation energy is obtained by fitting to the many body studies of Gell-Mann and Brueckner and Ceperly and Alder [21]. Modern LDA functional tend to be exceedingly similar, differing only in how their correlation contributions have been fitted to the many-body free electron gas data. The LDA is valid only for slowly varying densities. Experience with calculations of atoms, molecules, and solids shows that Eq.(2.7.4) can in general also be applied to these systems.

2.7.2 The Generalized Gradient Approximation

These are the second generation functionals (sitting on the second rung of Jacob's ladder) in which the gradient of the density, $\nabla\rho(r)$, at each coordinate is taken into account as well as the density itself:

$$E^{xc-GGA}[\rho(r)] = \int \rho(r)\varepsilon^{xc-unif}(\rho(r))\nabla\rho(r)d(r) \tag{2.7.5}$$

Thus GGAs are "semi-local" functionals, comprising corrections to the LDA while ensuring consistency with known sum rules. For many properties, for example geometries and ground state energies of molecules, GGAs can yield better results than the LDAs. Although for the properties of metals and their surfaces, GGA results are not necessarily superior to LDA results. The most widely used GGAs in surface physics are the PW91 [22] functional, and its close relative PBE [23].

2.7.3 Meta- GGA Functionals

These are the third generation functionals (third rung of Jacob's ladder) and use the second derivative of the density, $\nabla^2\rho(r)$, and or kinetic energy densities, $\tau_\sigma(\rho(r)) = \frac{1}{2}\sum_i \mid \nabla\phi i \mid^2$, as additional degree of freedom. In gas phase studies of molecular properties meta-GGAs such as the TPSS [24] functional have been shown to offer improved performance over LDAs and GGAs. However, a side from some benchmark studies of bulk materials and jellium surfaces, these functionals have not yet been exploited to any great extend in the solid state.

2.7.4 Hybrid Exchange Functionals

There is an exact connection between the non-interacting density functional system and the fully interacting many body system via the integration of the work done in gradually turning on the electron-electron interactions. The exact energy could be computed if one knew the variation of the density-density correlation function with the coupling constant, l. The LDA is recovered by replacing the pair correlation function with that for the homogeneous electron gas. The adiabatic integration approach suggests a different approximation for the exchange-correlation functional [25]. At $l = 0$ the non-interacting system corresponds identically to the Hartree-Fock ansatz, while the LDA and GGA functionals are constructed to be excellent approximations for the fully interacting homogeneous electron gas that is, a system with $l = 1$. It is therefore not unreasonable to approximate the integral over the coupling constant as a weighted sum of the end points that is, we might set:

$$E_{xc} \approx aE_{Fock} + bE_{xc}^{GGA} \tag{2.7.6}$$

Becke adopted this approach in the definition of a new functional with coefficients determined by a fit to the observed atomization energies, ionization potentials, proton affinities and total atomic energies for a number of small molecules [26]. The resultant (three parameter) energy functional is,

$$E_{xc} = E_{XC}^{LDA} + 0.2(E_x^{Fock} - E_X^{LDA}) + 0.72\Delta E_x^{B88} + 0.81\Delta E_C^{PW91} \tag{2.7.7}$$

Here ΔE_X^{B88} and ΔE_c^{PW91} are widely used GGA corrections [27] to the LDA exchange and correlation energies respectively.

2.8 Self consistence on the electron density

Self consistece fields are started from Solving the Kohn-Sham Equations here as,

$$\left(-\frac{1}{2}\nabla^2 + v_{ext}(r) + v_h[\rho^{in}(r)](r) + v_{xc}[\rho^{in}(r)](r)\phi_i(r)\right) = \epsilon_i\phi_i(r), \tag{2.8.1}$$

$$\rho^{out}(r) = \sum_{i\epsilon occupied} |\phi_i(r)|^2, \tag{2.8.2}$$

assuming a local exchange-correlation potential. In constructing the non-interacting KS system of electrons, the fundamental structure of the quantum mechanical equations has changed due to the introduction of the Hartree and exchange-correlation potentials. That is, the input to the KS equations now depends explicitly on the output non-linearly via the electron density. Therefore, in order to even begin solving the above system of equations, one must estimate an initial electron density to use as input, ρ^{in}. Once an initial input density has been specified, the (linear) KS equations can be solved Eq. (2.8.1) this involves digitalization of the KS Hamiltonian in some basis to find the occupied single particle orbitals. From these single particle orbital, the output electron density, ρ^{out}, is constructed using Eq. (2.8.2). The input and output densities are (in general) only equal if one has found the ground state electron density that solves the KS system. The computational journey one takes starting from an initial guess electron density, arriving at an electron density that solves the KS system is precisely what it means to achieve self-consistency. The above set of equations defines a non-linear system. That is, a map that takes an input ρ^{in} and generates an output ρ^{out} that is non-linearly related to the input,

$$F[\rho^{in}] = \rho^{out}, \tag{2.8.3}$$

where F hereafter defines the KS map. Solving this system amounts to finding a fixed point of the non-linear KS map, $\rho^* = \rho^{in} = \rho^{out}$, which is typically done using an iterative procedure. This iterative procedure acts to define a sequence, $\{\rho_1^{in}, ..., \rho_n^{in}\}$, such that $\rho^* = \rho_n^{in}$ within some defined tolerance. Ideally, this sequence is generated as robustly and efficiently as possible, which is to say, the sequence will eventually converge, and it does so such that n is minimized. In literature, this is often referred to as the self-consistent field (SCF) process, where here the self-consistent field is the density of a 3 dimensional real scalar field. It should be noted that self-consistency can be equivalently treated by defining a converging sequence of potentials, or wave functions; density has simply been chosen here. The reason being that, within CASTEP, the default method for achieving self-consistency explicitly operates by updating the electron density. This is not required, and indeed a reliable fall back method within CASTEP updates the single particle orbital directly in such a way that minimization in error is guaranteed between iterations [28]. and is extremely robust due to its variational nature, but not nearly as efficient as rivalling techniques. The default method for achieving self-consistency within castep is called density mixing, and combines the input and output densities at each iteration to estimate a new input density. However, before defining and exploring density mixing, a brief discussion of how KS DFT is implemented in software will be given. This will serve to motivate the need for and scope of improved density mixing methods.

2.9 Beyond the Local Density Approximation

At first sight a very natural extension of the LDA would be to recognize that in many systems the exchange contribution to the energy is dominant over the correlation energy and to compute the non-local exchange potential exactly as in Hartree Fock theory whilst approximating the correlation potential within the LDA [29]. This would yield a functional of the form:

$$E_{xc}(\rho) = E_{Fock} + E_c^{LDA} \tag{2.9.1}$$

The greater complexity [30] associated with the calculation of the non-local exchange potential would be offset by potentially significantly greater accuracy. However, the performance of the LDA is, in part, based on rather delicate cancelations between the exchange and correlation interactions and, in general, the use of the exact exchange interaction produces rather poor results. In the homogeneous electron gas the non-local exchange potential has effectively infinite range and its contribution to the electron-electron interaction diverges at the Fermi surface [31].

2.10 Pseudopotential

Pseudopotentials is well established that most physically interesting properties of solids are determined by the valence electrons rather than the core electrons. Mean while, the deeply bound core electrons within plane-wave basis sets, require a huge amount of basis functions for their description. To relieve this problem, the pseudopotential approximation replaces the strong ionic potential with a weaker pseudopotential. In general, there are two main purposes of the pseudopotential formalism [32]. First, to use a much weaker pseudopotential to replace core electrons which due to their deep potential need to be described by many plane-wave basis functions. Second, to eliminate the rapid oscillations of the valence electron wave function in the core region. we can see the pseudopotential is much weaker than the all-electron one and pseudo wave function has no radial node inside the core region. It is essential within the pseudopotential scheme that outside the core region, the pseudo potential and wave function becomes the same with the corresponding all electron ones. The most common general form of a pseudopotential is,

$$V_{ps} = \sum_{lm} \mid Y_{lm}\rangle V_l(r) \langle Y_{lm} \mid \tag{2.10.1}$$

where Y_{lm} are the spherical harmonics. One important class of pseudopotentials are so called norm-conserving pseudopotential. It require that the all-electron and pseudo wave function agree beyond a chosen radius (r_c) and the integrated density inside r_c

for the all electron wave function and pseudo wave function are the same (”norm conservation”).

$$\int_0^{rc} drr^2\psi^{*ps}(\vec{r}) = \int_0^{rc} drr^2\psi^{*}(\vec{r})\psi(\vec{r}) \tag{2.10.2}$$

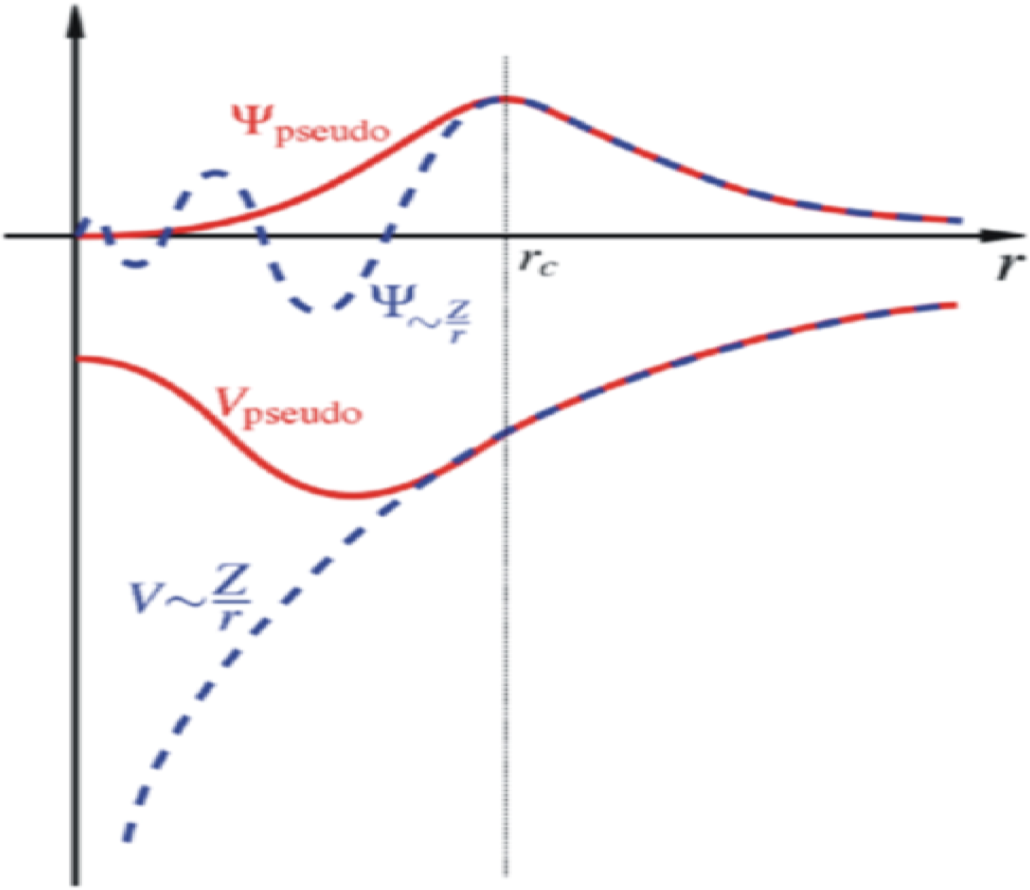

Figure 2.1: *Schematic illustration of the replacement of the all-electron wave function and core potential by a pseudo-wave function and pseudopotential*

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Chapter 3

Research Methodology

3.1 Methodology

In this section we study based on Density Functional Theory (DFT) with the Perdew-Burke- Ernzerhof (PBE) exchange-correlation functional, Vanderbilt ultra-soft pseudopotentials [33] together with the generalized gradient approximation and was calculating by using the Quantum-Espresso software package. Quantum-ESPRESSO is an integrated suite of computer codes for electronic-structure calculations and materials modeling based on density-functional theory (DFT), plane waves basis sets (PW) and pseudo potentials. It is freely available and distributed as open-source software under the terms of the GNU General Public License (GNU GPL or GPL).

Firstly, an initial guess for the electron density $\rho(r)$ is assumed, which is required for the calculation of $V_{eff}(r)$, the diagonilization of the Kohn-Sham equations, and the succeeded evaluation of $\rho(r)$ along with total minimum energy. As long as the convergence criterion is not fulfilled, the numerical procedure is continued with the last $\rho(r)$ instead of the initial guess. When criterion is satisfied, various output quantities [34] are computed.

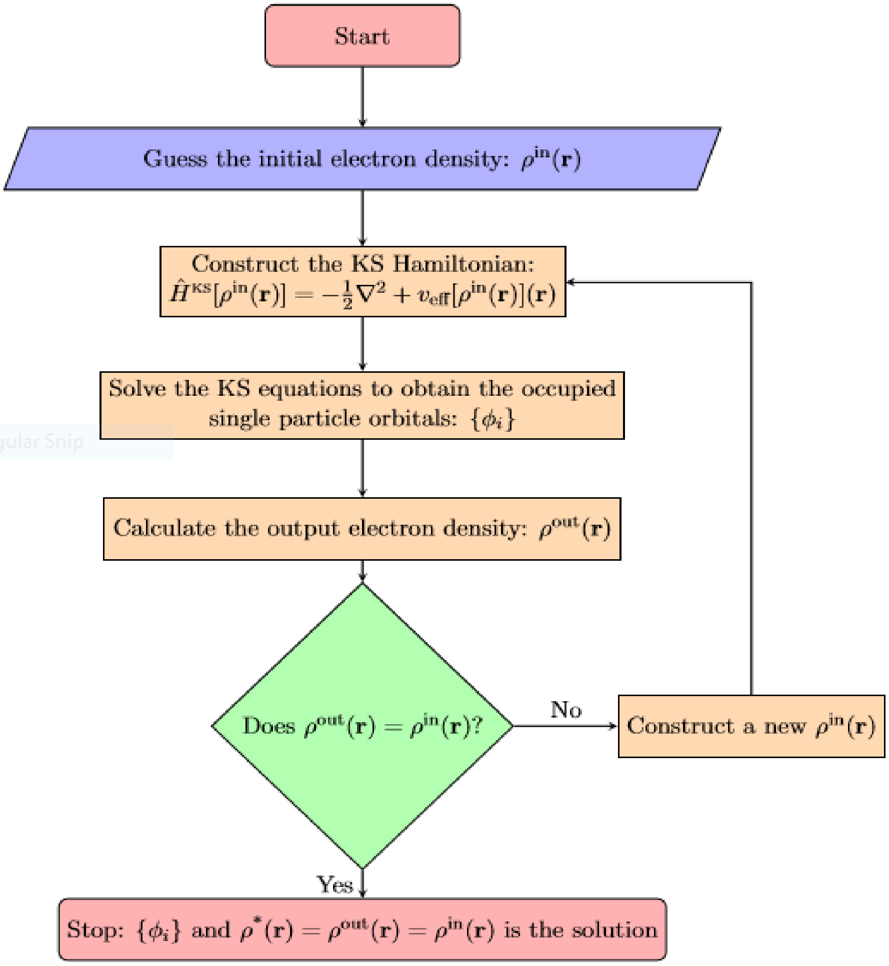

Figure 3.1: *Self Consistent Field of flow chart of the iteration scheme.*

Chapter 4

Results and Discussion

In this chapter, the structural and electronic properties of cuprous oxide (Cu_2O), is calculated within the frame work of the density functional theory. The important aspects in studied copper(I)oxide are the total minimum energy and total minimum force, lattice constant, band structure and density of state of Cu_2O. Results are mainly presented in figures. The first results are the total minimum energy per cell with respect to cutoff as well as K-points sampling and second results are total minimum forces values for three dimensional Cu_2O with respect to cutoff and K-points. In addition to this the results for the equilibrium lattice constants, band structure and density of state of Cu_2O. Graphs were plotted to obtain the optimized parameters for Cu_2O structure with in the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set.

4.1 Atoms in primitive unit cell of Cuprous oxide

The primitive unit cell of $2Cu_2O$ is shown in Fig.(4.1). A cubic unit cell with a lattice constant of a_1 = 4.27Å, i.e. the O ions are at the corners of the cube with a tetrahedral Cu_4O unit at the center, as shown in Figure(4.1) Cu_2O is consisting of two interpenetrating framework of copper ions in a face centered (Fcc) cube and oxygen ions in body-centered cube (bcc).

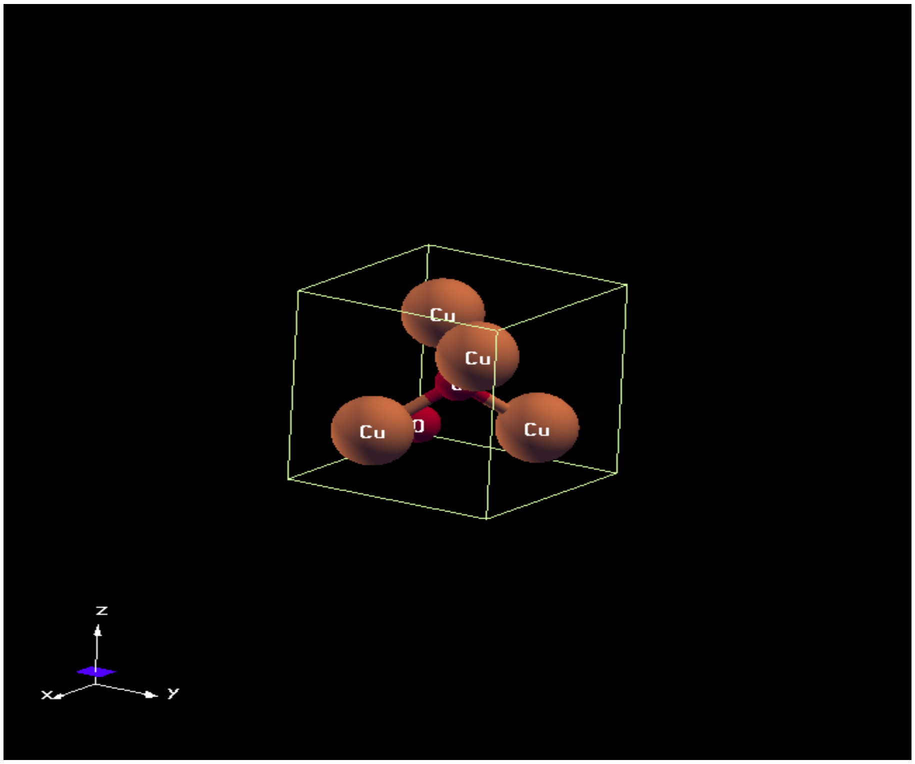

Figure 4.1: *Atoms in primitive unit cell of Cuprous oxide*

4.2 Convergence Test of Total Minimum Energy of Cu_2O with Respect to Energy Cutoff

The total minimum energy of Cu_2O is calculated as a function of energy cutoff. In this case the input code has $3 \times 3 \times 3$ K-points mesh and lattice constant of 4.27Å are fixed values. The calculation was done using different cutoff values, from 20 Ry to 120 Ry. An increment of cutoff energy for wave function is do until the convergence is achieved (i.e., the place where the energy becomes nearly constant). As we can see from the Figure 4.2, the total minimum energy converges at 50 Ry plane wave cutoff energy and the total ground state energy had its minimum at -935.56909926 Ry. Moreover, the total minimum energy is monotonically decreasing with increasing energy cutoffs for wave function. The accuracy of the ground state energy depends on the number of basis functions. However, we can get energy that close to ground state energy as the number of basis functions approaches infinity.

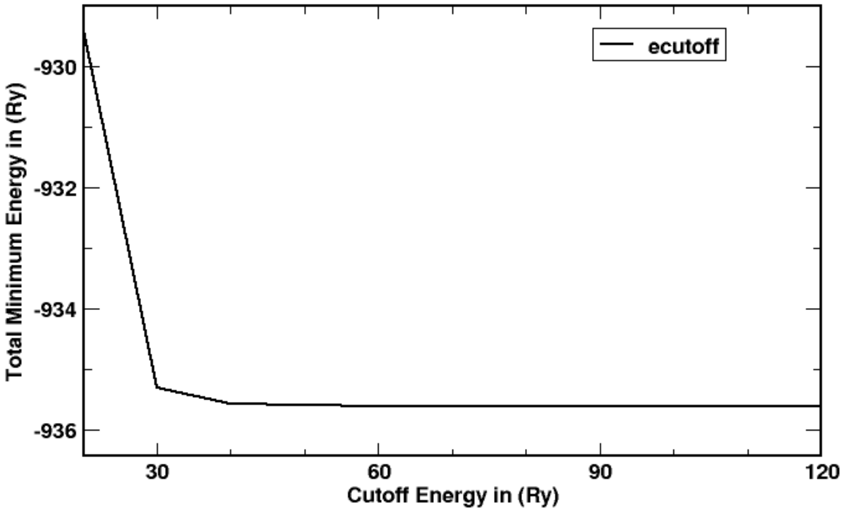

Figure 4.2: *Total minimum energy of Cu_2O with respect to energy cutoff*

4.3 Convergence Test of Total Energy of Cu_2O with Respect to K-point grid

In this case, the calculation was done using different k-point values from 3 × 3 × 3 to 9 × 9 × 9 k-points. The other variables such as lattice constant, energy cutoff, are kept constant. The total minimum energy of Cu_2O is calculated as a function of k-points grid size using PWSCF code. The total energy of Cu_2O versus k-points grid size is shown in Figure 4.3. It can be observed that the total minimum energy of Cu_2O converged at 7 × 7 × 7 K-points grid and the total ground state energy has its minimum at -929.28263773 Ry.

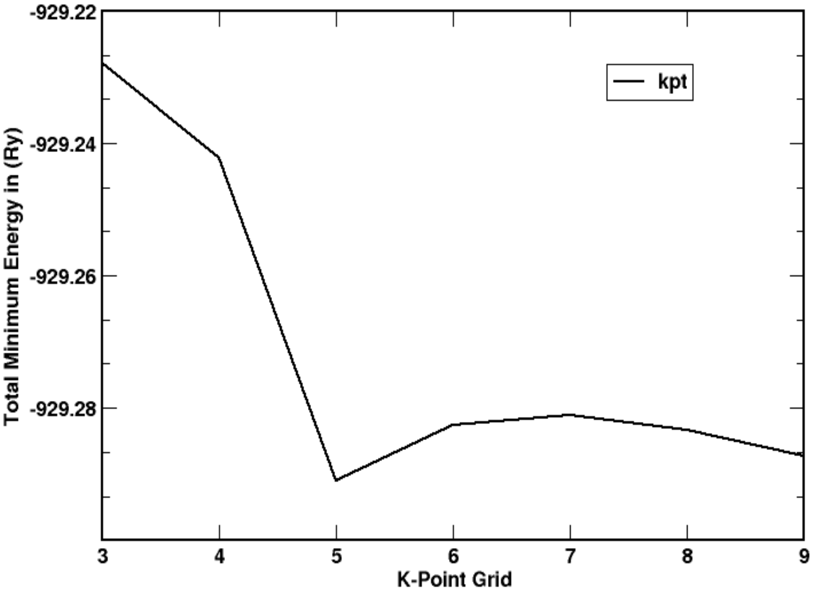

Figure 4.3: *Total minimum energy of Cu_2O with respect to k-point sampling*

4.4 Convergence Test of Total Force of Cu_2O with Respect to Energy Cutoff

In this calculations, we see that the forces on Cu_2O are zero in x, y and z directions. This is because of symmetry, which cancels out forces. However, it is possible to create forces by displacing a Cu atom $+0.05\AA$ in the z directions (fractional coordinates). Here we calculated total force on Cu_2O as a function of plane wave cutoff energy by keeping other parameters constant. For this calculation, we used the lattice constants $a = 4.27\AA$ and $3 \times 3 \times 3$ k-points grid.

In this simulation convergence is achieved when the energy cutoff is equal to 60 Ry.

A total force value at this energy cutoff is $0.174587 Ry/\AA$.

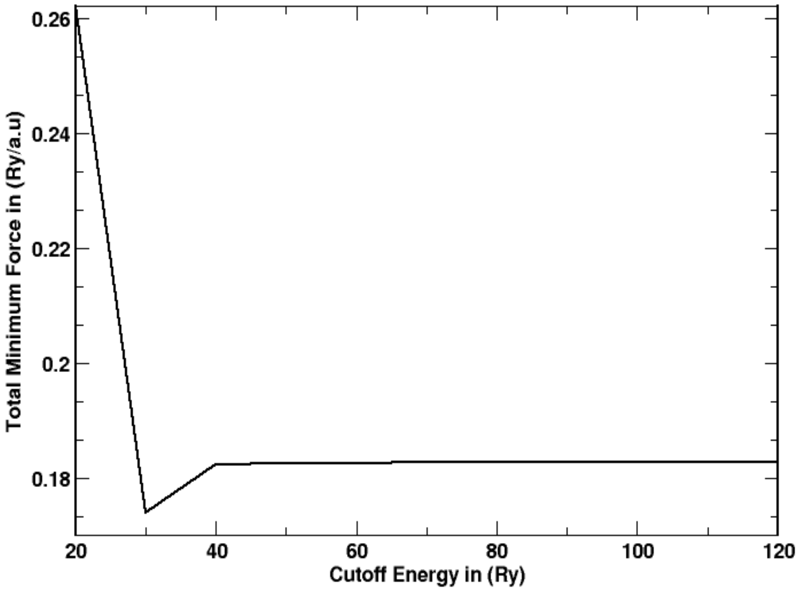

Figure 4.4: *Total force of* Cu_2O *with respect to energy cutoff*

4.5 Convergence Test of Total Force of Cu_2O with Respect to K-point grid

In this case, the calculation was done using different k-points value from $3 \times 3 \times 3$ to $10 \times 10 \times 10$. Here the other parameters are kept fixed. As it is plotted in Figure 4.5, the total force converges at the grid size of $9 \times 9 \times 9$ k-point mesh; and its value is 0.166427 $Ry/\AA$. Generally, it is true that different structural geometries will require different k-point meshes in order to reach convergence.

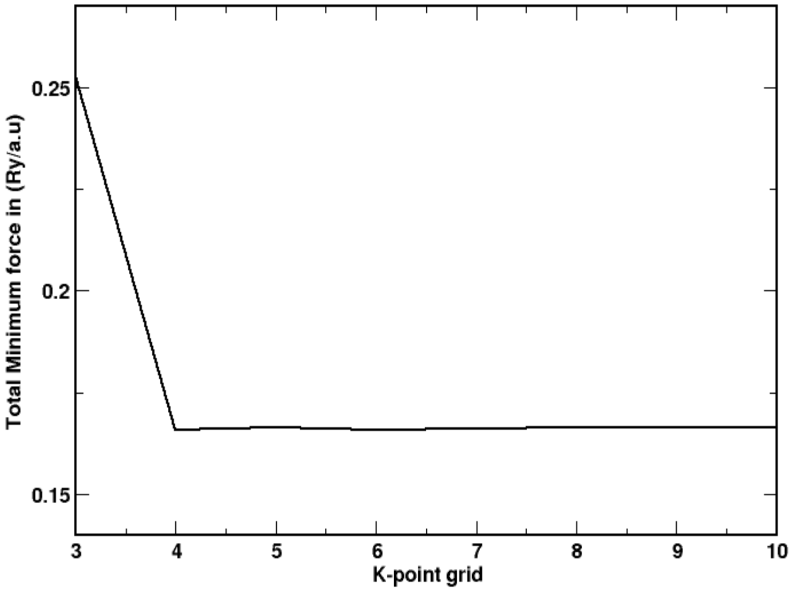

Figure 4.5: *Total minimum force of* Cu_2O *with respect to k-point sampling*

4.6 The Equilibrium Lattice Constant of Cu_2O

In figure 4.6 we show the equilibrium lattice constant of Cu_2O. To find the equilibrium lattice constant of Cu_2O we estimated serious of lattice parameters from 4.16 to 4.52. In this calculation the energy cutoff and the K-points sampling are made fixed (50 Ry and $7\times7\times7$ k-point) using the cutoff and k-point grid criteria for energy convergence respectively. The numerical calculation shows that the equilibrium lattice constant is $4.32\mathring{A}$. This result is 1.17% larger than the experimental value. This value in good agreement with experimental value of $4.27\mathring{A}$.

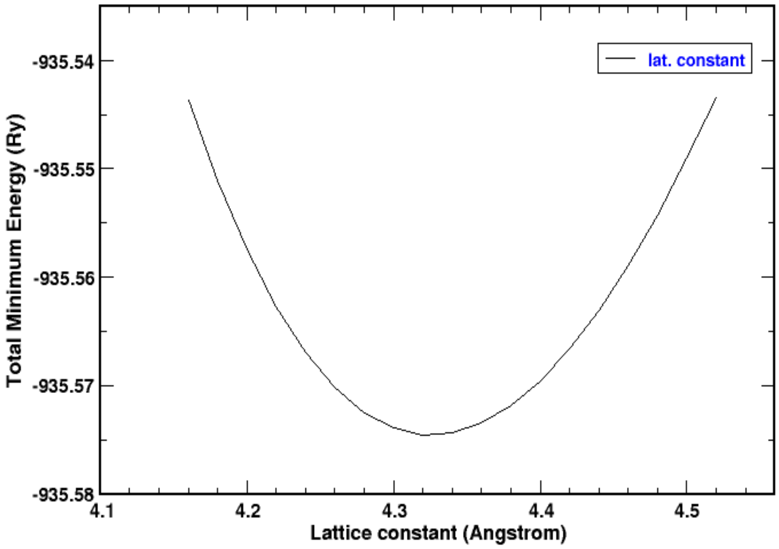

Figure 4.6: *Total energy of Cu_2O versus lattice constant*

4.7 Band Structure of Cu_2O

In this work, the energy cutoff and the BZ sampling were chosen to converge the total energy with a value of 30 Ry and we generated 71 K-points in crystal coordinate. The energy band structure of the primitive unit cell of Cu_2O is presented in Figure 4.7.

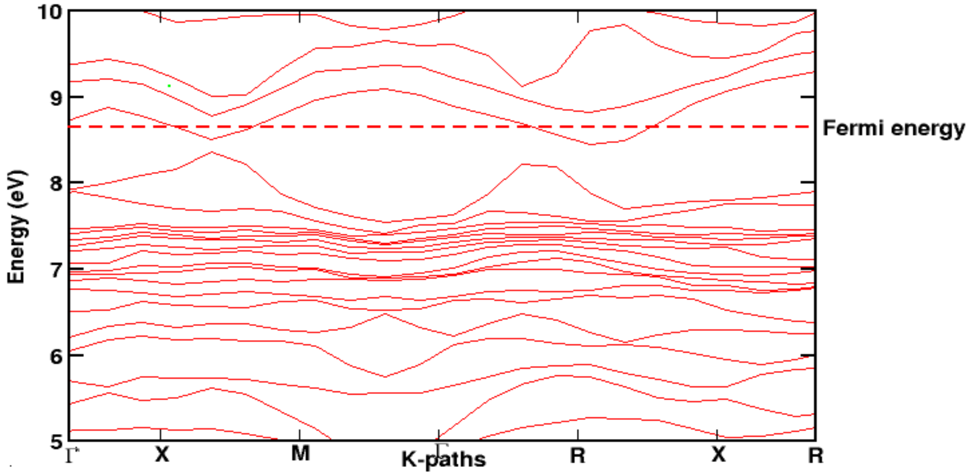

Figure 4.7: *Band Structure of primitive unit cell of 3D* Cu_2O

Energy gap between occupied and unoccupied energy levels is among the ways that we can determine the difference between electrical properties of semiconductor, insulator and metal. The calculated band gap of Cu_2O is a narrow gap semiconductor, with a direct band gap of 0.81 eV at Γ point. This value is smaller than the experimental values [3] which is 2.02 eV. It is well known that local density calculation always underestimate the band gap of a semiconductor. But, in the case of Cu_2O, the size of the gap is not settled until a much more careful analysis of optical data is performed. Our calculated value of this gap has an error of 59.9% relative to experimental value. So, Our calculation of energy gap of Cu_2O is failed in Density functional theory.

4.8 Density of State (DOS) of Cu_2O

The main issue of that calculating the density of states (DOS) of Cu_2O is the investigation of electronic transport properties of Cu_2O. The calculated DOS is displayed in Figure 4.8. It is clear that the valence band is dominated by the Cu 3d states. Cu 4p and 3s states are negligible components, while O 2s states are almost entirely absent. we see that before the Fermi level enters the conduction band. The Fermi level (E_f) was referenced at 8.6595 eV. The calculated energy gap of primitive unit cell of Cu_2O between the occupied and unoccupied energy levels was
almost 1 eV. This value is indicates our system is semiconducting materials. Semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the occupied level (valence band) and the energies of unoccupied level (conduction band).

Since so, our calculated value shows as our system is semiconductor.

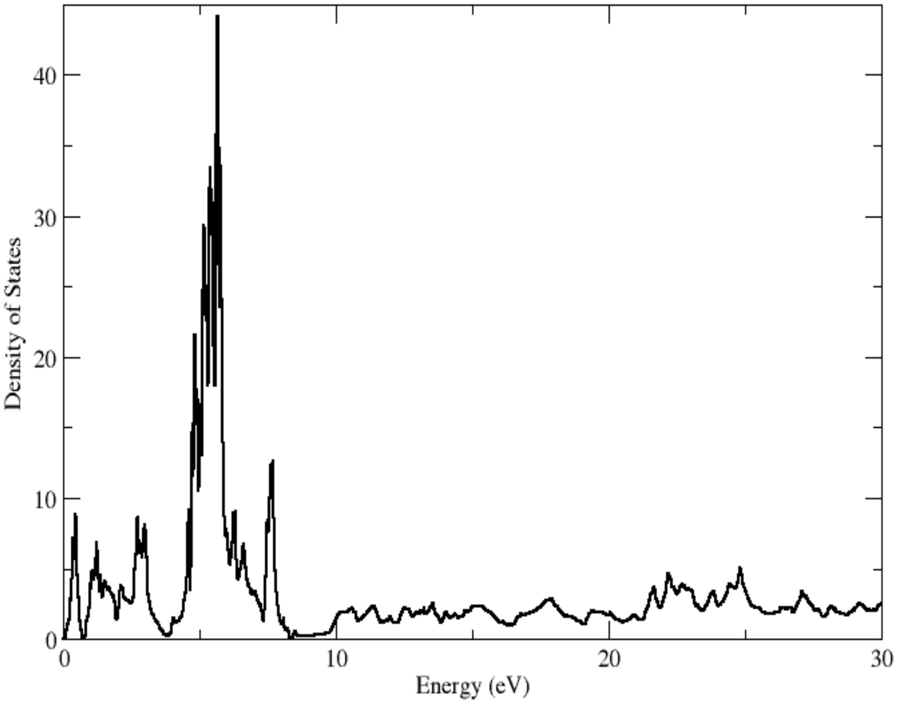

Figure 4.8: *Density of state of* Cu_2O

Chapter 5

Conclusion

In this thesis, we investigated structural and electronic properties of three dimensional Cu_2O using DFT. The electronic and structural properties of Cuprous Oxide Cu_2O was investigated within the frame work of the density functional theory (DFT) with the Perdew Burke-Ernzerhof (PBE) exchange-correlation functional, Vanderbilt (ultra soft) pseudopotentials and the plane wave basis set implemented in the Quantum-ESPRESSO open source code. All calculations have been carried out with Quantum Espresso package. The total minimum energy calculation is performed as a function of cutoff energy and K-points sampling, respectively. And the other parameters fixed. The total energy convergence test is achieved, at the energy cutoff 50 Ry for the energy cutoff case and at $7 \times 7 \times 7$ k-point grid size for the K-point sampling case. The total minimum energy is -935.56909926 Ry for the cutoff energy with respect to total energy and -929.28106386 Ry for the k point grid with respect to total energy. The total minimum force on Cu_2O as a function of cutoff energy and k-point(Monkhorst-Pack grid) is calculated by displacing Cu atom by $+0.05\AA$. Total force convergence test is achieved for the cutoff energy 60 Ry and for Monkhorst-Pack grid at $9 \times 9 \times 9$ k-point grid size. The numerical calculation shows that the equilibrium lattice constant is $4.32\mathring{A}$.

This result is 1.17% larger than the experimental value. This value is in good agreement with existing experimental value [3] which is $4.27\mathring{A}$.

In the case of investigating the band gap of Cu_2O, we shown that direct band gap of Cu_2O. This makes it interesting for applications in nanoelectronics. Also, experimentally the band gap of 3D Cu_2O is about 2.02-2.17 eV [3] and our numerical calculation shows 0.81 eV, This value is smaller than the experimental values 2.02 eV which has 59.9% of error. It is well known that Local density approximation underestimate the band gaps of semiconductor. Finally, the calculated density of states (DOS) of Cu_2O determines its electrical property. The calculated energy gap of primitive unit cell of Cu_2O between the occupied and unoccupied energy levels in case of DOS is 1 eV. This value shows as this system is semiconductor materials.

Bibliography

[1] N.N.Greenwood,A.Earnshaw,chemistry of the Elements,2nd ed.,Butterworth-Heinemann,Oxford,Uk,(1997).

[2] H.WayneRichardson "copper compounds in ullmann's Encyclopedia of Industrial chemistry (2002),Wiley-VCH,Weinheim.doi:10.1002/14346007.a07-567

[3] B.K. Meyer, A. Polity, D. Reppin, B. Becker, P. Hering, P.J Klar, T. Sander, C. Reindl, J. Benz, M. Eickhoff, C. Heiliger, M. Heinemann, J. Blaesing, A. Krost, S. Shokovets, C. Mueller, C. Ronning, Phys. Status Solidi B 249 (2012) 1487.

[4] L.O.Grondahl,Unidirectional current carrying device,parent,1927

[5] L. Hanke, D. Fröhlich, A.L.Ivanov, P.B. Littlewood, and H.stolz "LA-Phonoritons in Cu_2O "Phys.Rev.Lett.83, 4365 (1999).

[6] J. Brandt, D.Fröhlich, c.sandfort, M.Bayer, H.Stolz, and N.Naka, Ultranarrow absorption and two-phonon excitation spectroscopy of Cu_2O paraexcitons in a high magnetic field,Phys.Rev.Lett.99,217403(2007).doi:101103/PhysRevLett.99.217403.

[7] Z. Fang, D. Wang, P.Chang, W.Tseng and J.Lu, appl.Phys. Lett, 85, 5929 (2004).

[8] R. G. Parr and W. Yang , Density functional theory of atoms and molecules, Oxford university press, Inc. pp.336, 1989

[9] M. Born, R. Oppenheimer, Ann. Physik 84, 457 (1927).

[10] T. L. Gilbert, Phys. Rev. B 12, 2111 (1975)

[11] D. P. Taylor, W. P. Hess, and M. I. McCarthy, J. Phys. Chem. B 101, 7455 (1997).

[12] P. Baranek, G. Pinarello, C. Pisani, and R. Dovesi, Phys. Chem. Chem. Phys. 2, 3893 (2000).

[13] S. Casassa, A. Ferrari, M. Busso, and C.Pisani, J. Phys. Chem. B 106, 12978 (2002).

[14] P. Geerlings, F. D. Proft, and W. Langenaeker, Chem. Rev. 103, 1793 (2003).

[15] R. O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).

[16] M. R. Dreizler and E. K. U. Gross, Density Functional Theory :An Approach to the Quantum Many-Body Problem (Springer, Berlin, 1990).

[17] W. Kohn, Rev. Mod. Phys. 71, 1253 (1999).

[18] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).

[19] M. Levy, Phys. Rev. A 26, 1200 (1982)

[20] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[21] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).

[22] J. P. Perdew, K. Burke, and Y. Wang, Phys. Rev. B 54, 16533 (1992).27,58.

[23] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77,3865 (1996); 78, 1396 (1197).27,34,58,60

[24] J. M. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, Phys. Rev. Lett. 91, 146401 (2003).27

[25] D. Pines and P. Nozires, The Theory of Quantum Liquids (Benjamin, New York, 1966); J. Harris and R. O. Jones, J. Phys. F 4, 1170 (1974),O. Gunnarsson and B. I.Lundqvist, Phys. Rev. B 13, 4274 (1976).

[26] A. D. Becke, J. Chem. Phys., 98, 1372 (1993); A.D. Becke, Ibid.98, 5648 (1993)

[27] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

[28] D. Vanderbilt N. Marzari and M. C. Payne. Ensemble Density-Functional Theory for Ab Initio Molecular Dynamics of Metals and Finite-Temperature Insulators. Phys. Rev. Lett. 79 7, (1997).

[29] C. Adamo, M. Ernzerhof and G. E. Scuseria, J. Chem. Phys., 112, 2643 (2000)

[30] The exact exchange potential can be computed rather readily for periodic materials when a basis set Gaussian type orbitals is used as in the CRYSTAL software: R.Dovesi, V. R. Saunders, C. Roetti, M. Caus, N. M. Harrison, R. Orlando, C. M. Zicovich-Wilson, CRYSTAL98 User's Manual, University of Torino, Torino, 1998;(http://www.cse.dl.ac.uk/Activity/CRYSTAL).

[31] See, for instance, the discussion in Chapter 17 of, Solid State Physics, N. W. Ashcroft and N. D. Mermin, second edition, (HoltSaunders, Philadelphia, 1976)

[32] N. Troullier and Jos Luriaas Martins. Efficient pseudopotetials for plane wave calculations. Phys. Rev. B, 43:19932006, Jan 1991. doi:10.1103/PhysRevB.43.1993. URL http://link.aps.org/doi/10.1103/phyRevB.43.1993.

[33] D. Vanderbilt ,self-consistent pseudo potentials in a generalized eigenvalue formalism, Physical Review, Vol.41, pp.7892-7895. 1990

[34] K. Capelle. A Birds Eye View of Density Functional Theory , eprint arXiv. cond-mat/ 0211443, November 2002

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We the undersigned, number of the Board of Examiners of the final open defense by **Jewar Teyib Hussen** have read and evaluated his/her thesis entitled “**Investigation of Structural and electronic properties of Cuprous Oxide using Density Functional Theory**” and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfilment of the requirements for the degree Master of Science in **Physics (Condensed Matter Physics)**.

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DECLARATION

I hereby declare that this M.Sc thesis is my original work and has not been presented for a degree in any other University and that all source of materials used for the dissertation have been duly acknowledged.

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