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FIRST PRINCIPLE CALCULATION OF THE STRUCTURAL AND ELECTRONIC PROPERTIES OF COBALT USING QUANTUM ESPRESSO PACKAGE

BY

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Abbreviations of Terms

- SCF- Self Consistent Field

- DFT- Density Functional Theory

- PWSCF-Plane-Wave Self-Consistent Field

- DOS- Density of State

Acknowledgments

Abstract

In this thesis, the electronic structural properties of Cobalt (Co) was investigated with the density functional theory by using Quantum Espresso Package. The generalized gradient approximation (GGA) was used to compute the exchange correlation energy. The total energy of Cobalt is performed as a function of cutoff energy and Monk Horst- pack grid size. The results show that the total energy per cell is monotonically decreasing with increasing cutoff energy and converged 50Ry plane wave cutoff energy and the ground state energy had its minimum at -596.86253968 Ry. The total energy of Co per cell has converged at $8 \times 8 \times 8$ k-point grids with a ground state energy of -593.47698056 Ry. Besides, the optimized lattice constants of bulk Co have been determined to be a = 4.7 Bohr , c = 7.59168, and c/a = 1.615251 with respect to our computational calculation. The experimental values of bulk HCP cobalt is (a = 4.743212 Bohr, c = 7.691185 Bohr, and c/a = 1.622). The lattice constant determined using DFT calculation is compatible with an experimental result by an error of 1.29%. Moreover, different smearing calculations were made and it was observed that both mv and mp are much less dependent upon degauss and allow for faster convergence than simple Gaussian broadening. Finally, the band structure and density of state of HCP cobalt was computed. The band structure calculation shows that there is overlap between the conduction band and the valance band. This clearly shows that Co is purely metallic and zero band gap material. The density of state also shows that there is no discontinuity before and after the Fermi Level. The density of state is continuous and there is no an insulating regime.

Keywords: Cobalt,density functional theory,electronic structure,total energy

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Chapter One

1 Introduction

1.1 Background of the study

Cobalt is a chemical element with Co as its symbol and the ground state electronic configuration of $[Ar]3d^7 4s^2$. Cobalt is stable in air and is not affected by water. It is active chemically and dissolves in dilute sulfuric acid, nitric or hydrochloric acid. Alkalies have an effect on it as well. Cobalt is a hard, brittle metal. It is similar in appearance to iron and nickel. Cobalt has a magnetic permeability around two-third that of iron. Cobalt is found as a mixture of two allotropes over a wide temperature range. In its crystal structure Cobalt has a hexagonal close-packed (HCP) structure with cell parameters a = 4.743212 Bohr, c = 7.691185 Bohr, and c/a = 1.622 [1]
Cobalt forms many useful alloys. It is alloyed with iron, nickel, and other metals to form Alnico, an alloy with exceptional magnetic strength. Cobalt, chromium, and tungsten may be alloyed to form Stellite, which is used for high-temperature, high-speed cutting tools and dies. Cobalt is used in magnet steels and stainless steels. It is used in electroplating because of its hardness and resistance to oxidation. Cobalt salts are used to impart permanent brilliant blue colors to glass, pottery, enamels, tiles, and porcelain [2] Cobalt is used to make Sevres and Thenard's blue. A cobalt chloride solution is used to make a sympathetic ink. Cobalt is essential for nutrition in many animals. Cobalt-60 is an important gamma source, tracer, and radio-therapeutic agent. Cobalt is found in the minerals cobaltite, erythrite, and smaltite. It is commonly associated with ores of iron, nickel, silver, lead, and copper. Cobalt has the highest Curie Point of all metals. Cobalt also has valuable catalytic properties[3].
This study is aimed at the first principle calculation of cobalt using Density Functional Theory and Quantum Espresso packages as tools.

1.2 Statement of the problem

There is a great need for new methods to accelerate materials design. Many major industries depend on materials advancements to bring improved technologies to market. Often, these technological challenges relate to societal problems, such as cleanly generating and using energy, that are currently in need of materials breakthroughs within short time frames. However, materials innovations rarely appear overnight. Even after a new material demonstrates success in the laboratory, it takes about twenty additional years before its widespread adoption, largely due to the difficulties in building production capacities and lowering manufacturing costs from initial laboratory results [4]. It is therefore necessary to identify promising materials early on so that scale-up can begin as soon as possible. In addition, it is important to better understand the strengths and weaknesses of potential materials candidates early in the design process, as this helps avoid costly and time consuming materials optimization down the road [5-7]. In recent years, ab initio or first-principles computations (i.e., based on solving the fundamental equations of quantum mechanics have become ubiquitous in materials science, and it is nowadays hard to find a material of scientific interest that has not been studied computationally. The most popular approach to first-principles computations is currently by far density functional theory [8-12]. Although the theoretical roots of modern DFT trace back to Hohenberg–Kohn theorems of the last two decades of DFT research have been particularly important to materials design due to more accurate treatments of exchange and correlation effects of electrons, more powerful computational resources available to materials researchers, more efficient numerical algorithms. So the purpose of this study was to investigate the structural and electronic properties of Co with the help of density functional theory or ab-Initio techniques.

1.3 Research questions

This research tried to answer the following research questions:

1. What is the total energy of Co per cell with respect to cut-off energy?
2. What is the total energy of Co per cell with respect to k-point sampling?
3. What is the lattice constant of Co using DFT?
4. What does the smearing of the element looks-like?
5. What is the band structure of Co using DFT?
6. What is the density of state of cobalt?

1.4 Objectives of the study

The study has the following general and specific objectives.

1.4.1 General objective

The general objective of this study was to determine the electronic and structural properties of Co using density functional theory.

1.4.2 Specific objectives

specifically, the objectives of the study are:

1. to calculate the total energy of Co per cell with respect to cut of energy,
2. to calculate the total energy of Co per cell with respect to k-point sampling,
3. to determine the Lattice constant of Co using DFT,
4. to determine the smearing of Co,
5. to determine the band structure of Co using DFT and
6. to describe the density of state of Co

1.5 Significance of the study

This study may help to understand the first principle calculations of cobalt with respect to density functional theory and may help to get an insight of the quantities when compared to the experimental values. Moreover, it helps to understand different properties of Co which in turn helps its application in modern electronics and optical devices.

1.6 Scope of the study

This study is focused on the first principle calculation of cobalt using DFT as computational tool and focus on the total energies with respect to cut-off energy and k-point sampling and finding the lattice constant, band structure and the density of state for Co using Density Functional Theory. Besides, the study focused on finding the smearing of bulk Cobalt using Density Functional Theory.

Chapter Two

2 Literature Review

2.1 Introduction

DFT is used to study the electronic and structural properties of cells, molecules or bulk materials. The DFT provides a frame work to obtain the electronic, structural and the total energy using the concepts of quantum mechanics. DFT can also be used to address a vast variety of systems and problems in physics, chemistry, biology, and material science. Any problem in the electronic structure of matter is covered by Schrödinger equation including the time. In most cases, however, one is concerned with cells and molecules without time dependent interaction, so we may focus on the time independent Schrödinger equation [13]. Solving the Schrödinger equation to obtain energies and forces, require only the cell numbers of the constituents as input, and should describe the bonding between the cells with high accuracy. The Schrödinger equation for the complex many-cell, many-electron system is not analytically solvable, and numerical approaches have become invaluable for physics, chemistry, and materials science [14].

2.2 Schrödinger's Equation

All materials are composed of cellic nuclei and electrons. The macroscopic material properties that we observe only depend on the position of these electrons and ions. Thus knowing only the type of cells, the material is made of is in principle enough to calculate the wave function and energy of the system using the (time independent) Schrödinger equation. The stationary Schrodinger equation [15] is given by

$$H\Psi = E\Psi, \tag{1}$$

where H is the Hamiltonian and E the total energy of the system. The solution to this equation gives us the total wave function Ψ which in principle contains all wanted properties of the system and is, therefore, essential in quantum mechanics. The goal is, therefore, to find this wave function or equivalently, as in the case of DFT, the density $n(r) = |\Psi|^2$.

For the many-body problem of a system containing N electrons and K nuclei with charge Z_I the Hamiltonian calculated as [16, 17]

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

The first two terms represent the kinetic energy of the electrons and nucleons, T_e and T_n. The third term represents the electrostatic repulsion between the electrons, V_{ee}. The fourth term represents the electrostatic attraction between the electrons and nuclei, V_{ne}, and the last term between the nuclei, V_{nn}. m_e is the mass of the electrons, and M_I the mass of the cores. Z_I is the number of protons in each core, I. This looks rather complicated. It turns out that the stationary Schrödinger equation can only

be solved analytically for a one-electron system, e.g. the hydrogen cell or the ionized helium cell He^+. So, to be able to continue, certain approximations have to be made. As a first approximation one usually makes the Born-Oppenheimer approximation [18], which is justices by the fact that the nuclei (ions) are much heavier than the electrons, $M_I >> m_e$. In most cases, this justify a time-scale separation by saying that the electrons immediately adapt to changes in the positions of the ions. This means that the electronic and ionic system can be treated separately and for the electrons the ions can be regarded as fixed. We can, therefore, drop the ionic kinetic energy term and the ion-ion interaction term in the Hamiltonian and only consider the terms involving electrons.

$$H_{BO} = -\sum_{i=1}^{N} \frac{\hbar^2 \nabla_i^2}{2m_e} + \frac{1}{4\pi\epsilon_0} \sum_{i=1}^{N} \sum_{J>i}^{N} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_{I=1}^{K} \sum_{i=1}^{N} \frac{Z_I e^2}{|r_i - R_I|} \qquad (3)$$

If we denote the interaction of electron i with the ions $V_{ext}(r_i)$ and use Hartree cellic units $\hbar = m_e = e = \frac{1}{4\pi\epsilon_0} = 1$, we can write the Hamiltonian as

$$H = -\frac{1}{2} \sum_i \nabla_i^2 + \sum_i \sum_{J>i} \frac{1}{|r_i - r_j|} + \sum_i V_{ext}(r_i) \qquad (4)$$

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

2.3 Density functional theory

Density Functional Theory (DFT) is the model of choice for understanding condensed matter at low energies. It has achieved a certain status as a standard first-principles method. Indeed for many, though not all, significant condensed-matter phenomena. DFT is a powerful analytic tool for studying electronic, vibrational, magnetic, superconducting among others [19].

Density Functional Theory (DFT) is a quantum mechanical technique used in Physics and chemistry to investigate the structural and electronic properties of many body systems. DFT has proved to be highly successful in describing structural and electronic properties in a vast class of materials, ranging from cells and molecules to simple crystals and complex extended systems (including gasses and liquids). Furthermore DFT is computationally very simple. For these reasons DFT has become a common tool in first-principles calculations aimed at describing or even predicting properties of molecular and condensed matter systems [20, 21, 22].

Traditional methods in electronic structure theory, in particular Hartree-Fock theory and its descendants are based on the complicated many-electron wave function. The main objective of density functional theory is to replace the many-body electronic wave function with the electronic density as the basis quantity. Whereas the many-body wave function is dependent on 3N variables, three spatial variables for each of the N electrons, the density is only a function of three variables and is a simpler quantity to deal with both conceptually and practically [8].

The basic foundations of DFT were provided in 1964 by Hohenberg and Kohn with their two fundamental theorems. In 1965 the major milestone in the development of

DFT was introduced by Hohenberg, Kohn and Sham(HKS). They gave the proofs of these theorems by showing that DFT was an exact theory in same sense as the wave function theory [23].

2.4   The Hohenberg-Kohn theorems

The Hohenberg-Kohn formalism [23] of DFT is based on two theorems:
Theorem I
For any system of interacting particles in an external potential $V_{ext}(r)$, the potential $V_{ext}(r)$ is determined uniquely, up to a constant, by the ground state particle density, $n_0(r)$.

Theorem II
The second HK theorem defines energy functional for the system and proves that the correct ground state electron density minimizes this energy functional [24]. The energy functional of the density E[n] is:

$$E[n] = \int dr V_{ext}(r) n(r) + F[n], \tag{5}$$

where $F[n]$ is a universal functional of the density and incorporates the kinetic and the potential energy. Once the external potential $V_{ext}(r)$ has been fixed, the energy functional E[n] has its , the ground state energy E_0, at the physical ground state density $n_0(r)$:

$$E_0 = E[n_0]. \tag{6}$$

The Hohenberg-Kohn (HK) theorems have the limited purpose to prove that a universal functional of the electron density exists; they do not derive its actual expression. A direct minimization of the functional is usually not applicable, because no good expression for the kinetic energy as a functional of n is known, except for simple metals. The Kohn-Sham (KS) scheme, a reformulation of the theory based on the KS orbitals instead of the mere density, is the starting-point of most of the actual calculations.

2.5   Kohn-Sham equation

The Density Functional Theory (DFT), in the Kohn-Sham formalism, provides a powerful computational scheme, which allows to determine exactly the ground-state properties even of complex systems for interacting particles, simply solving a single particle like equation. Kohn-Sham density theory [25,26] is widely used for self consistent field electronic structure calculations of the ground state properties of cells, molecules, and solids. The Kohn and Sham equation as:

$$[-\frac{1}{2}\nabla^2 + \underbrace{\overbrace{V(r)}^{V_{ext}(r)} + V_H(r) + V_{xc}(r)}_{H_{KS}}] \psi_i(r) = \epsilon_i \psi_i(r), \tag{7}$$

where $V_{ext}(r)$ external potential,ψ_i eigenfunction.
Within the framework of Kohn-Sham DFT (KS DFT), the intractable many-body

problem of interacting electrons in a static external potential is reduced to a tractable problem of non-interacting electrons moving in an effective potential. The effective potential includes the external potential and the effects of the Coulomb interactions between the electrons, e.g., the exchange and correlation interactions. Modeling the latter two interactions becomes the difficulty within KS DFT [22].

2.6   Exchange-correlation energy

The KS DFT provides a practical procedure to solve the many-body problem by breaking the problem into a set of single-particle problems. This formalism is exact but practically still unsolvable since the many-body wave functions are still included in the exchange-correlation term $E_{XC}[n]$, whose exact form is not known.

To make the formalism useful, it is necessary to make some approximations for the exchange-correlation term $E_{XC}[n]$. The most common and straightforward approximation to $E_{XC}[n]$ is the Local Density Approximation (**LDA**) [23].
The idea of the **LDA** is assuming that the exchange-correlation energy per electron of a non-uniform system at any point in space is equal to the exchange-correlation energy per electron in a uniform electron gas having the same density at this point. In LDA the exchange-correlation functional can be written as

$$E_{XC}^{LDA}[n] = \int d\overrightarrow{r} \epsilon_{xc}[n] n(\overrightarrow{n})$$
(8)

$$\epsilon_{xc}[n] = \epsilon_{xc}^{uniform}[n].$$
(9)

By definition, the LDA is local because the exchange correlation energy $\epsilon_{xc}[n]$ at each point in space only depends on the electron density at the same point. The $\epsilon_{xc}[n]$ has been calculated and parameterized through Monte Carlo total energy calculation for a uniform electron gas with a variety of electron densities [27, 28].
Since the LDA is based on uniform electron gas, it is expected to be accurate only for systems in which the electron density varies slowly. It is clearly not suitable for the situations where the electron density undergoes rapid changes, as in the case of covalent bounded solids. To overcome this deficiency of the LDA, another form of exchanged-correlation functional has been developed, that is, the Generalized Gradient Approximation (GGA) [29-30]. The**GGA** functional depends on the local electron density as well as the spatial variation of the electron density that is represented by the density gradient. The **GGA** functional can be written as

$$E_{XC}^{GGA}[n] = \int d\overrightarrow{r} \epsilon_{xc}[n] F_{xc}[n, \overrightarrow{\nabla} n] n(r)$$
(10)

The $E_{XC}^{GGA}[n]$ is the exchange correlation energy per particle of an electron gas and F_{xc} is a functional of the electron density and its gradient. The GGA method gives better total energies, especially for small molecules, but computationally it is more time consuming than LDA [31]. Generally, **GGA** has the following advantages over **LDA** [32, 33-34]:

- GGA improves ground state properties for light cells, molecules and clusters.
- GGA predicts the correct magnetic properties of 3d transition metals such as body centered iron.

– Though GGA seems to be superior compared to LDA, it has several drawbacks. A GGA method fails to accurately treat the hydrogen bond. This defect is clearly manifested through expansion and hence softening of bonds [35].

2.7 Periodic system

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

2.7.1 Bloch's theorem

Bloch's theorem states that in a periodic solid each electronic wave function can be written as the product of cell-periodic part and wave like part[36].

$$\Psi_k(r) = e^{i\overrightarrow{k}.\overrightarrow{r}} u_k(r), \tag{11}$$

where $u_k(r)$ is periodic in space with the same periodicity as the supercell. That is, $u_k(r + n_1 a_1 + n_2 a_2 + n_3 a_3) = u_k(r)$ for any integers n_1, n_2, and n_3. This theorem means that it is possible to try and solve the Schrödinger equation for each value of k independently.

The cell-periodic part of the wave function can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are reciprocal lattice vectors of the crystal,

$$u_k(r) = \sum_G c_{i,G} e^{iG.r} \tag{12}$$

Where the reciprocal Lattice vectors G are defined by $G.l = 2\pi n$ for all l where l is a Lattice vector of the crystal and n is an integer. Therefor each electronic wave function can be written as a sum of plane waves,

$$\Psi_k(r) = \sum_G c_{i,k+G} e^{[i(k+G).r]} \tag{13}$$

The electronic wave functions at each k.point are now expressed in terms of a discrete plane wave basis set. In principle this Fourier series is infinite. However, in practice we cannot work with an infinite basis set, it has to be truncated. The number of plane waves can be restricted by placing an upper boundary to the kinetic energy of the plane waves. This boundary is called energy cut-off E_{cut}.

2.7.2 Energy Cutoffs

Our lengthy discussion of k space began with Bloch's theorem, which tells us that solutions of the Schrödinger equation for a supercell have the form

$$\Psi_k(r) = e^{i\overrightarrow{K}.\overrightarrow{r}} u_k(r) \tag{14}$$

where $u_k(r)$ is periodic in space with the same periodicity as the supercell. It is now time to look at this part of the problem more carefully. The periodicity of $u_k(r)$ means that it can be expanded in terms of a special set of plane waves:

$$u_k(r) = \sum_G c_{i,G} e^{iG.r} \tag{15}$$

where the summation is over all vectors defined by $G = n_1 b_1 + n_2 b_2 + n_3 b_3$ with integer values for n_i. These set of vectors defined by G in reciprocal space are defined so that for any real space Lattice vector l_i, $G.l = 2\pi n$.
Combining the two equations above gives

$$\Psi_k(r) = \sum_G c_{i,k+G} e^{[i(k+G).r]} \tag{16}$$

According to this expression, evaluating the solution at even a single point in k space involves a summation over an infinite number of possible values of G. This does not sound too promising for practical calculations! Fortunately, the functions appearing in the above equation have a simple interpretation as solutions of the Schrödinger equation: they are solutions with kinetic energy

$$E = \frac{\hbar^2}{2m} |k + G|^2. \tag{17}$$

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

$$E_{cut} = \frac{\hbar^2}{2m} G_{cut}^2 \tag{18}$$

The infinite sum then reduces to

$$\Psi_k(r) = \sum_{|G+k|<Gcut} c_{G+k} e^{[i(K+G)r} \tag{19}$$

This expression includes slightly different numbers of terms for different values of k. The discussion above has introduced one more parameter that must be defined whenever a DFT calculation is performed the cutoff energy, E_{cut}. In many ways, this parameter is easier to define than the k-points, as most packages will apply sensible default settings if no other information is supplied by the user. Just as with the k- points, it is good practice to report the cutoff energy used in your calculations to allow people to reproduce your results easily [37].

2.7.3   K-points sampling

The solution that is used most widely was developed by Monkhorst and Pack in 1976. Using these methods, one can obtain an accurate approximation for the electronic potential and the total energy of an insulator or semiconductor by calculating the electronic states at a very small number of k-points. The electronic potential and total energy are more difficult to calculate if the system is metallic because a dense set of k-points is required to define the Fermi surface precisely. The magnitude

of any error in the total energy due to inadequacy of the k-points sampling can always be reduced by using a denser set of k-points. The computed total energy will converge as the density of k-points increases, and the error due to the k-point sampling approaches zero.

In principle, a converged electronic potential and total energy can always be obtained provided that the computational time is available to calculate the electronic wave functions at sufficiently dense set of k-points. The computational cost of performing a very dense sampling of k-space can be significantly reduced by using the k-point total energy method [38-39].

2.7.4 Plane wave basis sets

Bloch's theorem states that the electronic wave functions at each k-point can be expanded in terms of a discrete plane-wave basis sets.

In principle, an infinite plane wave basis set is required to expand the electronic wave function. However, the coefficients $C_{i,k+G}$ for the plane waves with small kinetic energies. $\frac{\hbar^2}{2m}|K+G|^2$ are typically more important than those with large kinetic energy. Thus, the plane wave basis set can be truncated to include only plane waves that have kinetic energies less than some particular cutoff energy. If a continuum of plane wave basis states were required to expand each electronic wave function,the basis set would be infinitely large number matter how small the cutoff energy. Application of the Bloch theorem allows the electronic wave functions to expanded in terms of a discrete set of plane waves. Introduction of any energy cutoff to discrete plane wave basis set produces a finite basis set.

The truncation of plane wave basis set at a finite cutoff energy will lead to an error in the computed total energy. However, it is possible to reduced the magnitude of the error by increasing the value of cutoff energy. In principle, the cutoff energy should be increased until the calculated total energy has converged [40].

2.8 Pseudopotentials

From the earliest developments of plane-wave methods, it was clear that there could be great advantages in calculations that approximated the properties of core electrons in a way that could reduce the number of plane waves necessary in a calculation.

The most important approach to reducing the computational burden due to core electrons is to use pseudopotentials. Conceptually, a pseudopotential replaces the electron density from a chosen set of core electrons with a smoothed density chosen to match various important physical and mathematical properties of the true ion core. The properties of the core electrons are then fixed in this approximate fashion in all subsequent calculations; this is the frozen core approximation. Calculations that do not include a frozen core are called all-electron calculations, and they are used much less widely than frozen core methods.

A pseudopotential is developed by considering an isolated cell of one element, but the resulting pseudopotential can then be used reliably for calculations that place this cell in any chemical environment without further adjustment of the pseudopotential. This desirable property is referred to as the transferability of the pseudopotential.

The details of a particular pseudopotential define a energy cutoff that should be used in calculations including cells associated with that pseudopotential. Pseudopotentials requiring high cutoff energies are said to be hard, while more computationally efficient pseudopotentials with low cutoff energies are soft. The most widely used method of defining pseudopotentials is based on work by Vanderbilt; these are the ultrasoft pseudopotentials (USPPs). As their name suggests, these pseudopotentials require substantially lower cutoff energies than alternative approaches [37].

2.9 Self-consistent-field calculation

In (1897-1958) D.R. Hartree came up with the first idea of getting Self Consistent Field (SCF) solutions to a many-electron problem as a strategy to break the state. D.R. Hartree was helped by his father, William Hartree, in solving the numerical problems involved in solving the SCF problem [41,42-43]. Here we focus discussion on SCF in DFT calculations, the most time-consuming part of an SCF calculation is in matrix diagonalization, which consists of computing the self-consistent solutions of the following Kohn-Sham equation (in cellic units):

$$[-\frac{\nabla^2}{2} + V_{ext}(n(r), r)]\psi_i(r) = \varepsilon_i\psi_i,\tag{20}$$

where $\psi_i(r)$ is a wave function, ε_i is a Kohn-Sham eigenvalue. The external potential

$$V_{ext}(n(r), r) = V_{ion}(r) + V_H(n(r), r) + V_{xc}(n(r), r),\tag{21}$$

includes the ionic potential V_{ion}, the Hartree potential V_H and the exchange-correlation potential V_{xc}. In DFT the external potential depends only on $n(r)$the charge density. The charge density is given by

$$n(r) = 2\sum_{i=1}^{n_{occ}} |\psi_i(r)|^2,\tag{22}$$

where n_{occ} is the number of occupied states (half the number of valence electrons in the system) and the factor of two comes from spin multiplicity. Self-consistent iterations for solving this problem consist of starting with an initial guess of the charge density $n(r)$, then obtaining a guess for V_{ext} and solving Kohn-Sham equation for wave function $\psi_i(r)$ to update charge density and external potential. Then Kohn-Sham equation is solved again for the new wave function and the process is carried on until the difference between two consecutive external potential is below a certain tolerance (equivalently, the wave functions are close to stationary)[44].

2.10 Algorithm: self-consistent iteration

The SCF method is an iterative procedure which yields a self-consistent set of wave functions and orbital energies. It consists of the following steps.

1. An initial guess for the charge density.
2. Solve $[-\frac{\nabla^2}{2} + V_{ext}(n(r), r)]\psi_i(r) = \varepsilon_i\psi_i(r)$ for wave function $\psi_i(r)$, $i = 1, 2, ..$

3. Compute new charge density $n(r) = 2 \sum_{i=1}^{n_{occ}} |\psi_i(r)|^2$

4. Solve for new Hartree potential V_H.

5. Update V_{xc} and V_{ion}.

6. If the wave function does not satisfy the right boundary condition, we return to step 3 in order to make another guess for the energy $\varepsilon_i(r)$. If the wave function satisfies the right boundary condition, the calculation returns to step 2 and the newly obtained $\psi_i(r)$ plays the role of wave functions [45].

Chapter Three

3 Materials and Methods

3.1 Materials

The study was based on understanding the structural and electronic properties of cobalt, an intensive literature review is carried out. The main sources of literature review were the published articles, books, thesis and dissertations. Latex software and computers are additional instruments used to accomplish this project.

3.2 Methods

3.2.1 Computational method

In this thesis first-principles (ab-initio) calculations was used for performing the structural and electronic property of cobalt. This method of calculation is based on density functional theory. That is the structural and electronic property of cobalt is obtained based on the principles of density functional theory. The calculation was performed computationally using Quantum Espresso which is an open-source package for research in electronic structure, simulation and optimization. The Quantum Espresso distribution contains the core packages PWscf (Plane-Wave Self-Consistent Field) and CP (Car-Pirandello) for the calculation of electronic-structure properties within density-functional theory using a plane-wave (PW) basis set and pseudo-potentials.

Chapter Four

4 Results, and Discussion

Introduction
In this work, the structural and electronic properties of cobalt (Co) was calculated within the frame work of the density functional theory. One of the important aspects in studied cobalt was the total energy. Results are mainly presented in tables and figures under five parts. The first part presents the total energy of cobalt with respect to cutoff energy and the second part presents total energy of cobalt with respect to k-point sampling. The third part presents the equilibrium Lattice constant. The fourth part presents the smearing functions of Co and the last part presents the band structure and density of state of cobalt. The output files of the computations were used to deduce the tables of energy cutoffs, and Lattice constants against the total energies and graphs were plotted to obtain the optimized parameters for cobalt.

4.1 Total energy of Co per cell with respect to energy cutoffs

In this computation, the input parameters are $2 \times 2 \times 2 = 8$ cells and a Lattice constant of 4.7449 Bohr. To determine the total energy of Co per cell with respect to cutoff energy, different energy cutoff values from 20 Ry to 120 Ry were used and the respective total energies were computed and the result of the outputs was given by the table below.

Table 4.1: Ecut-off versus total energy

Ecut	Total Energy
20	-593.71073596
30	-596.77045398
40	-596.86052682
50	-596.86253968
60	-596.86325994
70	-596.86406201
80	-596.86497621
90	-596.86514847
100	-596.86531204
110	-596.89563505
120	-596.86579896

4.1.1 Convergence test for the total energy with respect to cutoff energy

The total energy of Co is calculated as a function of cutoff energy was investigated. The total energy of Co is monotonically decreasing with increasing energy cutoff until convergence is achieved. The total energy converges at 50 Ry plane wave cutoff energy and the ground state energy had its at -596.86253968 Ry. The plot of the cutoff energy and the total energy is shown in the figure below:
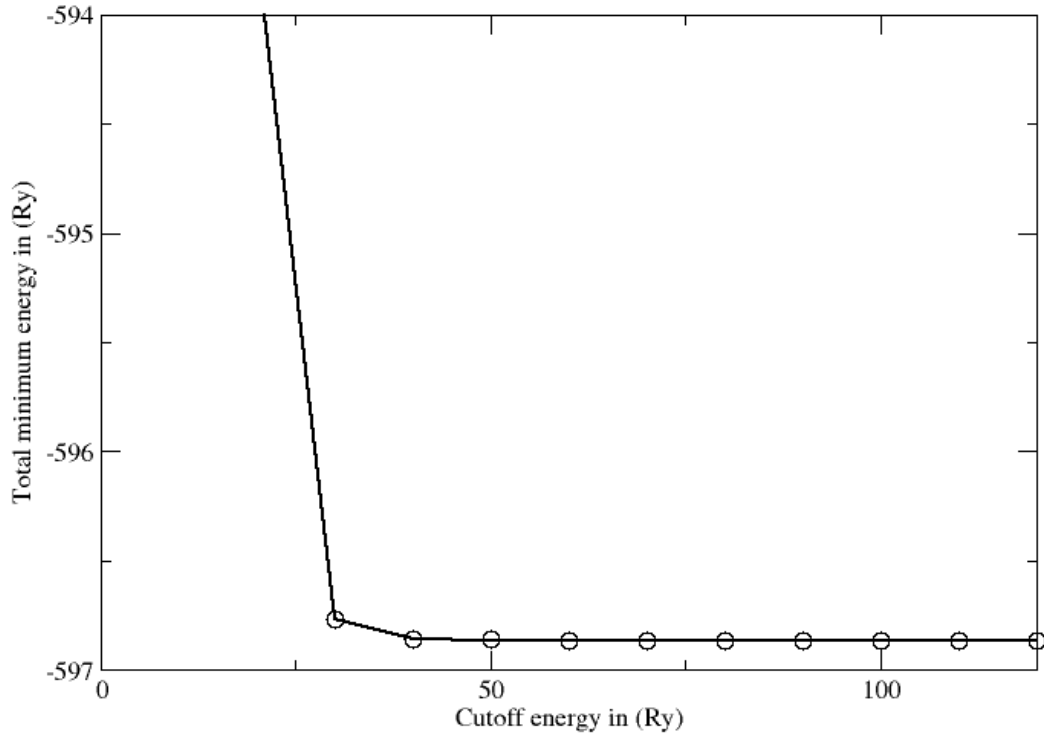
Figure 1: Ecut vs total energy

4.2 Total energy of Co per cell with respect to k-point sampling

To compute the total energy of Co per cell with respect to k-point grids, different k-point values are used starting from $2 \times 2 \times 2$ up to $12 \times 12 \times 12$ with step of 2 keeping the Cutoff energy at 20 Ry and lattice constant of 7.59168 Bohr whose out put is shown below

Table 4.2: k-point versus total energy

	Total Energy
$2 \times 2 \times 2$	-593.71073596
$4 \times 4 \times 4$	-593.55080583
$6 \times 6 \times 6$	-593.49527979
$8 \times 8 \times 8$	-593.47698056
$10 \times 10 \times 10$	-593.47945031
$12 \times 12 \times 12$	-593.49630534

4.2.1 Convergence test for total energy of Co

A convergence test of total energy for k-point sampling was performed on Co. The total energy of the Co cell was calculated using various sets of ranging from $2 \times 2 \times 2$ up to $12 \times 12 \times 12$. In each of these cases the plane wave kinetic energy cutoff of 20 Ry was used. The total energy of cobalt is calculated as a function of grid size using PWscf code. For this calculations, the other variables such as lattice constant and energy cutoff are kept constant. Convergence of the total energy is achieved at $8 \times 8 \times 8$ k-point grids and the total energy at this point is -593.47698056 Ry whose plot is shown below
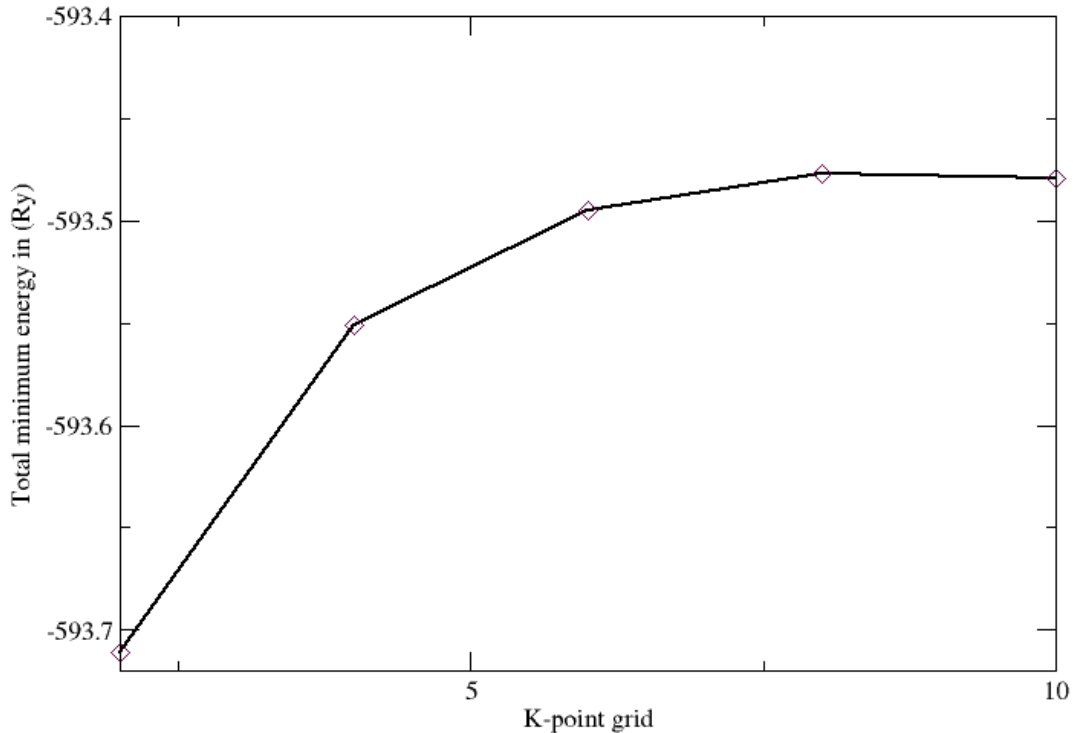

Figure 2: K-point vs Total Energy

4.3   The equilibrium lattice constant of cobalt

The equilibrium Lattice constant of Co was calculated by keeping the cutoff energy at 50 Ry and k-point grids at $8 \times 8 \times 8$. In this calculation the total energy of cobalt was computed by changing the lattice parameter from 4.2 Bohr to 5.5 Bohr in step of 0.05 and the result of the output is shown by the table below.

Table 4.3: Lattice parameter Vs total energy

Lattice parameter	Total Energy
4.2	-596.88332520
4.25	-596.90324315
4.3	-596.92114873
4.35	-596.93629454
4.4	-596.94877343
4.45	-596.95884646
4.5	-596.96691666
4.55	-596.97295561
4.6	-596.97721861
4.65	-596.97992028
4.7	-596.98116102
4.75	-596.98106221
4.8	-596.97979547
4.85	-596.97748339
4.9	-596.97428189
4.95	-596.9702578
5	-596.96552710
5.05	-596.96012041
5.1	-596.95415613
5.15	-596.94773314
5.2	-596.94088400
5.25	-596.93371280
5.3	-596.92608223
5.35	-596.91902047
5.4	-596.91164240
5.45	-596.90405842
5.5	-596.89630452

4.3.1 The equilibrium lattice constant

The total energy of cobalt was computed for different values of lattice parameters ranging from 4.2 to 5.5 Bohr under a constant cutoff energy of 50 Ry and k-point grids $8 \times 8 \times 8$. The result of the output shows that the total energy is decreasing untill the Lattice parameter is 4.7 Bohr and then start increasing from 4.75 Bohr up to 5.5 Bohr lattices. This shows that the total energy is converged at a lattice values of a= 4.7 Bohr and C/a value of 1.615251 Bohr. This was better shown in the plot below
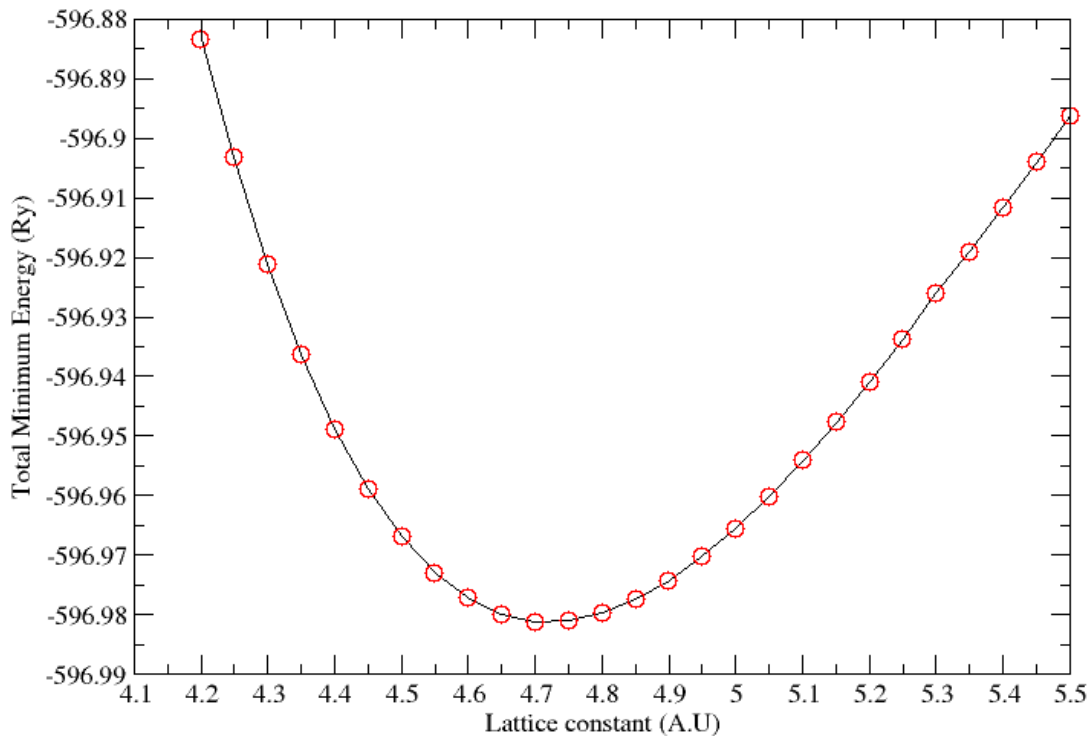

Figure 3: Lattice parameter vs Total Energy

4.4 Total energy of Co with respect to degauss/smearing

Degauss is the electronic temperature; it controls the broadening of the occupation numbers around the Fermi energy and smearing used to select occupation distribution. There are Four types of smearing; Gaussian, Methfessel-Paxton(M-P), Marzari-vanderbilt(m-v) and Fermi-Dirac smearing (fd). In this calculation, the plane wave cutoffs for wave functions are fixed at 20 Ry and Brillouin zone integration have been performed using different smearing from 0.001 up to 0.1 over shifted Monkhorst-Pack meshes of order $2 \times 2 \times 2$ for the HCP cobalt structure. In the case of smearing, the kinetic energy cutoff, the Lattice constant and the k-point grid are kept constant

4.4.1 Total energy with respect to gauss gmearing

The variation of the total energy with the change of smearing was analyzed by varing the degauss value from 0.01-0.1 and the output is given by table below.

Table 4.4: Output of smearing and total energy

Dag	T. Energy(ga)	MP	MV	FD
0.01	-593.712478	-593.7114587	-593.71146157	-593.717047
0.02	-593.7150704	-593.7117522	-593.7126236	-593.733281
0.03	-593.7188547	-593.71211	-593.7135202	-593.767266
0.04	-593.7240282	-593.7118947	-593.7121594	-593.822686
0.05	-593.7313762	-593.7106482	-593.7085632	-593.889021
0.06	-593.7416926	-593.7086581	-593.7034483	-593.962572
0.07	-593.7556938	-593.7063424	-593.698076	-594.042689
0.08	-593.7740293	-593.7042243	-593.6933783	-594.128745
0.09	-593.7964474	-593.7028233	-593.6898856	-594.22015
0.1	-593.8203524	-593.7025605	-593.6879312	-594.316384

4.4.2 Convergence test for energy

The result of the output for total energy for different values of the four types of smearing are shown below and it has been obtained that the Kinetic energy cutoff is achieved at 0.02 degauss value whose plot is shown below
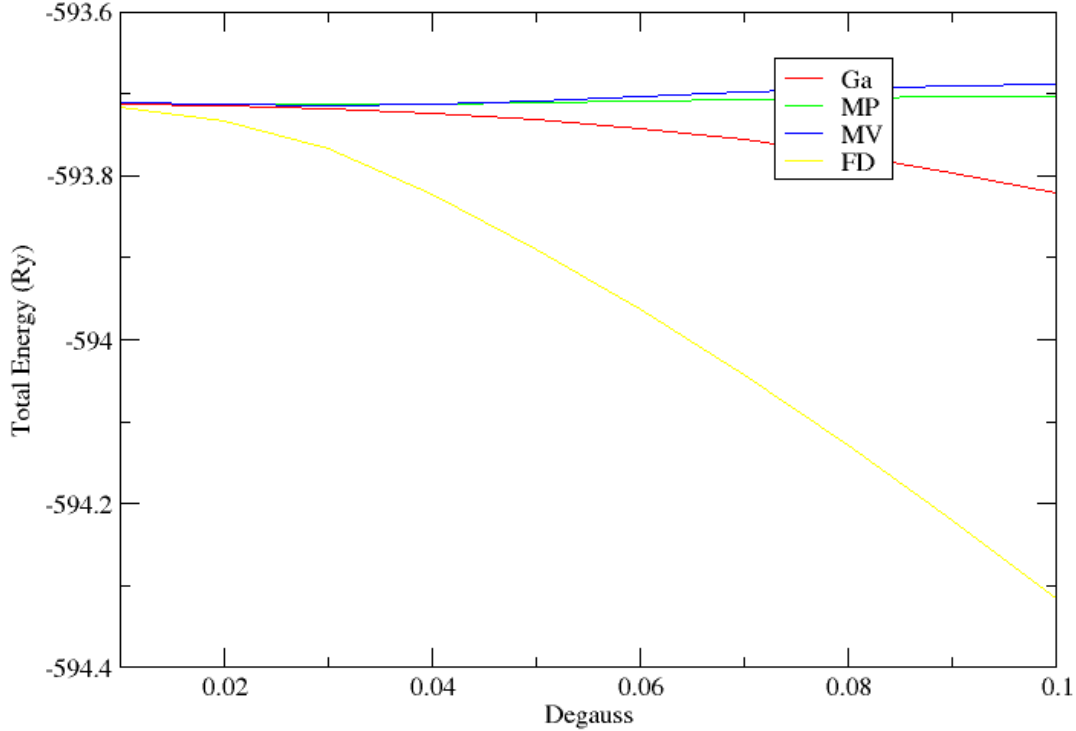
Figure 4: Smearing

Smearing describes occupied states. The procedure of smearing is to reduce the short distance fluctuations. Occupations, degauss, smearing, are particular details for the Brillioun zone integration for metals. Adding electronic temperature (degauss) smooth out the abrupt change of the occupation number and as a result total energy converges with fewer number of . Both m-v and m-p are much less dependent upon degauss and allow for faster and safer convergence than simple Gaussian broadening.

4.5 Band structure and density of state of cobalt

In solid state physics and condensed matter physics, the density of states (DOS) of a system describes the number of states that are to be occupied by the system at each level of energy. It is mathematically represented as a distribution by a probability density function, and it is generally an average over the space and time domains of the various states occupied by the system. The density of states is directly related to the dispersion relations of the properties of the system. High DOS at a specific energy level means that many states are available for occupation.

4.5.1 Band structure of cobalt

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties. A

useful way to differentiate between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitation can bridge the gap.The band structure of Cobalt is shown below
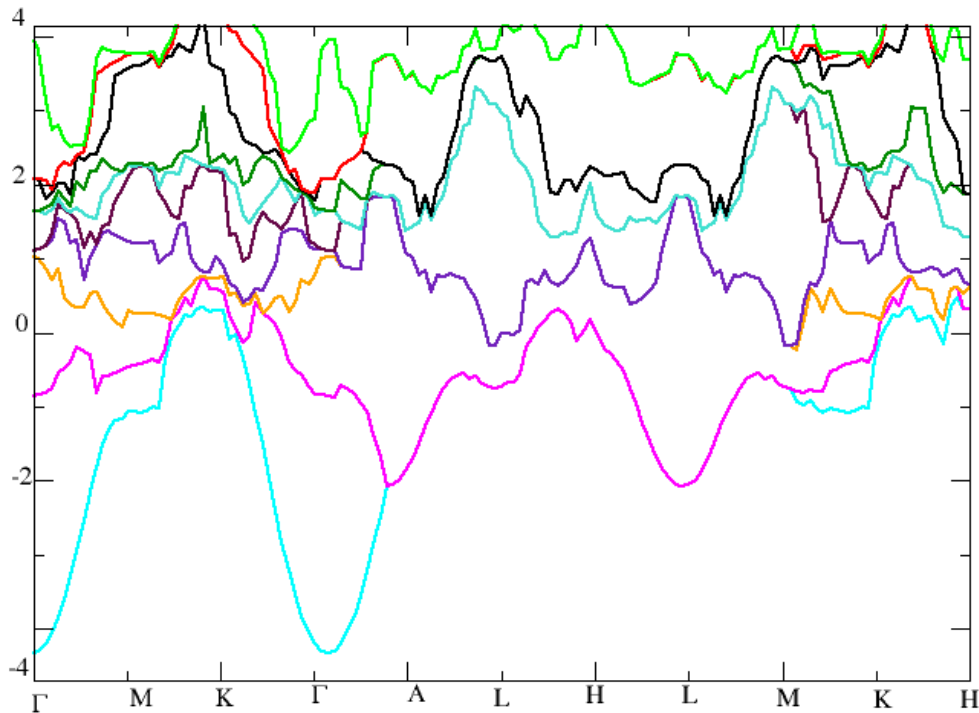
Figure 5: Band structure

From figure 5 one can observe that there is overlap between the valance and conduction bands. That is Co is pure metal and zero band gap material.

4.5.2 Density of State of Cobalt

Generally, the density of states of matter is continuous. In isolated systems however, such as atoms or molecules in the gas phase, the density distribution is discrete, like a spectral density. Local variations, most often due to distortions of the original system, are often called local density of states (LDOS). The DOS of cobalt is given below

Calculating the density of state of materials can also helps to differentiate either a material is a conductor or insulator. From figure 6 one can understand that the density of state is continious and there is no insulating regime.
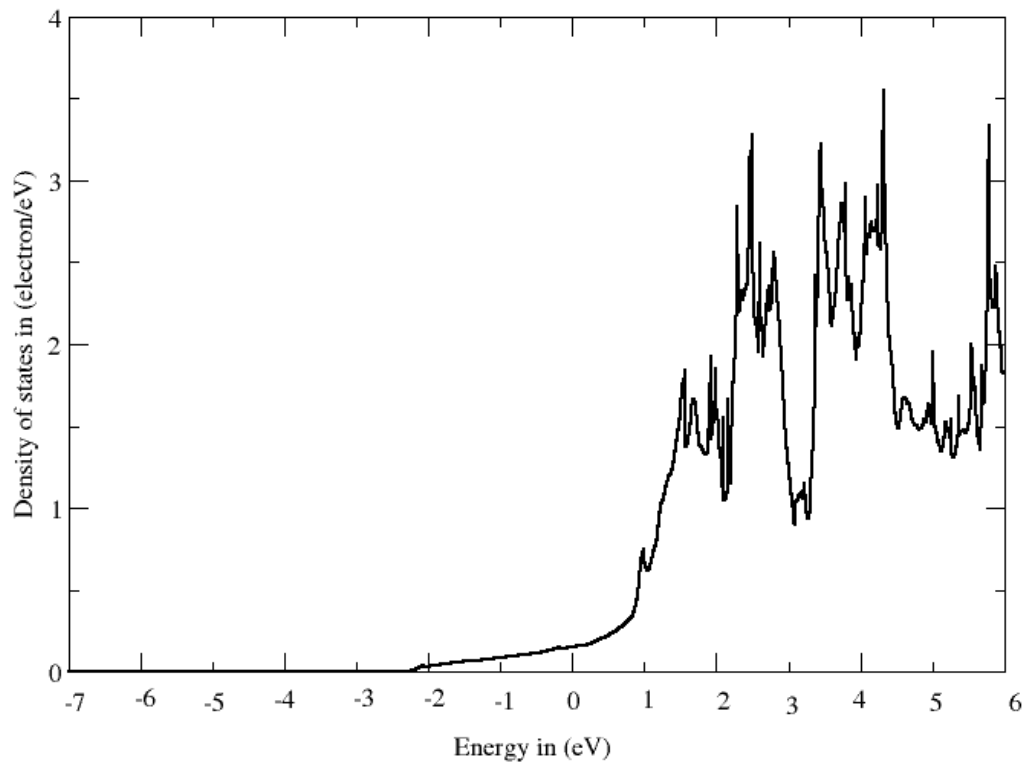
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Figure 6: DOS

Chapter Five

5   Conclusion

The electronic and structural properties of cobalt (Co) was investigated within the frame work of the density functional theory, plane wave basis sets, and pseudo potentials (ultrasoft). All calculations have been carried out with Quantum Espresso package (software). The total energy calculation is performed as a function of cutoff energy and Monkhorst pack-grid size, respectively, fixing the other parameters constant. The total energy convergence test is achieved, at the energy cutoff 50 Ry for the first case and at $8 \times 8 \times 8$ k-point grid size for the second case. The total energy is -596.86253968 Ry for the first case and -593.47698056 Ry for the second case. Besides, the optimization of lattice parameters was conducted with a $8 \times 8 \times 8$ k-mesh and the energy cutoff up to 50Ry. The optimized Lattice constants of bulk Co have been determined to be a = 4.7 Bohr, c = 7.59168 Bohr, and c/a = 1.615251 with respect to our computational calculation. The experimental values of bulk HCP-cobalt is (a = 4.743212 Bohr, c = 7.691185 Bohr, and c/a = 1.622). The Lattice constant determined using DFT calculation is compatible with an experimental result by an error of 1.29%. In addition, different smearing calculations were made and it was observed that both mv and mp are much less dependent upon degauss and allow for faster convergence than simple Gaussian broadening. Finally, the band structure and density of state of HCP cobalt was computed. The band structure calculation shows that there is overlap between the conduction band and the valance band. This clearly shows Co is purely metallic and zero band gap material. The density of state also shows that there is no discontinuity before and after the Fermi level. The density of state is continuous and there is no an insulating regime.

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