STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF CHROMIUM AND MOLYBDENUM

A Dissertation
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Requirements for the Masters of Science Degree in Physics

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DECLARATION

I, "Amrit Sharma", hereby declare that the work presented here is genuine work done originally by me and has not been published or submitted elsewhere for the requirement of a degree program. Any literature, data or works done by others and cited in this dissertation has been given due acknowledgement and listed in the reference.

Amrit Sharma
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RECOMMENDATION LETTER

This is to certify that the dissertation work entitled **STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF CHROMIUM AND MOLYBDENUM** has been carried out by **Mr. Amrit Sharma** as the partial fulfillment for the requirement of M.Sc. Degree in Physics under my supervision. To the best of my knowledge, this work is original and is not been submitted to any other degree in this institute.

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EVALUATION

ABSTRACT

We optimize lattice parameter and identify the nature and values of band gap of Chromium and Molybdenum by using quantum espresso. This work includes the general introduction on crystal structure and different models that work in the lattice constant and lattice dynamic. We also briefly include various theoretical details such as Born-Oppenheimer Approximation, Hartree-Fock Approximation, Density Functional Theory, Kohn-Sham approach, Local Density approximation, Generalized Gradient Approximation, and pseudo- potential. Finally, we discussed the fundamentals of Quantum Espresso computational program with the result and discussion on electronic properties, kinetic energy cut-off, lattice parameter, band gap, density of state and partial density of state of Chromium and Molybdenum.

We optimize lattice parameter and identify the nature and values of band gap of Chromium and Molybdenum. Optimized value of the lattice parameter, kinetic energy (cut off energy),K-point grid of Chromium is obtained as 5.4Bohr ,85Ry ,8×8×8 respectively. Similarly, Optimized value of the lattice parameter, kinetic energy (cut off energy),K-point grid of Molybdenum is obtained as 6.04 Bohr ,85Ry, 8×8×8 respectively. We used norm-conserving pseudo potentials; self consistent calculations employed Density Functional Theory (DFT) under Generalized Gradient Approximation (GGA) by using Quantum ESPRESSO package.

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LIST OF ABBREVIATIONS

BO	:	Born Oppenheimer
DFPT	:	Density Functional Perturbation Theory
DFT	:	Density Functional Theory
DOS	:	Density of State
FPMD	:	First Principle Molecular Dynamics
GGA	:	Generalized Gradient Approximation
HEG	:	Homogeneous Electron Gas
HF	:	Hartree-Fock
HK	:	Hohenberg-Kohn
KS	:	Kohn-Sham
LDA	:	Local Density Approximation
NSCF	:	Non-Self Consistent Field
PBE	:	Perdew, Burke and Ernzerhof
PDOS	:	Partial Density of State
PP	:	Pseudo Potential
PW	:	Plane Wave
QE	:	Quantum ESPRESSO
SCF	:	Self Consistent Field

CHAPTER 1

INTRODUCTION

1.1 General consideration

The transition metals, groups 3–12 in the periodic table, are generally characterized by partially filled ‘d’ sub shells in the free elements or their cations. Unlike the s-block and p-block elements, the transition metals exhibit significant horizontal similarities in chemistry in addition to their vertical similarities**.** As we go across the row from left to right, electrons are added to the 3d sub shell to neutralize the increase in the positive charge of the nucleus as the atomic number increases. With two important exceptions, the 3d sub shell is filled as expected based on the aufbau principle and Hund’s rule. In the second- and third-row transition metals, such irregularities can be difficult to predict, particularly for the third row, which has 4f, 5d, and 6s orbitals that are very close in energy. The increase in atomic radius is greater between the 3d and 4d metals than between the 4d and 5d metals because of the lanthanide contraction. Ionization energies and electro negativities increase slowly across a row, as do densities and electrical and thermal conductivities, whereas enthalpies of hydration decrease. Anomalies can be explained by the increased stabilization of half-filled and filled subs hells. Transition-metal cations are formed by the initial loss of ns electrons, and many metals can form cations in several oxidation states. Higher oxidation states become progressively less stable across a row and more stable down a column. Oxides of small, highly charged metal ions tend to be acidic, whereas oxides of metals with a low charge-to-radius ratio are basic.[1]

1.2 Study materials Chromium and Molybdenum

Chromium is a chemical element with the symbol ‘Cr ‘ and atomic number 24 and atomic mass 51.9961amu. It is the first element in group 6. It is a steely-Grey, lustrous, hard and brittle transition metal. The name of the element is derived from the Greek word *chrōma*, meaning color because many chromium compounds are intensely colored. Chromium minerals as pigments came to the attention of the west in the eighteenth century. On 26 July 1761, by Johann Gottlob Lehmann which he named *Siberian red lead in fact it is crocoite ore. It is chemically a compound of lead* *chromium and oxygen having molecular formula* $PbCrO_4$*.[2]*. In 1794, Louis Nicolas Vauquelin received samples of crocoite ore. He treated it with hydrochloric acid as a result he got chromium trioxide (CrO3). In 1797, Vauquelin discovered that he could isolate metallic chromium by heating the chromium trioxide (CrO3) in a charcoal oven, for which he is credited as the one who truly discovered the element.[3]

Table 1.1: Some Technical data of Chromium (Cr) [4]

Atomic Weight	51.9961 amu
Electron configuration	$[Ar]3d^5,4s^1$
Density	7.19 g/cm^3
Molar volume	7.2317×10^{-6}
Melting point	1907° C
Boiling point	2671° C
Electrical type	Conductor
Electrical conductivity	7.9×10^6 S/m
Electrical resistivity	1.3×10^{-7} mΩ
Atomic Radius	166 pm
Crystal structure	Body-centered cubic
Lattice angles	π/2, π/2, π/2
Lattice constants	291, 291, 291 pm
Space group name	Im_3m
Space group number	229
Known isotopes	^{42}Cr ^{43}Cr ^{44}Cr ^{45}Cr ^{46}Cr ^{47}Cr ^{48}Cr ^{49}Cr ^{50}Cr ^{51}Cr ^{52}Cr ^{53}Cr ^{54}Cr ^{55}Cr ^{56}Cr ^{57}Cr ^{58}Cr ^{59}Cr ^{60}Cr ^{61}Cr ^{62}Cr ^{63}Cr ^{64}Cr ^{65}Cr ^{66}Cr ^{67}Cr

Molybdenum is a chemical element with the symbol Mo and atomic number 42 and atomic mass 95.95amu. The name is from Neo-Latin *molybdenum*, from Ancient-Greek *molybdos*, meaning lead, since its ores were confused with lead ores.

Molybdenum minerals have been known throughout history, but the element was discovered in 1778 by Carl Wilhelm Scheele. The metal was first isolated in 1781 by Peter Jacob Hjelm.[5] the principal ore from which molybdenum is now extracted—was previously known as molybdena. Molybdena was confused with and often utilized as though it were graphite. Like graphite, molybdenite can be used to blacken a surface or as a solid lubricant. [6]. By 1778 Swedish chemist Carl Wilhelm Scheele stated firmly that molybdena was neither galena nor graphite.[7] Instead, Scheele correctly proposed that molybdena was an ore of a distinct new element, named *molybdenum* for the mineral in which it resided, and from which it might be isolated. Peter Jacob Hjelm successfully isolated molybdenum using carbon and linseed oil in 1781.[8].

Table 1.2: Some Technical data of Molybdenum (Mo) [4]

Atomic Weight	95.95 amu
Electron configuration	[Kr] $4d^5$,$5s^1$
Density	10.28 gm/cm^3
Molar volume	9.334×10^{-6}
Melting point	2623° C
Boiling point	4639° C
Electrical type	Conductor
Electrical conductivity	2×10^{7} S/m
Electrical resistivity	$4.9999999999997\times10^{-8}$ mΩ
Atomic Radius	190 pm
Crystal structure	Body-centered cubic
Lattice angles	π/2, π/2, π/2
Lattice constants	314.7, 314.7, 314.7 pm
Space group name	Im_3m
Space group number	229
Known isotopes	^{83}Mo ^{84}Mo ^{85}Mo ^{86}Mo ^{87}Mo ^{88}Mo ^{89}Mo ^{90}Mo ^{91}Mo^{993}Mo ^{99}Mo ^{101}Mo ^{102}Mo ^{103}Mo ^{104}Mo ^{105}Mo ^{106}Mo ^{107}Mo ^{108}Mo ^{109}Mo ^{110}Mo ^{111}Mo ^{112}Mo ^{113}Mo ^{114}Mo ^{115}Mo

1.3 Introduction to crystal structure

The crystal structure is a description of the ordered arrangement of atoms,ions or a molecules in a crystalline materials. The solidification or freezing of matter may lead to formation of ordered or disordered state in which ordered state is known as crystalline state where as the disordered one is termed the amorphous state. So, solids are either amorphous without form simply powered form or crystalline having fixed geometrical shape. Crystalline solids have definite, rigid shapes with clearly defined faces. The arrangement of atoms, ions or molecules are very ordered and repeat in three dimensions. Small repeating units in 3 dimensions are unit cells and are responsible for the order found in crystalline solids.

Crystal structure is described in terms of the geometry of arrangement of particles in the unit cell. The unit cell is defined as the smallest repeating unit having the full symmetry of the crystal structure. The geometry of the unit cell is defined as a parallelepiped, providing six lattice parameters taken as the lengths of the cell edges (a, b, c) and the angles between them (α, β, γ). The positions of particles inside the unit cell are described by the fractional coordinates (xi, yi, zi) along the cell edges, measured from a reference point. It is only necessary to report the coordinates of a smallest asymmetric subset of particles. This group of particles may be chosen so that it occupies the smallest physical space, which means that not all particles need to be physically located inside the boundaries given by the lattice parameters. All other particles of the unit cell are generated by the symmetry operations that characterize the symmetry of the unit cell. The collection of symmetry operations of the unit cell is expressed formally as the space group of the crystal structure.[9]. To understand the structure of most metals and a wide range of ionic compounds cubic system here will be explored in detail. In cubic crystal system three types of arrangements are found which are;

i. Simple cubic

ii. Body centered cubic

iii. Face centered cubic

The smallest group of particles in the material that constitutes this repeating pattern is the **unit cell** of the structure. The unit cell completely reflects the symmetry and structure of the entire crystal, which is built up by repetitive translation of the unit cell along its principal axes. The translation vectors define the nodes of the Bravais lattices. shape of crystals is referred to be the crystal lattice. The combinations of valance electrons with the neighboring electrons lead to the formation of chemical bond and hence the crystals are formed. Chemical bonds are of following types;

i. Ionic bond

ii. Covalent bond

iii. Metallic bond

iv. Hydrogen bond

v. Vander wall bond etc.

Ionic bond is generally formed in between the metals and nonmetals. The transfer of electron between each of the combining atoms (i.e. loose or gain of electrons) results ionic bond.

Metallic bond constitute the electrostatics attractive forces between the delocalized electrons called conduction electrons gathered in an electron cloud and the positively charged metal ions.

A hydrogen bond is formed when an atom of hydrogen is attracted towards respective electrons of the corresponding atom. This interferes with the crystal formation. Hydrogen after being bound to another atom is pulled towards the negative charge of the neighboring molecule. This confines the hydrogen atom between two negative charges.

A Vander wall bond is the weak interaction between the atoms of a substances resulting in soft consistency crystals. The outer orbit of the atom is completely filled with shared electrons but their charge keeps transferring Crystal of inert gases like “He” is made by this type of bond.

The crystal structure can be defined as it is composing from a pattern that is a set of atoms arranged in a particular way and a lattice exhibiting long range order and symmetry. Logically,

Crystal structure = lattice +basis

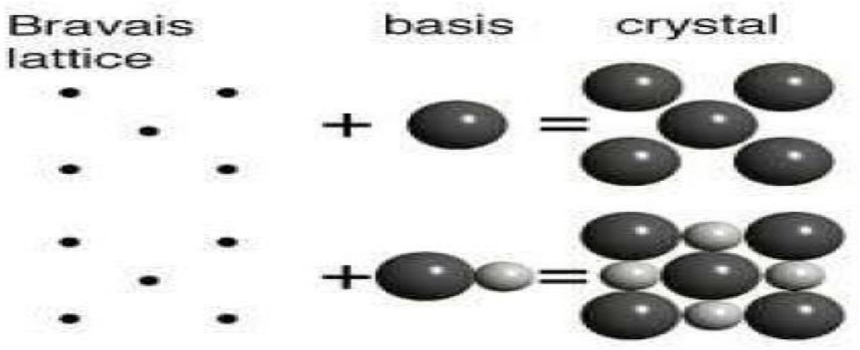

Fig: 1.1 Crystal Structure

The underlying order of crystalline solids can be represented by an array of regularly spaced points that indicates the location of the crystal basis structural units. This array is called crystal lattice. Crystal lattices are of course 3-dimensional but much of what we can say about them can be conveyed in simple two dimensional diagrams. Crystal lattice can be thought of as being built up from repeating units containing just a few atoms or molecules. These repeating unit s act much as rubbers stamp: press it on the paper, move it by an amount equal to the lattice spacing and stamp the paper again.

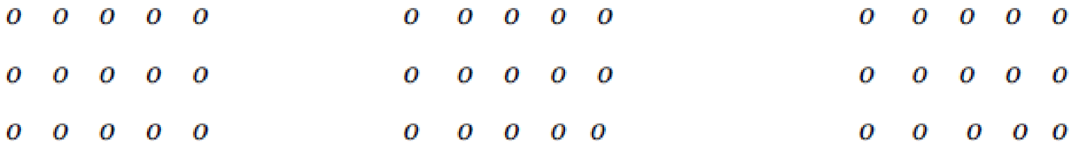

Fig : 1.2 square array of lattice points.

The circle represents the square array of lattice points. Square is the simplest unit cell that can be used to define the 2-dimensional lattice. And the building out the lattice by moving the unit cell in a series of steps is indicated by figure third.

Although the real crystal do not actually grow in this manner , this process is conceptually important because it allows us to classify a lattice type in terms of the simple repeating unit that is used to build it ,we call this shape the unit cell.

An ideal crystal is simply a form of infinite tessellation: a base pattern repeated over and over.

The base pattern is a group of atoms called the basis. The simplest basis is a single atom as in Cu, Fe, and Zn etc.

A lattice is a regular, periodic array of points in space as we discussed above. it can be defined in 3 dimension by 3 fundamental translational vectors a 1 ,a 2 ,a 3 and must satisfy the condition that for some position r in the crystal , the atomic arrangement looks exactly the same when observed at point r; where:

$$\vec{r}\,'=\vec{r}+u_1\vec{a}_1+u_2\vec{a}_2+u_3\vec{a}_3$$

The lattice comprises the points redefined by above equation where u_i are some integers,and α is a some constant.
$-\alpha<u_i<\alpha$
From this also crystal can be broken down as;

$$\text{lattice}+\text{basis}=\text{crystal structure}$$

We can perform a translation operation on a crystal by displacing it by an amount T where;

$$\vec{T}=u_1\vec{a}_1+u_2\vec{a}_2+u_3\vec{a}_3$$

Clearly, $\vec{r}+\vec{T}=\vec{r}\,'$ if it is satisfied in any arrangement s with fundamental vectors $\mathbf{a}_1$,$\mathbf{a}_2$,$\mathbf{a}_3$ by the all points, Then this arrangement is called the lattice as shown in figure in 2 dimensions.
We can see $\vec{T}$ as being the vector distance between two lattice point.

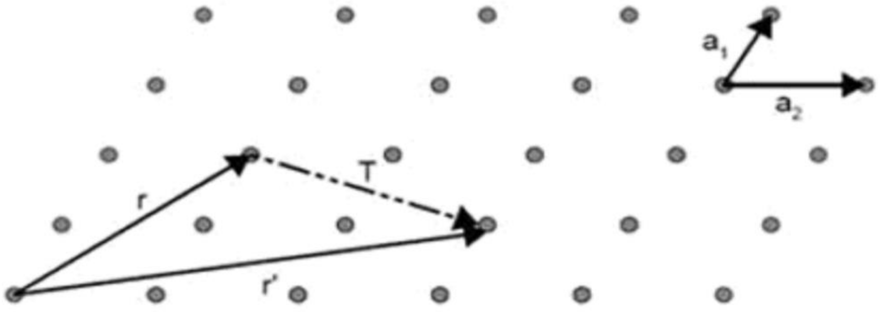

Fig: 1.3 Section of a 2-dimensional monoatomic crystal. The atomic arrangement at $\vec{r}$ and $\vec{r}\,'$ look the same to observes at these points, since $\vec{T}$ is a integer no. of primitive translation vectors a_1 and a_2 ($T = -a_1 + 2a_2$).

The primitive translation vectors [3], as shown in figure define the smallest possible volume (or in this case; area) of a cell that can be used as a base pattern for the crystal structure. Such a cell is a called primitive unit cell. There is always one lattice point per unit cell. Generally lattice points are shared by several cells, with the sum of the fraction of lattice points equaling 1(within one primitive cell).

In 3 dimensions the volume of the primitive cell is given by, $V_c = [a_1 .a_2 \times a_3]$. The basis of a primitive cell is called the primitive basis. No basis contains fewer particles than the primitive basis. Although the number of particles for a given crystal is always same as the choice of primitive cell in not unique. A unique and symmetric way of choosing the primitive cell is known as the wigner-seitz cell and is shown in figure given below.

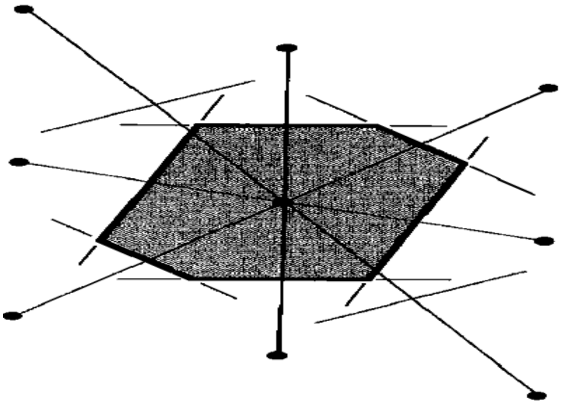

Fig: 1.4 Wigner- Seitz primitive cells

One way of choosing the primitive cell is as follows;

1. Draw lines to connect a particular lattice point to all nearby lattice points.
2. At the midpoints and normal to the lines, draw additional lines and planes.

The smallest volume enclosed in this process is actually wigner-seitz primitive cell. Four types of symmetry namely translational operation, rotation, reflection and inversion operation under which crystal lattice remain unchanged or repeating itself. The symmetry operation in 3 dimensions is inversion operation. The inversion and reflection operation are the point operation because under this the structure as well as identity of the lattice do not change.

Crystal lattice can be found having one, three, two, four, a and nd six fold symmetry but no fivefold symmetry. In two dimensions, rotation about a lattice point preserves the translational properties for a rotation (in radians) of: $\Theta= 2 /I$ where $I \in (1, 2, 3, 4, 6)$, any other rotation will not preserve the lattice symmetry.

The most general type of 2 dimensional lattice is an oblique lattice, which only preserves the lattice form under rotation of or 2. Although there are an infinite number of possible lattices due to the limited possible point operation, there are clearly 4 distinct restriction on the lattice (3 rotation, 1 reflection), leading to 4 special lattice type which have higher degree of symmetry than the oblique lattice. Along with oblique lattice there are five distinct lattices in 2 dimensions.

These lattices are known as bravais lattices i.e.; bravais lattice gave five lattices in 2 dimensionswhich are given below.

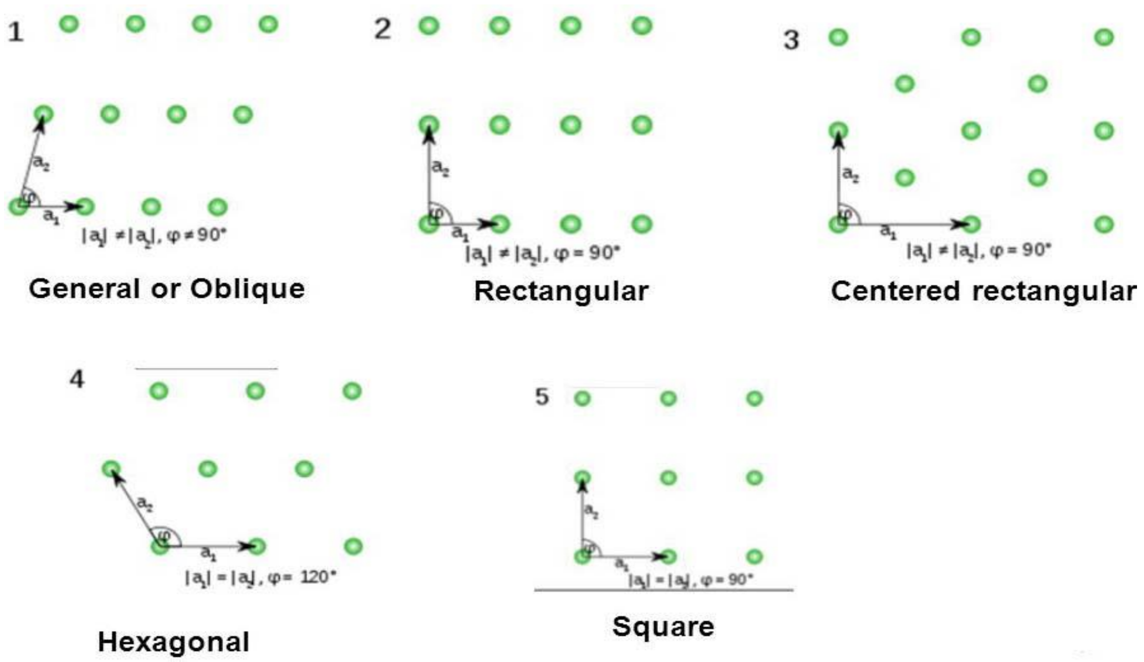

Fig: 1.5 The five-fundamental two-dimensional Bravais lattices.

Bravais showed fourteen types of lattice in three dimensions. These lattice are given below,

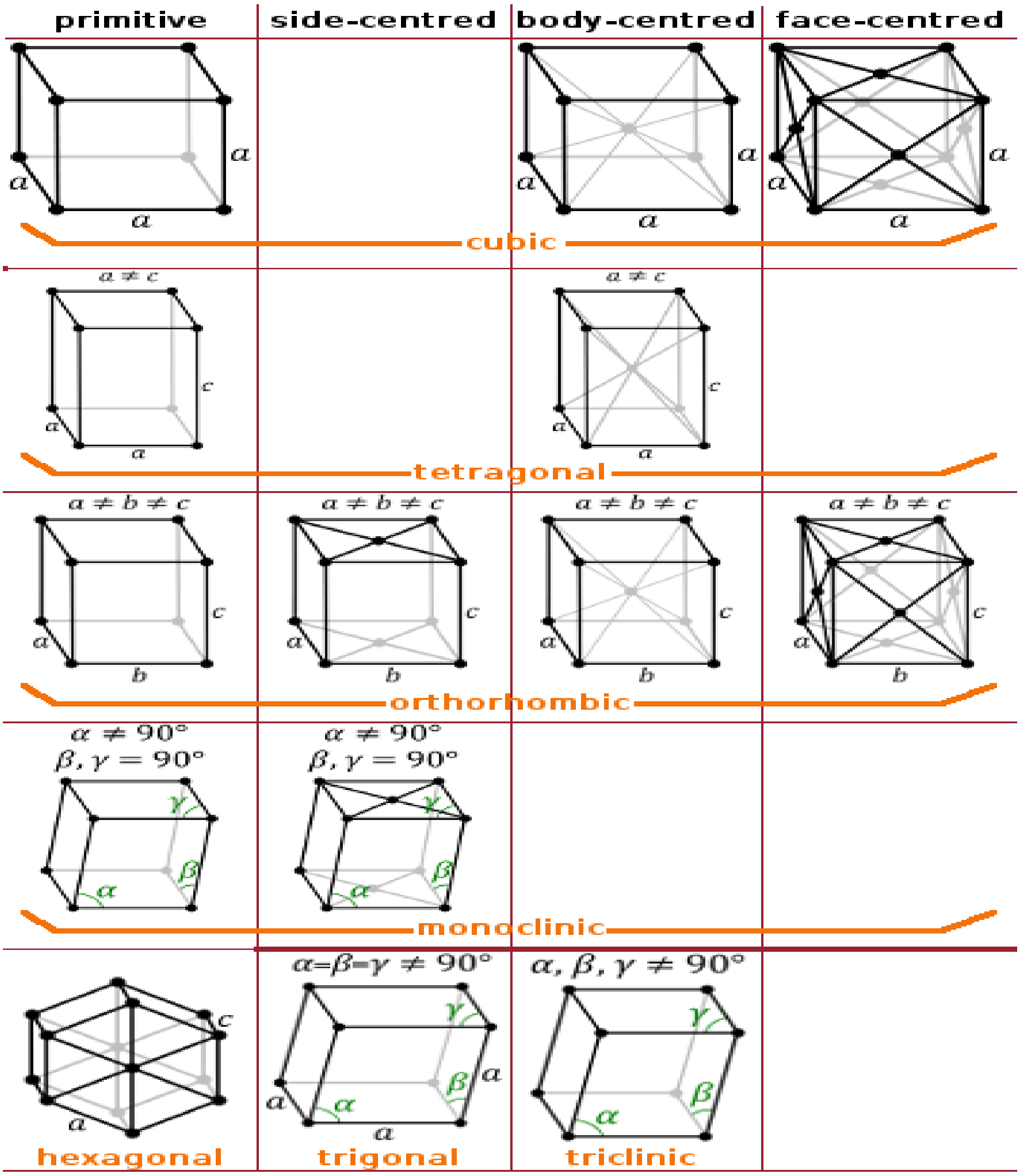

Fig: 1.6 Bravais lattice in three dimensions.

Altogether there are 7 types of crystal system in 3 dimensions. The most general is the triclinic system. The other six are; monoclinic, orthorhombic, tetragonal, cubic, trigonal and hexagonal. These are divided into fourteen bravais lattices. This is tabulated below;

Table: 1.3 Fourteen bravais lattice

System	Bravias Lattice	Unit Cell Characteristics	Characteristic Symmetry elements
Triclinic	Simple	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	None
Monoclinic	Simple Base Centered	$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$	One 2-fold rotation axis
Orthorhombic	Simple Base-centered Body-centered Face-centered	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Three mutually orthogonal 2-fold rotation axes
Tetragonal	Simple Body-centered	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	One 4-fold rotation axis
Cubic	Simple Body-centered Face-Centered	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Four 3-fold rotation axes (along cube diagonal)
Trigonal (rombohedral)	Simple	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	One 3-fold rotation axis
Hexagonal	Simple	$a = b \neq c$ $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	One 3-fold rotation axis

The coordination number of an atom or ion within an extended structure is defined as the number of nearest neighbor atoms (ions of opposite charges) that are in contact with it. In Sc, FCC and bcc the coordination number are 6, 12 and 8 respectively.

The important characteristics of unit cell of SC, FCC, HCP and diamond Crystal structure are given below.

Table: 1.4 Characteristics of different Cubic Structures

S.N.	Characteristics	SC	BCC	FCC	HCP	DC
1	No of atoms per unit cell	1	2	4	6	8
2	Atomic radius R	$a/2$	$a\sqrt{3}/4$	$a/2\sqrt{2}$	$a/2$	$a\sqrt{3}/8$
3	Nearest neighbour distance (2r)	A	$a\sqrt{3}/2$	$a/\sqrt{2}$	A	$\sqrt{3}/4$
4	Coordination number	6	8	12	12	4
5	Unit cell volume	a^3	a^3	a^3	$(a\sqrt{3}/2)a^3$	a^3
6	Packing Factor	0.52	0.68	0.74	0.74	0.34
7	Examples	Po,KCl	Fe,Ba,Cr	Al,Cu,Pb,Au	Mg,Zn,Cd	Ge,Si,C, Diamond

The number of atoms per unit cell is given by n i +(1/8)n c +(1/2)n f ,where n i =number of atoms inside a unit cell, n f = no of atoms faces of unit cell andn c = no of atoms on the all corner of unit cell.

Also the light if sprayed over the term packing fraction, it also then adds some flavor to the knowledge of crystal structure. It is actually the ratio of total volume of atoms in unit cell to the volume of unit cell. i.e.;

$$Packing fraction = \frac{(Volume\ of\ atom\ in\ a\ unit\ cell)}{Volume\ of\ unit\ cell}$$

$$= \frac{no.\ of\ \ atoms\ \ per\ unit\ cell \times volume\ of\ atom}{(volume\ of\ unit\ cell)}$$

It shows how closely the atoms are packed in a unit cell. If P.f. is 52%, it means 52% space is covered by atoms crystal and 48% is empty.

Crystal contains infinite no of planes in different spacing and orientation miller introduced the three numbers (hkl) called miller indices to know the position of the particular planes.

It represents the infinite no of parallel planes in same direction and orientation but not for single plane. These different sets of lattice planes can cause diffraction. If we draw normal to each set of planes from a common origin in such a way that the length of normal being proportional to the reciprocal of the interplaner spacing of the corresponding set., then end points of these forms a lattice which is called the reciprocal lattice. Each point in the reciprocal lattice represents the characteristics of the corresponding set of planes. Its direction with respect to origin represents the orientation of the planes and its distance from origin represents the interplaner spacing.

Hence we can say that every crystal structure has two lattices associated with it, these are the direct lattices and reciprocal lattices. Every direct crystal lattice space is associated with the reciprocal lattice that relates in similar geometrical manner with direct lattice. The diffraction pattern of the crystal is a map of reciprocal lattice of the crystal. To describe the diffraction properties of the crystal that means for the description of electron energy band Brillouin has introduced the idea of brillouin zone.

Brillouin zones are important characteristics of crystal structures. The construction and illustration of brillouinzones for a 3-dimensional lattice are somewhat difficult to follow. The construction of brillouin zones for a two dimensional lattice is much easier to follow. The first brillouin zone for a point in a lattice is the set of points that are closer to the point than the Braggs plane of any point. The second brillouin zone is defined as the points which may be reached from the first brillouin zone by crossing only one Bragg'splane; this can be generalized to define the n th brillouin zone as the set of points, not in the previous zones, that can be reached from one (n-1) th zone by crossing one and only one Bragg'splane. The first brillouin zone is defined to be the Wigner-Seitz primitive cell of the reciprocal lattice that is a zone described by the set of planes that are perpendicular bisectors of the reciprocal lattice vector. Any wave which has the wave vector '**K**' in the direction of reciprocal lattice vector **G** will suffer diffraction from the crystal if the following condition is satisfied by **G** and **K**. i.e. $2\mathbf{K}.\mathbf{G}=G^2$

So, that the brillouin zone construction gives the all wave vector which suffer diffraction from the crystal.

If $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$ are the primitive translation vectors of any simple cubic with $\mathbf{a_1 = a_i}$, $\mathbf{a_2 = a_j}$, $\mathbf{a_3 = a_k}$ then the primitive translation vectors of reciprocal lattice vectors $\mathbf{b_1}$, $\mathbf{b_2}$, $\mathbf{b_3}$ are given by,

$$\overrightarrow{b_1} = 2\pi \frac{(\overrightarrow{a_2} \times \overrightarrow{a_3})}{(\overrightarrow{a_1} \times \overrightarrow{a_2} \times \overrightarrow{a_3})} \quad \overrightarrow{b_2} = 2\pi \frac{(\overrightarrow{a_3} \times \overrightarrow{a_1})}{(\overrightarrow{a_1} \times \overrightarrow{a_2} \times \overrightarrow{a_3})} \quad \overrightarrow{b_3} = 2\pi \frac{(\overrightarrow{a_1} \times \overrightarrow{a_2})}{(\overrightarrow{a_1} \times \overrightarrow{a_2} \times \overrightarrow{a_3})}$$

Any points in reciprocal lattice now is given as :

$\mathbf{G} = v_1 \mathbf{b_1} + v_2 \mathbf{b_2} + v_3 \mathbf{b_3}$

Where; v_1, v_2 and v_3 are integers which define the reciprocal lattice points, 'G' is called reciprocal lattice vector.

In case of direct lattice of BCC crystal, If 'a' be the length of each side then the lattice is described as a simple bravais lattice where the three edges of the primitive cell i.e. primitive lattice vectors $\mathbf{a_1}$, $\mathbf{a_2}$, $\mathbf{a_3}$ are given by,

$$\overrightarrow{a_1} = \frac{a}{2}\left(-\hat{\imath} + \hat{\jmath} + \hat{k}\right) \quad \overrightarrow{a_2} = \frac{a}{2}\left(\hat{\imath} - \hat{\jmath} + \hat{k}\right) \quad \overrightarrow{a_3} = \frac{a}{2}\left(\hat{\imath} + \hat{\jmath} - \hat{k}\right)$$

Where $\hat{\imath}$, $\hat{\jmath}$ and $\widehat{k}$ are unit vectors along the side of cube.

So, the reciprocal lattice basis vectors of the BCC crystal are given by the relation,

$$\overrightarrow{b_1} = 2\frac{\pi}{a}\left(\hat{\jmath} + \hat{k}\right) \quad \overrightarrow{b_2} = 2\frac{\pi}{a}\left(\hat{\imath} + \hat{k}\right) \quad \overrightarrow{b_3} = 2\frac{\pi}{a}(\hat{\imath} + \hat{\jmath})$$

This is of course the BCC lattice implying that the reciprocal lattice of BCC is FCC lattice.

The general reciprocal vectors are given by;

$\mathbf{G} = v_1 \mathbf{b_1} + v_2 \mathbf{b_2} + v_3 \mathbf{b_3}$

$= \frac{2\pi}{a}[(v_2+v_3)\, \hat{\imath} + (v_1+v_3)\, \hat{\jmath} + (v_1+v_2)\, \hat{k}]$

Therefore, the shortest twelve reciprocal vectors are given as;

$$\frac{2\pi}{a}[\pm v_2 \pm v_3]; \frac{2\pi}{a}[\pm v_1 \pm v_2]; \frac{2\pi}{a}[\pm v_1 \pm v_3]$$

The first Brillouin zone boundaries are determined by the twelve planes normal to those vectors at their midpoints. The vectors from the origin to the center of each face are:

$$\frac{\pi}{a}[\pm v_2 \pm v_3];\frac{\pi}{a}[\pm v_1 \pm v_2];\frac{\pi}{a}[\pm v_1 \pm v_3]$$

The unit cell of BCC lattice with lattice constant 2a is shown in figure;

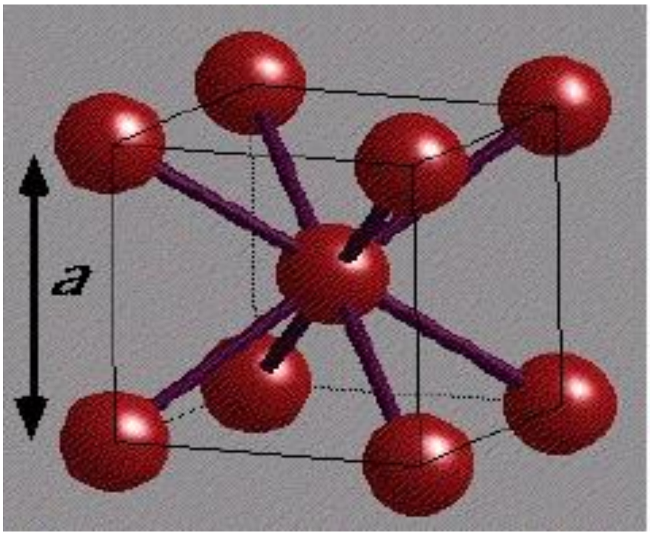

Fig: 1.6 A unit cell and primitive cell of BCC lattice

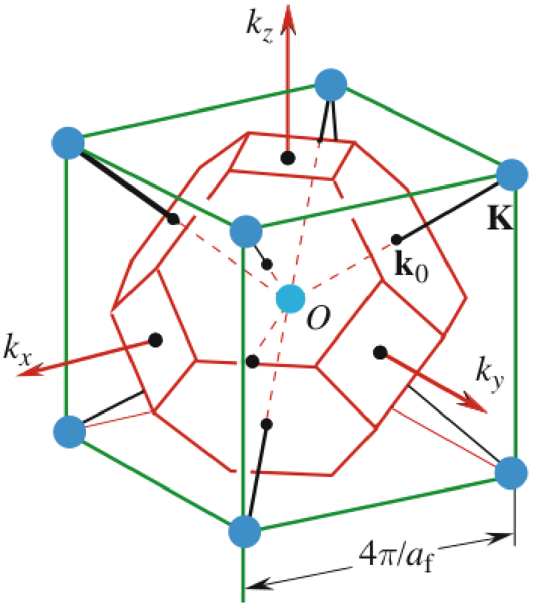

Fig:1.7 Reciprocal lattice vector of BCC lattice

The reciprocal lattice vectors for each direct lattice can be given in terms of primitive lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$,$\mathbf{a}_3$ by the Laue equation that is,$\mathbf{a}_i\ \mathbf{b}_j = 2\ \square_{ij}$ where $\mathbf{b}_j$ are the basis vectors of reciprocal lattice . And i , j = 1, 2, 3 and δ_{ij} is the kronecker delta function given as;

δ_{ij}= 0 if; i≠j

= 1 if; i=j

The co-ordinates of first neighbor of the reference atom situated at the origin of the co-ordinate system are shown below in table;

Table: 1.5 Coordinate of first neighbors at different index atoms

Index of atom	X-coordinate	Y-coordinate	Z-coordinate
0	0	0	0
1	+a	+a	A
2	+a	+a	-a
3	+a	-a	A
4	+a	-a	-a
5	-a	+a	A
6	-a	+a	-a
7	-a	-a	A
8	-a	-a	-a

Here the lattice constant is ‘a’ and (0, 0, 0) is the coordinate of atom at origin when it is taken as reference atom. The coordinate of the second nearest neighbors can be written as,

Table: 1.6 Coordinate of second neighbors at different index atoms

Index of atom	X-coordinate	Y-coordinate	Z-coordinate
9	2a	0	0
10	0	2a	0
11	-2a	0	0
12	0	-2a	0
13	0	0	-2a
14	0	0	-2a

In the body centered cubic (BCC) structure the unit cell contains eight atoms at the corner and one atom at the centre of the body. The volume of primitive cell is given as;

$V = |\mathbf{a_1} .(\mathbf{a_2} \times \mathbf{a_3})| = \frac{1}{2} a^3$

Where, ‘a’ is the half of the lattice parameter.

From above table it is seen that the primitive cell of BCC lattice contains only one atom. Each atom has eight nearest neighbors at a distance ‘a’ and six next nearest neighbors at a distance ‘2a’. Thus the zone formed is a regular twelve face solid, rhombic dodecahedron.

1.4 Scope of the present work

The study of properties of solid is one of the most interesting and fruitful branches of physics. By knowing the lattice dynamics, we can predict different physical properties of solid and help to uses these solid in daily life application, which we can easily observed in this time period.

In this present work, we have studies the density of state (DOS) of transition metal Chromium and Molybdenum. From the study of DOS, we can get idea about nature of the solid and magnetic properties.

The main objective of our study are:

1. To study about the crystal structure done by previous worker.
2. To estimate the lattice parameter of Cr and Mo.
3. To study and plot the density of state of Cr and Mo
4. To study and plot band structure of Cr and Mo
5. To study and plot the partial density-of-states of Cr and Mo

1.5 How we Approach?

Mainly this research work is done is computational by using Quantum ESPRESSO (QE) package. First, we optimized structure of Transition metal by optimizing lattice parameters, then we study the band structure, DOS and PDOS of Chromium and Molybdenum. In this study, we choose body centre cubic structure because of its computational cost and simplicity of structure.

The outline of the present work is summarized as follows:

In this work, Chapter 1 includes general introduction about crystal structure and lattice dynamics with attachment of objective and scope of work. In chapter 2, we discuss about the literature review of this work as complete by previous researcher. In chapter 3 the theoretical models of the method employed in calculations such as Born-Oppenheimer, Hartree-Fock method, Density functional theory with local density approximation (LDA), General gradient approximation (GGA) and Pseudopotential. In chapter 4 we described some detail about Quantum ESPRESSO and its execution. Then in chapter 5 we discuss and present about main finding of this research. Finally, in chapter 6 we summarize our results and mention about further advantage of same field research. Reference are listed at end of chapter 6.

CHAPTER 2

LITERATURE REVIEW

In 1961 M. Asdente and J. Friedel study about the electronic structure of the 3d band in Cr is calculated in the tight-binding approximation; the effect of the nearest-neighbor interaction and of the second-nearest-neighbor interaction on the energy surfaces in the Brillouin zone and on the density-of-states curve g(E) is investigated.[10]

In 1984 J.A. Leiro & E.E.Minni study about the X-ray photoemission (XPS) spectra of the valence band and 2p core lines of metallic chromium are presented. A considerable deviation is observed in the shape of the valence band between the experimental spectrum and the theoretical one-electron spectrum. This discrepancy is mainly due to the d band being too broad in the one-electron band structure calculation. Correlation effects are expected to narrow the theoretical 3d band of Cr considerably.[11]

In 1986 P. E. S. Persson and L. I. Johansson study about the bulk band structure of paramagnetic chromium, calculated with use of the linear augmented plane-wave method, is presented and discussed. The calculated band structure is used for interpreting the data obtained in angle-resolved photoemission experiments carried out on Cr(110). Experimentally determined band locations and dispersions are found to agree fairly well with the theoretically predicted values. Calculations of the photocurrent-simulating recorded photoemission spectra have also been made with the use of two different methods.[12]

In 2013 Parwana Habibi, Cyrille Barreteau, Alexander Smogunov study about the Electronic and magnetic structure of the Cr(001) surface. Density functional theory (DFT) calculations are carried out to study the electronic and magnetic structure of the (001) surface of chromium. [13]

In 1988 A. R. Jani, G. S. Tripathi, N. E. Brener, and J. Callaway study about the band structure and related properties of molybdenum. Self-consistent, all-electron, local-density calculations are reported for bcc molybdenum, using the linear combination of Gaussian orbitals (LCGO) method. We obtain the density of states, the Fermi surface, charge form factors, the Compton profile, and the optical conductivity. Results are compared with other calculations and with experiments where these exist.[14]

In 1989 Jani, Tripathi, Brener,Callaway study about Band structure and related properties of molybdenum. Self-consistent, all-electron, local-density calculations are reported for bcc molybdenum, using the linear combination of Gaussian orbitals (LCGO) method. We obtain the density of states, the Fermi surface, charge form factors, the Compton profile, and the optical conductivity. Results are compared with other calculations and with experiments where these exist.[15]

In 2009 Ning Wu, Yaroslav B. Losovyj, Zhaoxian Yu, Renat F. Sabirianov, Wai-Ning Mei, N. Lozova, J. A. Colón Santana, and Peter A. Dowben study about the surface relaxation and band structure of Mo(112).The experimental and theoretical surface band structures of Mo(112) are compared. This surface band structure mapping is presented with corrections included for the lattice relaxation of the Mo(112) surface. Quantitative low energy electron diffraction (LEED) has been used to determine the details of the Mo(112) surface structure.[16]

In 2013 Jolayemi O. R. and Idiodi J. O. study about the Electronic and surface properties of Molybdenum. First principle calculations are performed using the super cell method with pseudopotentials and plane waves based on the Density Functional Theory (DFT) for surface structural properties at T = 0 K and also for electronic properties of bulk Molybdenum. Relaxation, surface energy, and work function of the Mo (100) surface as well as the band structure, density of state, projected density of state and charge density of bulk Molybdenum are presented. Consistent results are obtained with the Generalized Gradient Approximation (GGA) for the exchange-correlation functional and they compare well with experimental and other theoretical works.[17]

CHAPTER 3

RESEARCH METHODOLOGY

3.1 General Consideration

In this chapter, we discuss about Schrödinger equation, the development and invention of Hartree-Fock (HF) approximation and density function theory and methods of Phonon and IR calculations. This theory starts with the Born-Oppenheimer approximation where the KE due to nucleus is neglected and the repulsion between nuclei are omitted. But since exact wave functions are not known for atoms with higher atomic number, next method is required. The Hartree-Fock self-consistent method is one-electron approximation in which the motion of each electron in the effective field of the other electrons is governed by a one electron Schr¨odinger equation [18]. In the Hartree-Fock approximation, the antisymmetric product of one-electron wave functions is used, i.e. it takes into account of the correlation arising due to electrons of same spin, however, the motion of the opposite spin remains uncorrelated [19,20]. Beyond Hartree-Fock approximation, the methods which deals with the phenomenon associated with the many electron system are known as electron correlation methods. One of the first-principles method which take account of electron correlation is DFT, in which the electronic orbitals are solution to a Schr¨odinger equation which depends on the electron density rather than on individual electron wave functions. In this theory, the exchange-correlation is expressed as a functional of the electron density and the electronic states are solved for self-consistency as in the Hartree-Fock approximation. The exchange-correlation potential includes the exchange interaction arising from the antisymmetry of the wave functions and the dynamic correlation effect arising due to the Coulomb repulsion between the electrons. In principle, DFT theory is exact but it treats the exchange and dynamic correlation effects only approximately [21, 22, 23].

3.2 Theoretical Details

3.2.1 Born-Oppenheimer Approximation

The Schrödinger equation is exactly solvable for any one electron atom. But the Schrödinger equation for many electron atom and molecule cannot be solved exactly [19, 20] because of the inter-electronic repulsion term in the Hamiltonian. Therefore some approximate methods are required for the calculation of energies and other relevant parameters. Thus we need an approximate solution of the time independent, non-relativistic Schrödinger equation of N electrons and M nuclei:

$\hat{H}\psi_i(r_1\ \sigma_1, ..., r_N\ \boldsymbol{\sigma}_N, R_1, R_2, ..., R_M) = E_i\psi_i(r_1\ {}_s\sigma_1, ..., r_N\ \boldsymbol{\sigma}_N, R_1, R_2, ..., R_M)$ (3.1) Where r_i's and σ_i's are space and spin coordinates of electrons respectively. R_i's are the nuclear positions and $\hat{H}$ is the Hamiltonian operator for a system consisting of N electrons and M nuclei in absence of the electric and magnetic field. Ψ_i is the wave functions of i^th state of the system which depends on 4N coordinates of electrons (r_i) (i.e. 3N space co-ordinates and N spin co-ordinates) and 3M coordinates of the nuclei (R_i).

The Hamiltonian of the system consisting of N-electrons and M-nuclei can be written as [20]:

$$\hat{H} = -\sum_{i=1}^{N}\frac{\hbar}{2m_e}\nabla_i^2 - \sum_{\alpha=1}^{M}\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 - \sum_{i=1}^{N}\ \sum_{\alpha=1}^{M}\frac{Z_\alpha e^2}{|r_i - R_\alpha|} + \sum_{j>1}^{N}\ \sum_{i=1}^{N}\frac{e^2}{|r_i - r_j|} + \sum_{\beta>\alpha}^{M}\ \sum_{\alpha=1}^{M}\frac{Z_\alpha Z_\beta e^2}{|R_\alpha - R_\beta|} \tag{3.2}$$

In Eq. (3.2), i, j refers to the electrons and α, β refers to the nuclei. The first and second term of the Eq. (3.2) represents the kinetic energies of the electron and nuclei respectively. The third term represents the coulomb attraction between electrons and nuclei, the fourth term represents the coulomb repulsion between the electrons, and the last term represents the coulomb repulsion between nuclei.

In fact nuclei are much heavier than electrons ($M_\alpha/m_e >> 10^3$[19], hence the electrons move much faster than the nuclei, and to a good approximation, we can regard the nucleus as fixed while electrons carry out their motions. This approximation is known as Born-Oppenheimer approximation [19, 20]. Thus considering the nuclei as fixed, nuclear Kinetic energy terms from Eq. (3.2) can be neglected and the repulsion between nuclei is taken as constant. This constant to the Hamiltonian does not affect the eigen function but adds a constant term to the eigenvalue. So with this approximation, the Hamiltonian in Eq. (3.2) reduces to:

$$\hat{H} = -\sum_{i=1}^{N}\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i=1}^{N}\ \sum_{\alpha=1}^{M}\frac{Z_\alpha e^2}{|r_i - R_\alpha|} + \sum_{j>1}^{N}\ \sum_{i=1}^{N}\frac{e^2}{|r_i - r_j|} \tag{3.3}$$

3.2.2 The Hartree-Fock Approximation

For hydrogen atom, we know the exact wave function. Similarly for helium and lithium, approximate wave function have been calculated by including inter-electronic distances in the variation function [20]. So we can solve their problems approximately using the Schrödinger’s equation with Born-Oppenheimer approximation. But for the system containing higher atomic number, the best approach to finding a good wave function lies in first calculating an approximate wave function using the Hartree-Fock self-consistent field approach [20]. The Hartree-Fock method is the main basis for the usage of atomic and molecular orbitals in many electron systems. This method is superior to the Hartree method of self-consistent fields, in a respect that simple product of wave function of Hartree neglects the contributions in the motion of electrons caused by the asymmetry of the complete wave function [19].

In the Hartree’s Self-consistent Field (SCF) model of the atom, each electron moves in the potential field of the nucleus plus (N-1) others electrons treated as overlapping charge clouds [18]. The Hartree equation neglects the spin direction of electrons. To account spin direction of electron we have to go through Hartree-Fock approximation [25] taking anti symmetric wave function in Slater determinant form. So Hartree-Fock equation is as follows [26];

$$[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \sum_{i=1}^{N}\sum_{\alpha=1}^{M}\frac{Z_\alpha e^2}{|r_i - R_\alpha|} + \sum_{j\neq i}\int dr'\,\psi_j^*(r')\frac{e^2}{|r-r'|}\psi_j(r')\,]\,\psi_i(r) - \sum_{j\neq i}\int dr'\,\psi_i^*(r')\frac{e^2}{|r-r'|}\psi_i(r')\delta_{\sigma_i\sigma_j}\,]\,\psi_j(r) = \varepsilon_i\psi_i(r) \qquad (3.4)$$

Third term represents Coulomb potential due to interaction between inter-penetrating charge distributions. The last term in the right hand side of Eq. (3.4) represents the exchange potential and this vanish if ψ_i and ψ_j have different spins. The exchange potential is related to the interactions between all the electrons with same spin in the system and so it is difficult to derive.

Although the Hartree-Fock wave function satisfies the anti-symmetry requirements of the Pauli’s exclusion principle and hence includes the correlation effect arising from the electrons of same spin, the motion of the electron with opposite spins remains uncorrected [20]. This means the Hartree-Fock (HF) approximation must be improved to account for the electron dynamic correlations.

The Hartree-Fock wave function includes the correlation effect that arises from the electrons of same spin, but the motion of electrons with opposite spin remains uncorrelated which overestimate the electron-electron repulsion. It also satisfies the anti- symmetric nature of fermions i.e. electrons. There are two types of electron repulsion: the first one is the classical coulomb repulsion that arises from electric charge and the second one is Fermi repulsion due to Pauli's exclusion principle. So, it cannot be stated that HF method cannot explain the correlation effect due to dynamic nature of electrons. The repulsion energy between two electrons is calculated between an electron and the average electron density for the other electron in HF method. This discrepancy arises due to the fact that the electron will push away the other electrons as it moves around by diminishing the repulsion energy. So the correct solution of Schrödinger equation is not obtained from HF method. The difference between the exact solution of Schrödinger equation and Hartree-Fock limit energy is known as correlation energy.

So, to explain the dynamical behavior of electron (electronic correlation) HF approximation must be improved. The method like DFT, MP2 etc are used to account correlation of electrons.

3.2.3 Density Functional Theory

It is a method arise due to a major limitation and drawback from the Hartree-Fock method. A Hartree-Fock method takes into account the interaction between electrons only in an average way, but the motion of electrons of opposite spins is not considered. The Hartree-Fock approximation can be improved by considering the electron correlation which is mainly caused by the instantaneous interaction between electrons. The difference between the exact (within the Born-Oppenheimer approximation and neglecting the relativistic effect) ground state energy E_0 and the HF ground state energy E_{HF} is called the correlation energy E_{corr} [20].

i.e., $$E_{corr} = E_0 - E_{HF} \tag{3.5}$$

One of the most useful and fundamental approaches to take into account of electron correlation is Density Functional theory. In DFT, the electron density $\rho_0(r)$ plays a central role, and it replaces the wave function of Schrödinger equation and Hartree-Fock approximation. Density functional theory is the quantum-mechanical theory of correlated many body system used to investigate the electronic structure of systems, in particular atoms, molecules and the condensed phases [27].

The fundamental tenet of the density functional theory is that any property of a system or many interacting particles can be viewed as a functional of ground state density $\rho_0(r)$ i.e. one scalar function of position $\rho_0(r)$, in principle, determines all information of the many-body wave functions for ground state and all excited states. In the density functional theory the emphasis shifts from the ground-state wave function to the much more manageable ground-state electron density $\rho_0(r)$ [21]. The modern formulation of the density functional theory originated in a famous paper written by P. Hohenberg and W. Kohn in 1964 [18]. Later in 1965, W. Kohn and L. Sham developed a formalism with the introduction of atomic orbitals that is the foundation for the current application of DFT in the computational approach [28].

This formalism yields a pragmatic and practical way to solve a system of interacting electrons. Thus Kohn and Sham showed in quantum many body system, the density can be considered as basic variable i.e. all the properties of the system can be considered to be unique functional of ground state density. Actually, the first attempt to use the electron density rather than the wave function for obtaining information about atomic and molecular systems are the method of Thomas and Fermi proposed in 1927 [21]. Although their approximation is not accurate enough for present day electronic calculations, the approach illustrates the way density functional theory works.

The method of Thomas and Fermi, proposed in 1927, is the original density functional theory. In the Thomas-Fermi method the kinetic energy of the system of electrons is approximated as an explicit functional of density, idealized as non-interacting electron in homogeneous gas with density equal to the local density at any given point. Both Thomas and Fermi neglected exchange and correlation among electrons, however this was extended by Dirac in 1930 who formulated the local approximation for the exchange among electrons [21].

In Thomas-Fermi approach certain ideas will be borrowed from quantum mechanics, but otherwise one operates with normal functions instead of quantum mechanical operators, i.e. it is semi-classical. The condition for the semi-classical approach to be applicable is that spatial variations of the de Broglie wavelength in a system must be small [29].

i.e., $\left|\frac{d\lambda(x)}{dx}\right| << 1$ (3.6)

3.2.4 The Hohenberg-Kohn Theorems

The Density functional theory (DFT) for many body systems is based on two fundamental mathematical theorems proved by Hohenberg and Kohn [23]. The first theorem states that the wave function, which has a central position in standard quantum theory, used as a fundamental tool can be replaced by the ground state electron density without any loss of information. The second Hohenberg-Kohn theorem is more or less the equivalent of the variation principle in standard quantum mechanics. For a system of N interacting electrons total Hamiltonian can be decomposed into the sum of an “internal” part (kinetic energy of the electrons plus electron-electron Coulomb interactions) and “external” part (external part is given by the electronic-nuclear interactions). We have,

$$H = H_{int} + H_{ex}$$
$$= T + V_{ext} + V_{ee} \quad (3.7)$$

Where the first term represents the kinetic energy of electrons, the second term represents the Coulomb attraction between electrons and nuclei and the third term is for the Coulomb repulsion among electrons. The second term in Eq. (3.7) for N electrons and M nuclei system can be written as:

$$V_{ext} = \sum_{i=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|r_i - R_\alpha|} = \sum_{i=1}^{N} v(r_i) \quad (3.8)$$

Where $v(r_i) = \sum_{\alpha=1}^{M} \frac{Z_\alpha}{|r_i - R_\alpha|}$ is called the external potential on the ith electron due to M nuclei present in the system. The first and third terms (i.e. T and V_{ee}) in Eq. (3.7) are universal operators, hence they are same for any system while the second term (V_{ext}) uniquely determines the Hamiltonian of system.

First Hohenberg-Kohn Theorem

The first Hohenberg-Kohn theorem states that ground state electron density ρ_0(r) of a bound system of interacting electrons in some externals potential v(r) determines this potential uniquely. This can also be stated as 'there exist one to one correspondence between external potential and ground state electron density.' Since, in turn, v(r) fixes the Hamiltonian operator, the ground state of many interacting system is a unique functional of ground state density ρ_0(r). That means, the basic variable is the ground state electron density which uniquely determines the Hamiltonian operator characterizing the ground state system.

For the proof of this theorem, let us consider two external potentials v(r_i) and v_0(r_i) which differ by more than a constant (since the wave function and hence the charge density is unaltered if a constant is added to the potential) with two different ground state wave functions Ψ and Ψ_0 but give rise to the same density ρ(r). Ψ and Ψ_0 can't be same since they satisfy different Schrödinger equation. Now if we denote the Hamiltonian and ground state energies for these wave functions by $\hat{H}$,$\hat{H}_o$ and E, E_0 respectively, then from minimal property of ground state energy:

$$E < \langle \psi' | \hat{H} | \psi' \rangle$$

$$= \langle \psi' | \hat{H}' | \psi' \rangle + \langle \psi' \,|\, \hat{H} - \hat{H}' \,|\, \psi' \rangle$$

This yields,

$$E < E' + \int \rho(r))\{v(r_i) - v'(r_i)\}dr \qquad (3.9)$$

Interchanging the primed with unprimed quantities and solving as before, we get,

$$E < E' + \int \rho(r))\{v'(r_i) - v(r_i)\}dr \qquad (3.10)$$

Adding eq. (3.9) and (3.10) leads to the inconsistency,

$$E + E' < E + E' \qquad (3.11)$$

This concludes that there cannot be two different v(r_i) that yield the same ground state electron density or in other words, v(r_i) is a unique functional of ρ(r), since in turn v(r_i) fixes $\hat{H}$, we see that the full many-particle ground state is a unique functional of ρI [23,24]. So in place of Eq. (3.3) writing ground state energy E_0 for E to make explicit dependence on ρ_0,

$$E_0[\rho_0] = T[\rho_0]+V_{Ne}[\rho_0]+V_{ee}[\rho_0]$$

$$=\int \rho_0(r)v(r)dr + F_{HK}[\rho_0] \tag{3.12}$$

Where,

$$F_{HK}[\rho_0] = T[\rho_0] + V_{ee}[\rho_0] \tag{3.13}$$

The term F_{HK} also referred as universal functional, in the sense that their form is independent of N, Z and R_α. We should note here that the ground state density uniquely determine the Hamiltonian operator, which characterizes all states (ground and excited) of the system.

Second Hohenberg-Kohn Theorem

The second Hohenberg-Kohn theorem can be stated as: The exact ground state energy (E_0) of a system with an external potential v(r) is given by the global minimum value of the energy functional E[ρ] and the density that minimizes the functional is the exact ground state density $\rho_0(r)$. The functional E[ρ] in terms of density ρ(r) can be defined for any external potential v(r).

Now, as it is proven that ρ(r) contains all the necessary information for the entire system, it follows that all observables are certain functionals of ρ(r). The total energy $E_v[\rho]$ and its constituents, the total kinetic energy T[ρ], the total external potential energy $V_{ext}[\rho]$ and the total electron-electron interaction energy $V_{ee}[\rho]$ are now written as,

$$E_v[\rho] = T[\rho] + V_{ext}[\rho] + V_{ee}[\rho] \tag{3.14}$$

Rewriting this in the form of

$$E_v[\rho] = \int v(r)\rho I dr + T[\rho] + V_{ee}[\rho]$$

$$= \int v(r)\rho I dr + \langle\psi|\hat{T} + \hat{V_{ee}}|\psi\rangle \tag{3.15}$$

We can see that integral part is system dependent. For the other part which is universal functional, valid for any number of particles and any external potential, we define a new HK function as

$$F_{HK}[\rho] = \langle \psi | \hat{T} + \hat{V}_{ee} | \psi \rangle$$
$$= T[\rho] + V_{ee}[\rho] \qquad (3.16)$$

So that equation (3.15) becomes

$$E_v[\rho] = \int v(r)\rho I dr + F_{HK}[\rho] \qquad (3.17)$$

Although this functional $F_{HK}[\rho]$ appears to be just another formulation, it is actually the very important as it is applicable to each and every system. If it were known exactly, it would have been possible to solve the Schrödinger equation accurately, and there would have been no need of approximations.

However, it contains the functions for the kinetic energy $T[\rho]$ and the electron-electron interaction energy $V_{ee}[\rho]$, for both of which the explicit forms are unknown. It can be convenient to extract the classical Coulomb energy $J[\rho]$ from $V_{ee}[\rho]$ and write,

$$V_{ee}[\rho] = J[\rho] + G[\rho]$$

$$= \frac{1}{2}\int \frac{\rho(r)\rho(r\prime)}{|r-r\prime|} dr dr' + G[\rho] \qquad (3.18)$$

Where $G[\rho]$ is a (unknown) universal functional containing all the non-classical contributions. The main idea of the Hohenberg-Kohn theorem is presented in the Fig: (3.1).

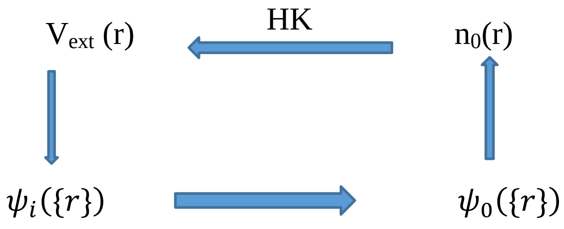

Figure 3.1: Schematic representations of the Hohenberg-Kohn theorem [26].

In the figure, the smaller arrows denote the usual solution of the Schrödinger equation where the potential $V_{ext}(r)$ determines all states of the system $\psi_i(r)$, including the ground state $\psi_o(r)$ and ground state density $\rho_o(r)$. The long arrow labeled HK denotes the Hohenberg Kohn theorem, which completes the cycle.

3.2.5 The Kohn-Sham approach

W. Kohn and L. Sham, in 1965, developed an approach with the introduction of atomic orbitals which is the foundation for the current application of DFT in the computational modern physics and chemistry fields. This approach yields a practical way to solve the Hohenberg-Kohn theorem for a set of interacting electrons. The purpose of introducing orbitals is to compute the ground state electron density ρ_0 and to provide a framework to compute the kinetic energy functional T[ρ]. For this purpose, W. Kohn and L. J. Sham introduced the idea of a reference system of non-interacting electrons that are influenced by a local effective potential $v_{eff}(r)$.

This effective potential is chosen such that the system of N non-interacting electrons exhibits the same ground state density ρ_0 as the real system of interacting electrons [25]. The Hamiltonian operator that defines the system of non-interacting electrons is defined as a sum of one-electron Hamiltonian operators

$$\hat{H}_s = \sum_i^N \hat{h}_i^{KS} \tag{3.19}$$

Where the one electron Hamiltonian operator is defined as

$$\hat{h}_i^{KS} = \frac{-1}{2}\nabla_i^2 + v_{eff}(r_i) \tag{3.20}$$

Since the exact wave functions of non-interacting electrons for the non-degenerate states are Slater determinants, the ground state wave function of the Hamiltonian operator given by (3.19) can be represented as

$$\phi_s = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(x_1) & \phi_2(x_1) & .. & .. & \phi_N(x_1) \\ \phi_1(x_2) & \phi_2(x_2) & .. & .. & \phi_N(x_2) \\ .. & .. & .. & .. & .. \\ \phi_1(x_N) & \phi_2(x_N) & .. & .. & \phi_N(x_N) \end{vmatrix} \tag{3.21}$$

The spin orbitalsϕ_i's are termed as Kohn-Sham orbitals and are given by

$$\hat{h}_i^{KS}\phi_i = \varepsilon_i\phi_i \qquad (3.22)$$

Where $\hat{h}_i^{KS}$ is the one-electron Kohn-Sham operator given by Eq. (3.20) and ε_i's are Kohn-Sham orbital energies unlike the molecular orbital energies.

The effective local potential v_{eff} of non-interacting reference system is chosen such that the ground state electron density ρ(r) of the reference system equals to the ground state electron density ρ_0I of the real system and is given by

$$\rho(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 = \rho_0(r) \qquad (3.23)$$

Which is subjected to conservation condition

$$\int \rho(r)dr = N \qquad (3.24)$$

The kinetic energy of the non-interacting reference system with the same density as the real interacting one can be obtained by the expression

$$T_s = \frac{-1}{2}\sum_{i=1}^{N} \langle\phi_i|\nabla^2|\phi_i\rangle \qquad (3.25)$$

The approximate kinetic energy term $T_s[\rho(r)]$ which is the kinetic energy of N non-interacting electrons is not equal to the kinetic-energy of N interacting electrons system.

$$T_s[\rho(r)] \leq T[\rho(r)] \qquad (3.26)$$

In KS-DFT, the difference between the true kinetic energy T[ρ(r)] and the non-interacting kinetic energy $T_s[\rho(r)]$ along with the non-classical electrostatic contribution G[ρ(r)] are collectively defined as the exchange-correlation functional [40].

$$E_{xc}[\rho(r)] = T[\rho(r)] - T_s[\rho(r)] + G[\rho(r)] \qquad (3.27)$$

From Eq. (3.18) and (3.27), we have

$$E_{xc}[\rho(r)] = (T[\rho(r)] - T_s[\rho(r)]) + (V_{ee}[\rho(r)] - J[\rho(r)]) \qquad (3.28)$$

Where $(T[\rho(r) - T_s[\rho(r)])$ is the residual part of the true kinetic energy which is not covered by Ts and G[ρ(r)] is the non-classical contribution to the electron-electron interaction. The exchange-correlation energy functional $E_{xc}[\rho(r)]$ contains all the unknown terms; non-classical effect of self-interaction correction, exchange and correlation to the potential energy of the system and a portion of kinetic energy. The energy expression of non-interacting system contains only two terms: the kinetic energy (T_s) and the energy due to the interaction with the external potential v(r). According to Hohenberg-Kohn theorems, the total energy must be a functional of electron density ρI. Hence, T_s must be also a functional of electron density ρ(r). Thus, the total energy of the reference system can be expressed as

$$E_s[\rho] = T_s[\rho] + \int \rho(r)v(r)dr \tag{3.29}$$

Now, the energy expression for real interacting system can be written as

$$E[\rho(r)] = T_s[\rho(r)] + J[\rho(r)] + E_{xc}[\rho(r)] + V_{ext}[\rho(r)] \tag{3.30}$$

Writing explicit forms for J[ρ(r)] and V_{ext}[ρ(r)], Eq. (3.30) can be expressed as

$$E[\rho(r)] = T_s[\rho(r)]\frac{1}{2}\int\int\frac{\rho(r)\rho(r')}{|r-r'|}drdr' + E_{xc}[\rho(r)] + \int \rho(r)v(r)dr \text{ ....(3.31)}$$

Since the ground state energy of a many-electron system can be obtained by minimizing the energy functional (3.31), subject to the Constraint (3.24), i.e.,

$$\delta\{E_v - \mu[\int \rho(r)dr - N]\} = 0$$

$$\delta\{\int v(r)\rho(r)dr + T_s[\rho] + J[n] + E_{xc}[\rho] - \mu\mu\,[\int \rho(r)dr - N]\} = 0$$

$$v(r) + \frac{\delta T_s[\rho]}{\delta\rho} + \frac{\delta J[\rho]}{\delta\rho} + \frac{\delta E_{xc}[\rho]}{\delta\rho} - \mu = 0 \tag{3.32}$$

Defining

$$v_{eff}(r) \equiv v(r) + \frac{\delta J[\rho]}{\delta\rho(r)} + \frac{\delta E_{xc}[\rho]}{\rho(r)} \tag{3.33}$$

And

$$v_{xc}(r) \equiv \frac{\delta E_{xc}[\rho]}{\delta\rho(r)} \tag{3.34}$$

We thus get the Euler-Lagrange equation

$$\mu = v_{eff}(r) + \frac{\delta T_s[\rho]}{\delta\rho(r)} \tag{3.35}$$

With the Kohn-Sham effective potential:

$$v_{eff}(r) = v(r) + \int \frac{\rho(r\prime)}{|r-r\prime|}dr' + v_{xc}(r) \tag{3.36}$$

The Eq. (3.22), (3.23), (3.36) together are the well-known KS equations, which must be solved self-consistently because v_{eff}(r) depends on the density through the XC potential. Usually, one begins with an initial guessed ρ(r), constructs a v_{eff}(r) from (3.36), solves for ϕ_i using (3.22) and finally gets a new ρI from (3.23). This process continues until the density converge, i.e. until self-consistency is achieved.

The flow chart for self-consistency is shown in the Fig. (3.2).

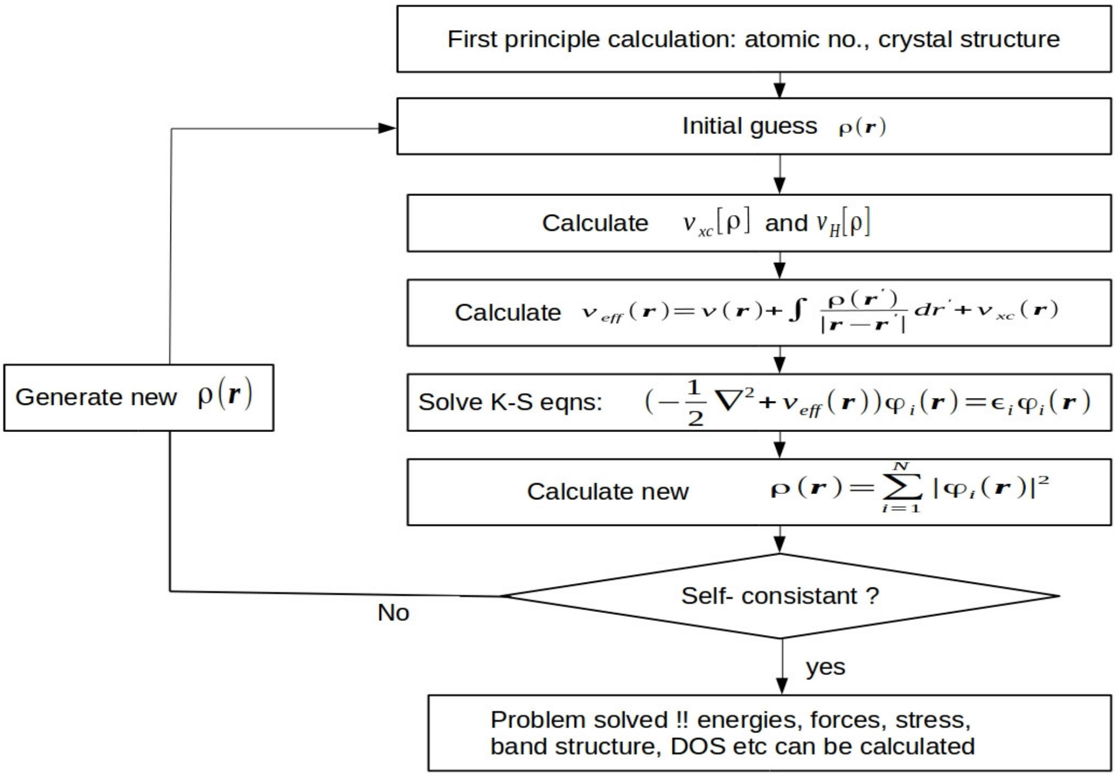

Figure 3.2: Self-consistency flow chart.

Thus if exact forms of E_{xc} and v_{xc} were known, the Kohn-Sham approach would lead to the exact energy i.e. the correct eigenvalue of the Hamiltonian operator $\hat{H}$ of the Schrödinger equation. It is noted that the approach that we have illustrated does not contain any approximation as of yet. The approximation only enters when we have to decide on an explicit form of the unknown functional for the exchange-correlation energy E_{xc} and the corresponding potential v_{xc}.

The brief description of the Kohn-Sham approach and it's relation with the Hohenberg-Kohn theorem is illustrated in the Fig. (3.3) [21].

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$$\begin{tikzcd}
V_{\text{ext}}(\mathbf{r}) \arrow[d, Rightarrow] \arrow[r, Leftarrow, "\text{HK}"] & n_0(\mathbf{r}) \arrow[r, Leftrightarrow, "\text{KS}"] & n_0(\mathbf{r}) \arrow[r, Rightarrow, "\text{HK}_0"] & V_{\text{KS}}(\mathbf{r}) \arrow[d, Rightarrow] \\
\Psi_i(\{\mathbf{r}\}) \arrow[r, Rightarrow] & \Psi_0(\{\mathbf{r}\}) \arrow[u, Rightarrow] & \psi_{i=1,N_e}(\mathbf{r}) \arrow[u, Rightarrow] & \psi_i(\mathbf{r}) \arrow[l, Rightarrow]
\end{tikzcd}$$

Figure 3.3: Schematic representations of the Kohn-Sham approach

In the figure, the notation HK_o denotes the Hohenberg-Kohn theorem applied to the non-interacting potential. The arrow labelled KS provides the connection in both directions between the many-body and independent particle systems, so that the arrows connect any point to any other point. Therefore, in principle, solution of the independent-particle Kohn-Sham problem determines all properties of the full many-body system [21].

3.2.6 The Local Density Approximation

The main problem with the Kohn-Sham procedure described above is the introduction of the unknown exchange-correlation functional. As long as there is no expression for this term, it is impossible to solve the KS equations. Therefore, several approximations have been devised to get an explicit form for this functional.

The most widely used approximation in solid state physics are the local density approximation (LDA) and the generalized gradient approximation (GGA).

The exchange-correlation potential $v_{xc}(r)$, also known as the Kohn-Sham potential, is a local potential in general cases. But for a real system, the exchange-correlation potential has non local dependence on the density. For slowly varying electron density $\rho(r)$, the exchange-correlation energy functional $E_{xc}[\rho(r)]$ may be considered to depend only on the local value of the density ρ(r) and not on its gradients. This is called the local density approximation (LDA) [21]. In local density approximation, the XC energy per electron at a point r is considered the same as that for a homogeneous electron gas (HEG) that has the same electron density at the point r.

In the local density approximation (LDA), the exchange-correlation functional $E_{xc}[\rho(r)]$ is approximated in the form,

$$E_{xc}^{LDA}(\rho) = \int \rho(r)\varepsilon_{xc}[\rho(r)]dr \qquad (3.37)$$

Where $\varepsilon_{xc}[\rho(r)]$ is a function that gives the exchange- correlation energy per particle of a uniform gas of interacting electrons of density ρ(r).

3.2.7 The Generalized Gradient Approximation

The accuracy of LDA is often considered satisfactory in condensed-matter systems, but it is much less so in atomic and molecular physics, for which highly accurate experimental data are available. Also, LDA overestimates (∼ 20% and more) cohesive energies and bond strengths in molecules and solids, and as a consequence bond lengths are often underestimated. Such problems are mostly corrected by the introduction of gradient corrections. The exchange-correlation functional is written as a function of the local density and of the local gradient of the density.

Also, as the LDA approximates the energy of true density by the energy of a local constant density, it fails in the situation where the density undergoes rapid changes such as in molecules. The first logical step to go beyond LDA is the use of not only the information about the density of the electron, n(r) at a point~ r, but also to supplement the density with information about the gradient of density, ∇_n(~ r) in order to account for the non-homogeneity of the true electron density. This approximation is called generalized gradient approximation (GGA). Symbolically this can be written as,

$$E_{XC}^{GGA} = E_{XC}\left[\rho(r), \nabla_\rho(r)\right] \qquad (3.38)$$

Which can also written as:

$$E_{XC}^{GGA}[\rho] = \int \rho(r)\, \varepsilon_{XC}\left[\nabla_\rho(r), \rho(r)\right]dr \qquad (3.39)$$

There are two sets of functional forms widely used in exchange correlation energy, introduced respectively by Perdew and Wang in 1992 (pw91) [30] and Perdew, Burke, and Ernzerhof in 1996 (PBE) [29]. It is observed that GGA in PBE form give rather accurate results for most of the periodic systems.

Both LDA and GGA perform badly in materials where the electrons tend to be localized and strongly correlated such as transition metal oxides and rare-earth elements and compounds. This drawback leads to approximations beyond LDA and GGA.

3.3 Pseudo-potentials and applications

Generally single particle wave function is taken into account to solve Kohn-sham equation in the solid on plane wave basis. Due to Wiggling nature of core electron, to express them in plane waves, it requires an extremely large number of basis sets. Since core electron are mostly localized to an ion and are less important in determining physical and chemical properties of the material. Because of this, they can be considered as external effective potential for the valance electrons. However, classification of valance and core electrons on certain atoms may not be straight forward. Thus the pseudo-potential method equivalently transform all the electron problem into valance electron problem only.

In our study within QE method, we make use of pseudo-potentials. The pseudo-potential method is an attempt to replace the complicated effects of the motion of core electrons and nucleus of an atom with an effective potential term.

It means an effective potential is used as an approximation for the simplified and explicit description of complex systems, the chemically active valence electrons are dealt explicitly, while the core electrons are frozen with nuclei as rigid non-polarizable ion cores. The core states are eliminated, and the valence electrons are described by pseudo-wave functions to be described with far fewer nodes, thus making plane-wave basis set practical to use. The representation of wave function and potential in the pseudo-potential methods is shown in the Fig. (3.4) below. There are much pseudo-potential currently in use. Out of them the ultra-soft and norm-conserving pseudo-potentials are widely used [32]. The developers of the pseudo-potentials do not guarantee the usefulness of their product for any system under study and the researchers have to use them at their own risk. In the ultra-soft pseudo-potential method, the system takes the contributions from some core states, thus the name ultra-soft. While in norm-conserving pseudo-potential method, we define the core states and valence states ourselves and the system does not take any contribution from the core states.

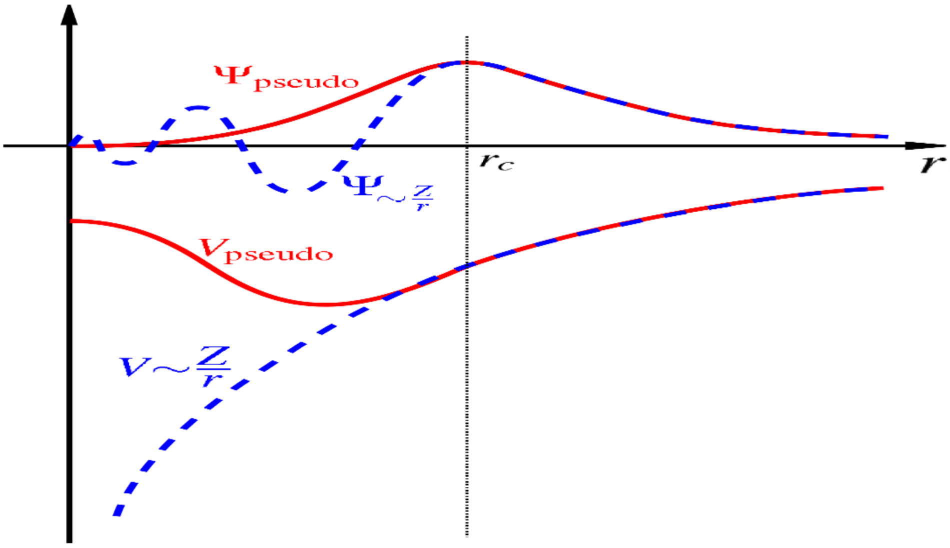


Figure3.4: Comparison of a wave function in the Coulomb potential of the nucleus (blue) to the one in the pseudo-potentials (red). The real and the pseudo wave function and potentials match above a certain cut off radius rc

3.3.1 Norm-conserving pseudo-potentials

First-principles pseudo-potentials are generated by solving all-electron radial Kohn-Sham equation within the density functional theory

$$\left[\frac{-1}{2}\nabla^2 + \frac{l(l+1)}{2r^2} + V^{ks}(r)\right]\psi_l^{AE}(r) = \varepsilon_l \psi_l^{AE}(r) \qquad (3.40)$$

Where $V^{KS}(r) = V_{ext} + V_H[n(r)] + V_{xc}^{LDA}[n(r)]$ is the self-consistent, one-electron potential with V_{xc}^{LDA} being the exchange correlation potential within LDA, and $\psi_l^{AE}(r)$ is the atomic radial wave function for angular momentum l.

We then replace the atomic wave function ψ^{AE} l by a pseudo-wave function ψ_l^{PS}within the pseudization radius of $r_{c,l}$, which will satisfy the following conditions[34]

- Pseudo-wave function ψ_l^{PS} contain no nodes.

- $\psi_l^{PS} = \begin{cases} \psi_l^{AE} if r > r_{c,l} \\ r^{l+1} f(r) if r \leq r_{c,l} \end{cases}$ (3.41)
- Norm conserving, i.e. . $\int_0^{r_{c,l}} \left|\psi_l^{PS}\right|^2 r^2 dr = \int_0^{r_{c,l}} \left|\psi_l^{AE}\right|^2 r^2 dr$
- Pseudo-potential eigenvalue $\varepsilon_l^{PS} = allelectroneigenvalue \varepsilon_l^{AE}$

Here, $f(r) = \sum_{i=0}^{12} c_i r^i$ for even i only is the Troullier-Martin's method [35]. This method is an improved version of Kerker [34] and mostly focus on the smoothness of pseudo-potential. The coefficients ci are calculated with norm conserving condition, continuity of $\psi_l^{PS}(r)$ and its derivatives up to the fourth order at $r_{c,l}$, and zero curvature of screened pseudo-potential at the origin.

Another advance in generating pseudo-potential is due to Rappe and others (RRKJ) [20]. In RRKJ pseudization the optimized pseudo wave function is expressed as a sum of Bessel functions instead of polynomial as in Ref [33], which is equal to all-electron wave function outside the cut-off radius r_c and fI+cI inside r ≤ r_c. The expression for f(r) is given below:

$$f(r) = \sum_{i=1}^{3(4)} \alpha_i j_l\,(q_i r) \tag{3.42}$$

Where the coefficients α_i and parameters qi are found from normalization condition and the continuity conditions between pseudo wave function and

$$\phi_l^{AE}(r) atr = r_{c,l}. c(r)$$

is also the sum of Bessel functions whose coefficients are chosen to minimize the kinetic energy beyond q_c and it vanishes at r_c.

Once the pseudo wave function is determined as above, we invert the Schrödinger equation to obtain the screened (mixed with Hartree and exchange correlation potential) pseudo-potential as follows

$$V_l^{scr}(r) = \varepsilon_l - \frac{l(l+1)}{2r^2} + \frac{1}{2\psi_l^{PS}(r)} \frac{d^2\psi_l^{PS}(r)}{dr^2} \tag{3.43}$$

Once we remove the Hartree and exchange-correlation part from Equation (3.43), we obtain the ionic pseudo-potential. Pseudo-potential thus generated is called norm-conserving pseudo-potential (NC-PP).

3.3.2 Ultrasoft pseudo-potential (USPP)

In norm conserving pseudo-potential it is difficult to deal with highly localized orbitals such as 2p in first row atoms, 3d in transition metal atoms and 4f in rare-earth atoms due to very large number of plane wave basis sets. This difficulty can be overcome by relaxing the direct norm-conserving condition inside the cut-off radius r_c [35]. This will allow one to choose the larger cut-off radius than used in NC-PP. To achieve such condition the valence charge density is compensated by an augmented charge density in the self-consistent calculation. The pseudo-wave function in this method is the solution of generalized eigenvalue problem. Method is the solution of generalized eigenvalue problem.

$$H|\,\psi_{n,k}^{PS}\rangle = \varepsilon_{n,k}S|\,\psi_{n,k}^{PS}\rangle \qquad (3.44)$$

where H is the usual Hamiltonian and S is the non-local overlap operator, which ortho-normalize the pseudo wave function as below

$$\langle\psi_{n,k}^{PS}|\hat{S}|\psi_{n',k}^{PS}\rangle = \delta_{n,n'} \qquad (3.45)$$

The form of operator is given by

$$S = 1 + \sum_{i,j} Q_{i,j}|\,\beta_i\rangle\langle\beta_j\,| \qquad (3.46)$$

Where β_i are constructed local function from $\psi_i^{PS}(r)$,

The matrix $Q_{i,j} = \psi_i^{*AE}(r)\psi_j^{AE}(r) - \psi_i^{*PS}(r)\psi_j^{PS}(r)$, which relax the direct norm conserving condition. This kind of pseudo-potential must be updated at each self-consistent iteration.

3.3.3 Band Structure

If we knew the potential $V_P(r)$, and could solve the one-electron Schrödinger equation $(\frac{-\hbar^2}{2m_e}\nabla^2\psi(r) + V_P(r)\psi(r) = E\psi(r)$

we could ascertain the energies E of the entirety of the different potential states. There are a few different ways of moving toward such figurings from first standards, and we won't go into those here. The after effects of such counts give what is known as a band structure. The electronic conditions of precious stones are portrayed by the band hypothesis of solids. The external orbital's of the molecules in a thickly stuffed strong cover with one another as the synthetic bonds that hold the gem together are framed. This causes the discrete vitality levels of the free ion as to be expanded into groups. The differentiation between a protector and a semiconductor is identified with the size of the band gap. Semiconductors have littler band holes than encasings. The free electrons in the conduction band can direct power effectively in a similar way as the free electrons in metals. Semiconductors, hence, have a higher conductivity than encasings, yet a littler conductivity than metals as a result of the modest number of free electrons [21]. There are various groups in a band structure(in actuality a limitless number), yet generally, just a couple are significant indeciding specific properties of a material. Fig. 8.4 outlines a basic band structure. Each band has an all outnumber of permitted k-states equivalent to the number of unit cells in the precious crystal.

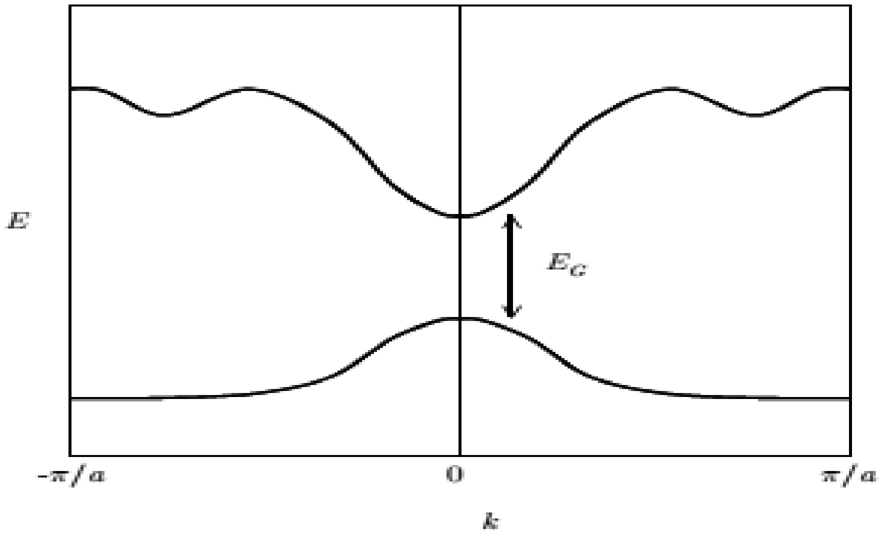


Fig. 3.5: Figurative illustration of a semiconductor band structure, plotted along one crystal direction

The upper "band" (line) will be essentially empty of electrons, and is called the conduction band; the lower band will be essentially full of electrons, and is called the valence band.

Fig. 2.4 illustrates a simplified band structure. In each band, we only have to plot *k*-values from $-\pi / a$ to π / a. The band structure in Fig. 2.4 is also drawn to be symmetric about $k = 0$. Band structures are often symmetric in this way. In our simple one-electron model, neglecting magnetic effects, the existence of symmetries like this is easily proved [22].

3.3.4 GW approximation

While we have given some justification to utilizing a straight forward LSDA band structure way to deal with assessing excitation energies, various materials with intriguing attractive properties include firmly corresponded electronic states, and other estimated approaches have been created to go past the LSDA. For the quasiparticle issue, the focal issue is a sufficient estimation for the self-vitality administrator, $\Sigma_{GW}(r,r';E)$. A working technique for tackling this issue is the purported GW estimation. On the off chance that the pinnacle is sufficiently sharp, well-defined quasiparticle vitality can be acquired. Where the self-energy is

$$\Sigma_{GW}(r,r';t) = iG(r,r';t)W(r,r':t) \qquad (2.1.39)$$

The self-vitality in the GW A has a similar structure as that in the Hartree-Fock estimate aside from that it relies upon the vitality and contains a term that relies upon abandoned states as an outcome of relationship impacts. In this manner, the GW A can be deciphered as a speculation of the Hartree-Fock estimate with a potential that contains dynamical screening of the Coulomb potential. The GWA has been fruitful in treating the quasiparticle frameworks, for example, free-electron like metals and semiconductors It can be demonstrated that the GWA hypotheses might be identified with a Hartree-Fock hypothesis with a recurrence and orbital-subordinate screened Coulomb association and, at any rate for confined states, for example, d or f orbital's of progress metal or uncommon earth metal particles [23].

CHAPTER 4

METHODOLOGY

4.1 General Consideration

In this chapter, we discuss details about our present work with the first principle pseudopotential-based density functional calculations including norm-conserving pseudo-potential in the DFT approach by using The quantum ESPRESSO (QE) computational package. Some practicable commands along with their functions are well detailed here.

4.2 Quantum Espresso Program

In this activity, you will use the Density Functional Theory (DFT) to investigate the properties of different materials. DFT is broadly utilized in industry, and in the scholastic research network since it is one of the computational techniques that can (roughly) tackle reasonable quantum mechanical issues numerically [24]. Quantum ESPRESSO-a condensing for Quantum Open-Source Package for Research in Electronic Structure, Simulation, and Optimization program is a multi-reason and multi-stage PC coding program for electronic-structure figurings and materials demonstrating. This bundle is essentially utilized in the stomach muscle ab-initio estimations of dense issue frameworks. In a controlled issue material science, its ordinary application in the stomach muscle ab-initio estimations like-basic advancements (both at zero and limited temperature), direct reaction computations (Phonons, flexible constants, dielectric, and some more) and so forth stretches out to high-temperature atomic elements. The significant element of the bundle remembered for the product are :

(i) Plane Wave self-consistent field (PWscf)
(ii) First-Principles Molecular Dynamics (FPMD) and
(iii) Car-Parrinello (CP). QE, based on DFT, implements a variety of methods and algorithms for a chemically realistic modelling of materials from the Nano scale upwards
(iv) Chemical reactivity and transition-path sampling, using Nudged Elastic Band (NEB) method.

(v) Computational microscopy (STM). This package uses a plane waves (PWs) basis set for the expansion of electronic wave function, a pseudopotentials (PPs) to represent electron-ion interactions and DFT for the description of electron-electron interaction.

Some basic computations/simulations that can be performed by this package include:

- Calculations of the Kohn-Sham (KS) orbitals and energies for isolated and extended systems, and of their ground states energies.
- Structural modelling (equilibrium structures of molecules, crystals, surfaces).
- Atomic forces and stresses.
- Ground state studies of magnetic or spin-polarized systems.
- Dynamical modeling (first-principles molecular dynamics) either in the electronic ground state (Born-Oppenheimer) or with fictitious electronic kinetic energy (Car-Parrinello).

Density-Functional Perturbation Theory (DFPT) used in the package to calculate the energy derivatives and related quantities. QE package are used as our first — principles code. QE is a full ab- initio package implementing electronic structure and energy calculation, linear response method (to calculate dielectric constants, Born effective charge and phonon dispersion curves) and third order an-harmonic perturbation theory. It also contains two molecular- dynamics codes, CPMD (Car-Parrinello Molecular Dynamics) and FPMD (First Principles Molecular Dynamics). Among them, to perform the total energy calculations, PWscf code is used, which used both norm-conserving pseudopotential (PP) and Ultra soft Pseudo-potentials (US-PP) within DFT. In our case, we use Quantum ESPRESSO integrated module of codes, based on DFT by using plane basis set for expansion of wave function and pseudopotential with required content in first-principle method of calculation to calculate total energies and optimize geometries of transition metal Cr and Mo. Also, by using this package, band structure is calculated and partial density of states (PDOS) is used to find the nature of material.

4.2.1 PWscf

PWscf stands for Plane Wave self-consistent field (which in earlier releases included PHonon and PostProc), developed by Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso (SISSA) Paolo Giannozzi (Univ. Udine), and many others [25]. PWscf implements an iterative approach for self-consistency, in the framework of the plane-wave pseudo potential method. This package uses the well-established LDA and GGA exchange-correlation functionals, including spin-polarizations. The main feature of PWscf calculation is the self-consistency calculations, structural relaxation, electronic structure calculations, variable cell molecular dynamics calculation, etc, performed by invoking executable file called pw.x. The structural optimization is performed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) [26].

Some of the most important parameters in the input file of the Quantum espresso are as indicated below.

- &CONTROL: general variables controlling the run
- &SYSTEM: structural information on the system under investigation & ELECTRONS: electronic variables: self-consistency, smearing
- ibrav : 3, this keyword generates body centered cubic (bcc) structure.
- celldm(1): specifies the lattice constant of the crystal and are usually given in atomic unit. · ecutwfc: kinetic energy cutoff (Ry) for wavefunctions (1 Ry=13.6ev).
- nat: number of atoms in the unit cell .
- ntyp: number of types of atoms in the unit cell.
- nbnd: represents the number of electronic stated (bands) to be calculated.
- Atomic Species: It specifies the symbols of the atoms, their corresponding masses (in amu) and the name of the files containing the pseudo-potentials.
- Atomic Positions: specifies the atomic co-ordinates of the atoms which are defined for the proper structure.
- k-points: represents the rectangular grid of points of dimensions, spaced evenly throughout the Brillouin zone and this keyword requires appropriate unit.

4.2.2 Post-Processing

The package called Postprocessing was Originally developed by Stefano Baroni, Stefano de Gironcoli, Andrea Dal Corso (SISSA), Paolo Giannozzi (Univ. Udine), and many others. After the Self Consistent calculation has been converged, we use many small calculations such as plotting of band, density of states (DOS) etc.

The main post processing codes which extract the specified data/files from the PWscf calculations and perform further calculations are as follows;

- pw.x: We use this command to run the input files of scf and nscf calculations of energy and wave functions at each k-points, which extracts the output files for the energy calculation at every k-points.
- bands.x : This extracts the files from PWscf calculation and records its eigenvalues at different K-points with corresponding energies values ready for further processing. The code bands.x also performs the symmetry analysis of the band structure.
- plotband.x : The output file of bands.x is directly read and converted to plottable format by auxiliary code plotband.x. The value of k-points must be correctly put in a sequence, otherwise unpredictable plots may result if k-points are not in sequence along lines or if two consecutive points are same. Thus, proper choice of sequence of k-points is important.
- dos.x : This code helps us to calculate the electronic density of states at different k-points. • projwfc.x : This code calculates projections of wave functions over atomic orbitals. It gives the contributions of the atomic orbitals s, p, d, f.

CHAPTER 5

RESULTS AND CONSIDERATION

5.1 General Consideration

This thesis has describes the comparative study of element Chromium (Cr) and Molybdenum (Mo). One of the main challenges in first principle calculation is the geometric optimization of structures. We have taken out the energy minimization of Cr and Mo, followed by the study of electronic band structures and the density of states. The calculation has been carried out using density functional theory using generalized gradient approximation. At first, in the GGA method, energy minimization is done with respect to the lattice parameter then the same lattice parameter corresponding to the minimum energy state is used to carry out further calculations. In-band structure calculations, We plotted the graph of energy versus the high symmetry k-points and then analyzed the properties of the substance on the basis of band lines and band gap. To view the individual contribution of different orbital electrons, we study the conduction band edge and valance band edge. Likewise, the Density of states (DOS) is performed to get information about the nature of the bandgap and the Partial Density of states (PDOS) gives information about the origin of bands. In all these self-consistent fields (SCF) calculations, we have used the convergence criteria as the difference between energy in the order of 10^6 Rydberg.

In this chapter, we discuss about:

- Calculation of lattice parameter.
- Calculation of Density of states (DOS) as well as Partial Density of States (PDOS) and plotting.

Then we have performed the series of following convergence tests and energy minimization:

5.2 Structural Optimization:

We carried out the self- consistent field (scf) calculations to determine basic parameters:

kinetic energy cut-off for the plane wave basis and k-points grid by testing the convergence of total energy with these parameters individually and calculation of lattice parameter by energy minimization.

5.2.1 Kinetic Energy cut-off (ecutwfc)

The plane wave scf code implemented in the Quantum Espresso expand the electron wave-function in terms of the infinite basis function that are plane waves. The value of the kinetic energy cut-off corresponds to the neighbouring interactions in the periodic system. If we take this cut-off energy large, we include long range interactions and the results will be more accurate, but this takes more computing resources. If we take this energy small, the results could be inaccurate though computationally cheap. Therefore, we have to take optimum value of this cut-off energy. It is expressed in unit of the energy Ry. The plane wave expansion in the reciprocal space is

$$\psi_k(r) = \frac{1}{\Omega}\sum_G C_{k.G^{e^{i(k+G).r}}} \tag{4.1}$$

where Ω is the volume of the box, G are the reciprocal lattice vectors defined by $G.l = 2\pi m$ for all l, where l is a lattice vector of the crystal and m is an integer, $C_{k.G}$are the coefficients for the plane waves and k represent the reciprocal space vectors within the first Brillouin zone of the periodic cell.

In principle, we need infinite numbers of plane waves but in order to reduce the computational cost we have to truncate the plane wave expansion from some acceptable value. To make the plane wave expansion (4.1) finite, we truncated according to the condition.

$$\frac{|k+G|^2}{2m} \leq E_{cut} \tag{4.2}$$

We performed the scf calculations using the experimental value of the lattice parameter (a=5.4 Bohr) and some arbitrary k-point mesh in the scf input file for Cr. The scf calculations were performed for different values of the ecutwfc ranging from 40 Ry to 100 Ry. At these different values of cut-off energy, we found different values of total scf energy. Then we plot the graph between the scf total energy versus kinetic energy cut-off value and the appropriate value of kinetic energy cut-off is chosen from which the convergence of total energy starts to occur. In the case of Chromium, it is found to be 85 Ry, which is shown in the Fig. (4.1). So, for further calculations, the value of ecutwfc = 85 Ry is appropriate to use for Chromium. In our case, the pseudopotential used is Cr.pbe-spn-kjpaw_psl.1.0.0.UPF pseudo-potentials generated using “atomic” code by A. Dal Corso (espresso distribution).

When a graph was plotted for the relationship between cut-off energy along X-axis versus total energy along Y-axis of Cr, following graph was obtained.

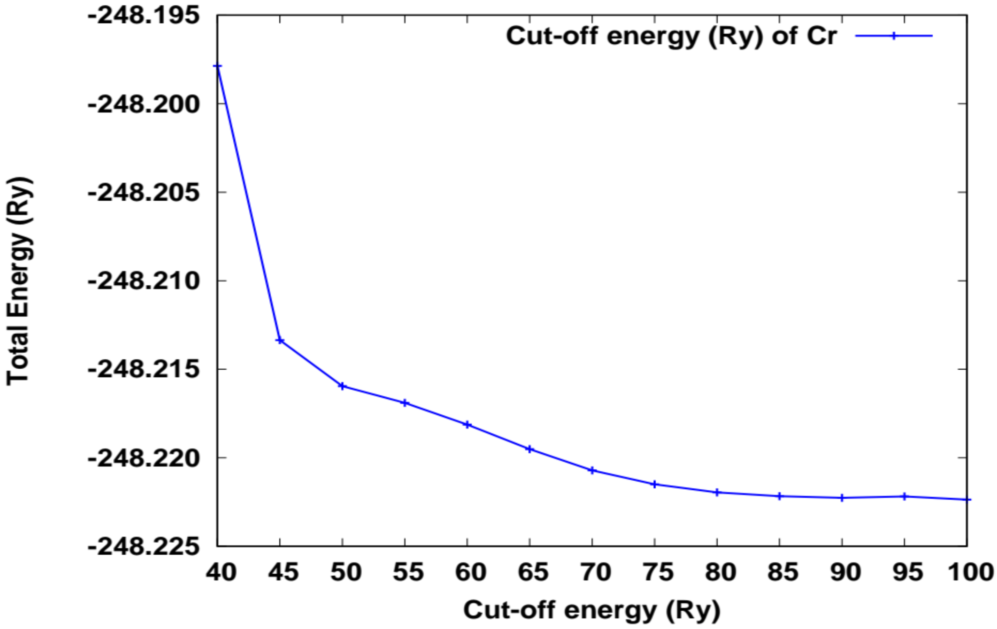


Figure 4.1 : The plot of Total energy with cut-off energy of Cr.

To determine the value of kinetic energy cut-off we performed the scf calculation using lattice parameter a=6.04 from literature and some arbitrary k-point mess (8, 8, 8) in scf input file for Mo. Similarly we perform same ecutwfc range as Cr in this case and we get different values of total energy in self-consistent field. Then plot of total energy versus kinetic energy cut-off value for BCC structure of Mo is shown in Figure (4.2). Clear from the Fig. (4.2) that there is nominal variation in total energy above 85 Ry. Therefore in the rest of calculations, our cut-off energy is 85 Ry.

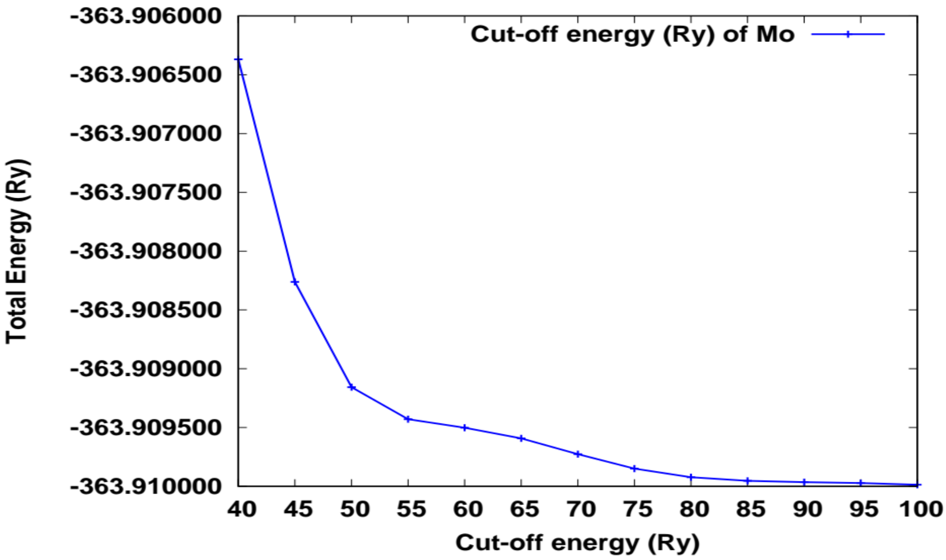


Figure 4.2: The plot of Total energy with cut-off energy of Mo.

5.2.2 Lattice Parameter

Lattice constant is a property of crystal lattice i.e. periodic arrangement of atoms in three dimensions whether it is not a property of atoms. Basically, the lattice constant is the length of periodicity of the lattice repeats itself, for most crystals the lattice constant are few angstroms. After the calculation and value of ecutwfc and, we performed a convergence test for lattice parameter by using the converged value of ecutwfc for both Cr and Mo. For Cr, we performed the scf calculations for total scf energy with different value of lattice parameters ranging from 5 to 6 Bohrs to optimizing lattice parameter by using optimized value of ecutwfc. Then we plot a graph between total energy with lattice parameter which is shown in Fig. 4.3.

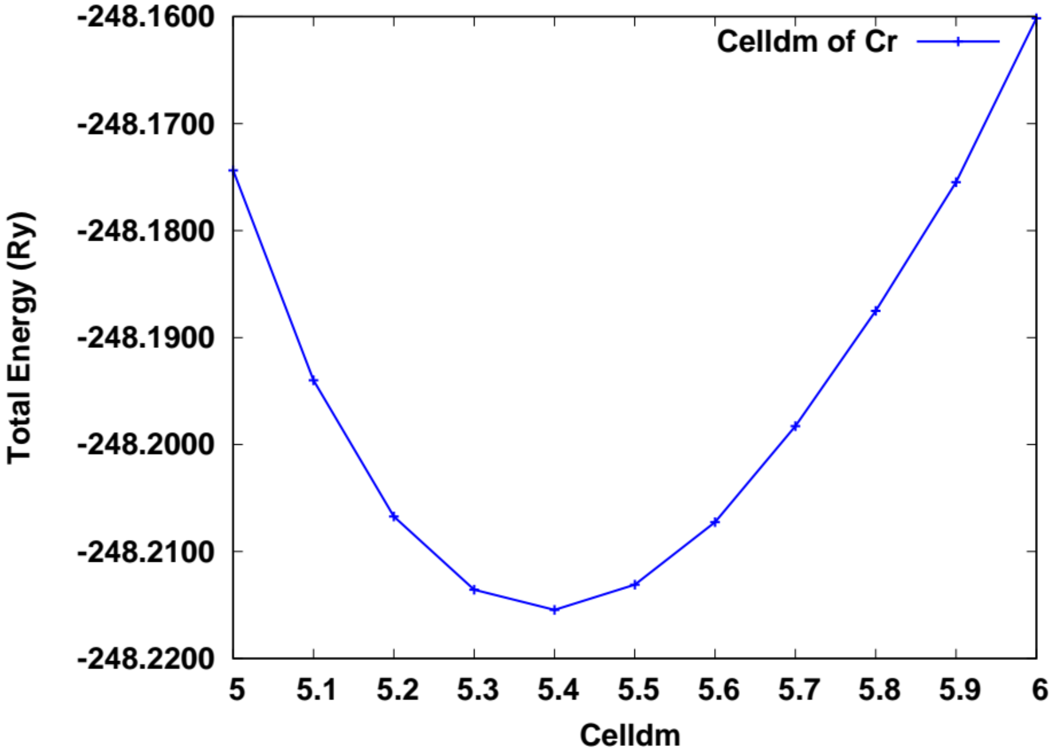


Figure 4.3: The plot of Total energy with lattice parameter of Cr

At different value of lattice parameter we found different value of total energy. Then, we obtained the suitable value of parameters for the input file at which the total energy is minimum. From Fig. 4.3, the appropriate value of lattice parameter is at which the minimum total energy is at 5.4 Bohr. The experimental value of lattice parameter is 5.5 Bohr which is closer to our calculate value of lattice parameter and we get 1.81% error from previous work [27].

For Mo, we performed the scf calculations for total scf energy with different value of lattice parameters ranging from 5.4 to 6.6 Bohr by using optimized ecutwfc. Then we plot a graph between total energy with lattice parameter which is shown in Fig. 4.4.

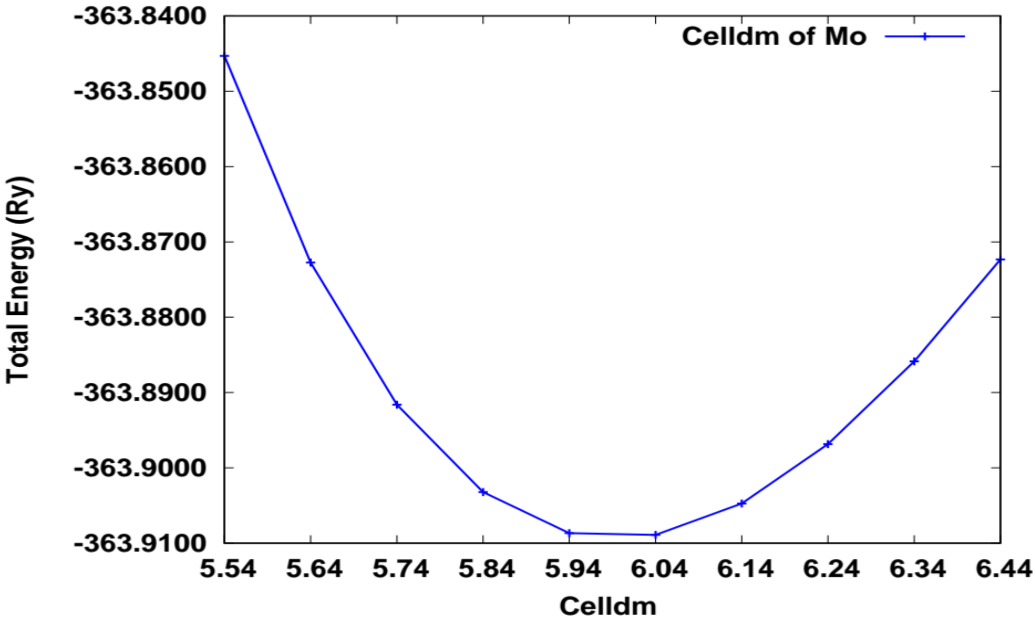


Figure 4.4: The plot of Total energy with lattice parameter of Mo.

Then, we obtained the suitable value of parameters for the input file at which the total energy is minimum. From Fig. 4.4, the minimum total energy is at 6.04 Bohr. The experimental value of lattice parameter is 5.95 Bohr which is closer to our calculate value of lattice parameter and we get 1.51% error from previous work [29].

5.2.3 k-point grid

In order to perform the Brillouin zone interaction in discrete scheme, it is essential to have a large number of grid points. But in practice, due to limitations of computational resources, we optimize the number of k-points grids. By calculating total energy versus k-point grids the rectangular grid of points of dimensions Kx×Ky×Kz, spaced evenly throughout the Brillouin zone is called k-points grid. More the number of the grid points sampling will be more finer and accurate but computationally expensive. Here, the size of grid required depends on the system under study. We can estimate appropriate size by means of total energy calculation. Our approach of k-point sampling is as suggested by Monkhrost and Pack [26]. At first, we performed the scf calculations of Cr for total scf energy with different values of k-points grid starting from 2×2×2 to 18×18×18. The calculated data of k-point grid vs its corresponding total scf energy is shown in Fig. 4.5.

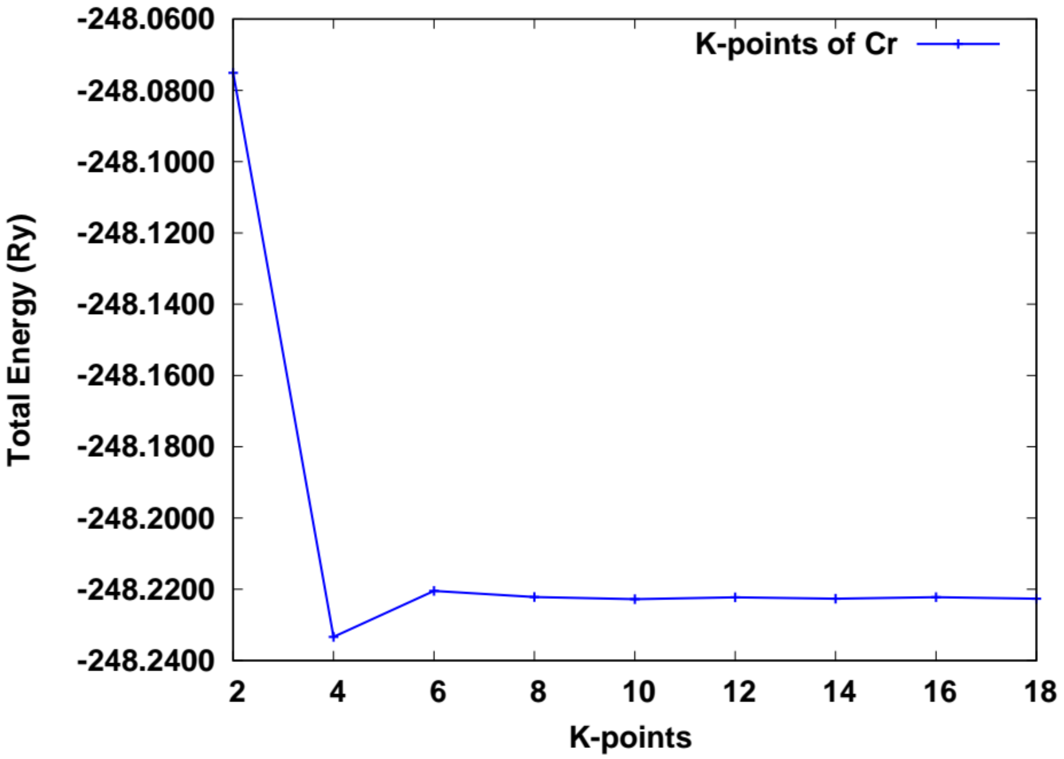


Figure 4.5: The plot of Total energy with k-point grid of Cr

From Fig. 4.5 it is clearly seen that total energy of Cr remains almost constant from the k-point grid 8×8×8. So, it is appropriate to use the value of k-point grid as 8×8×8 for our further calculation. Then we performed the scf calculations of Mo for total scf energy with different values of k-points grid starting from 2×2×2 to 18×18×18. The calculated data of k-point grid vs its corresponding total scf energy is shown in Fig. 4.6.

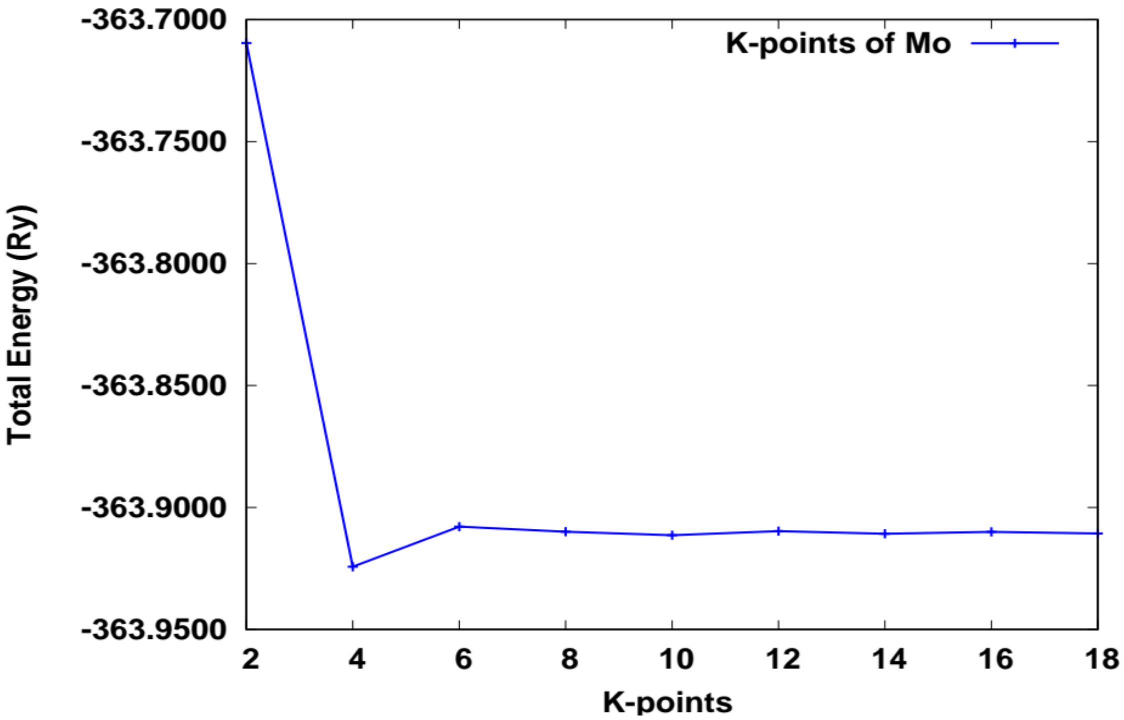


Figure 4.6: The plot Total energy with k-point grid of Mo

From Fig. 4.6, it is clearly seen that total energy remains almost constant from the k-point grid 8×8×8. So, it is appropriate to use the value of k-point grid as 8×8×8 for our further calculation.

5.2.4 Degauss

In the case of degauss, you should use the smallest value at which your calculation does not struggle to converge. After optimization of all Structure of Cr and Mo, we are intended to study the effect of degauss on elements. To account the degauss, we have taken all optimized value and apply degauss in the range of 0.001 to 0.06. Then we plotted a graph between degauss value vs total kinetic energy which is shown in Figure 4.7 and figure 4.8 for Cr and Mo respectively. From the graph it is observed that degauss is constant to 0.04 for Cr and 0.05 for Mo, so further calculation take place by using degauss 0.04 for Cr and 0.05 for Mo..

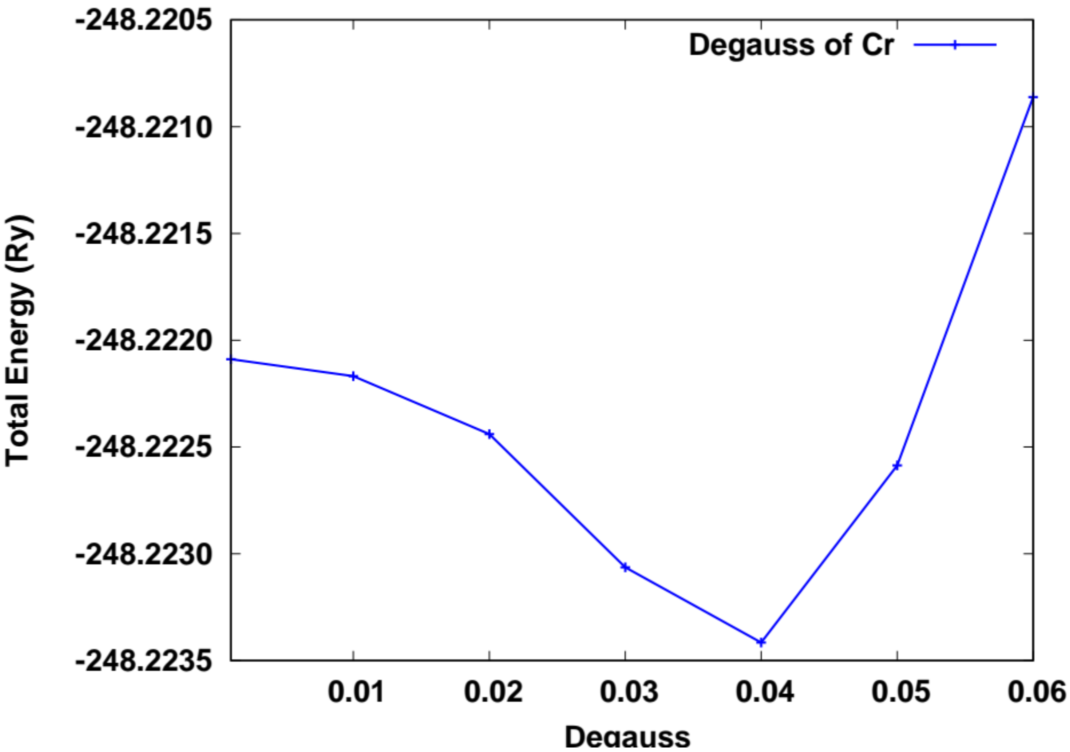


Figure 4.7: The plot of Total energy with degauss of Cr

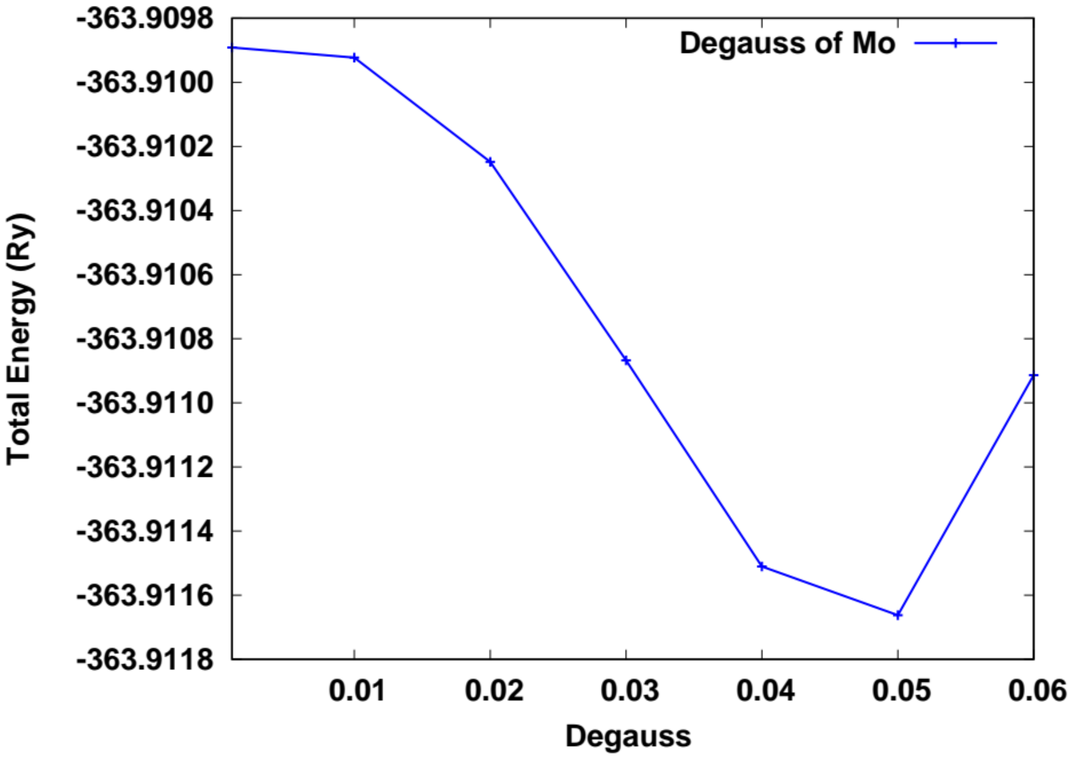


Figure 4.8: The plot of Total energy with degauss of Mo

We have also calculated the band structure of Transition Metal Cr and Mo. For other calculations of Cr and Mo, we took (8×8×8) and (8×8×8) respectively k-points along specific direction of irreducible Brillouin zone in order to obtain fine band structure which is performed by executable pw.x. Then, we performed post processing calculations with executable plotband.x in order to obtain band structure of Chromium Cr and Molybdenum Mo. Further, we have calculated the DOS and PDOS for both Cr and Mo structure. Finally we performed scf calculation and then nscf calculation; we used denser k-point mesh in order to obtain smooth partial density of states curve. These calculations were performed using the executable pw.x. Then, we performed PDOS calculation using executables projwfc.x command. In this section, we discussed the results of the first principles calculations carried out to obtain: Band structure calculation of Cr and Mo, Density of states of structure of Cr and Mo and Partial Density of states of structure of Cr and Mo.

5.3 Band Structure

In the first principles electronic structure calculation of crystals, the electronic band structure is one of the most widely applied analytical tools especially within the Kohnsham framework of density functional theory. The band structures of solid are helpful to determine different electronic properties of solid. It contains the basic ingredients to almost all the crystal properties. Since the atoms in a solid are closely packed the interaction between them perturbed the initial atomic levels when a large number of atoms are brought together. Electrons in the orbitals are filled up according to Pauli's exclusion principle i.e. no two electrons can occupy the same energy state. A bands constitutes a sort of energy continuum, in which separate level due to individual atoms cannot be identified. In the process of inter atomic interaction, the inner shell electron stated are the least affected. Whereas the valance electron, which are closest to neighbouring ions, are the most affected. The effect of bringing one atom closer to the other is to split a single sharp level. The bands structures of solids are helpful in determining different electronic and optical properties of the solid.

The band structure is calculated by pseudo potential and plane wave basis set method within the Density functional theory (DFT), treating exchange- correlation functional with generalized gradient approximation (GGA) in the form of PredewBerke- Erzndof (PBE) functional. All pseudo potential used in the calculations were norm- conserving scalar relativistic and full relativistic pseudo potentials. All calculation was performed within the Quantum- ESPRESSO package, plane wave kinetic energy cut-off were set at 85 Ry for both Cr and Mo. We took uniform grid of k-vector (k-points) in X-Y plane ranging from 1 to 1 in the unit of 2π /a .

The band structure calculation of Cr is shown in Fig. 4.9

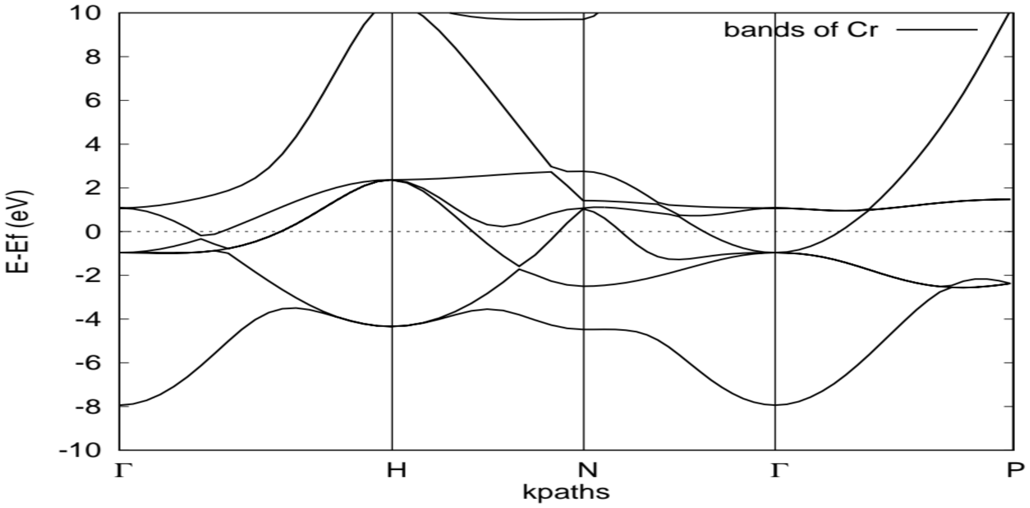


Figure 4.9: the plot of energy gap between conduction and valence band of Cr.

The band structure calculation of Mo is shown in Fig. 4.10.

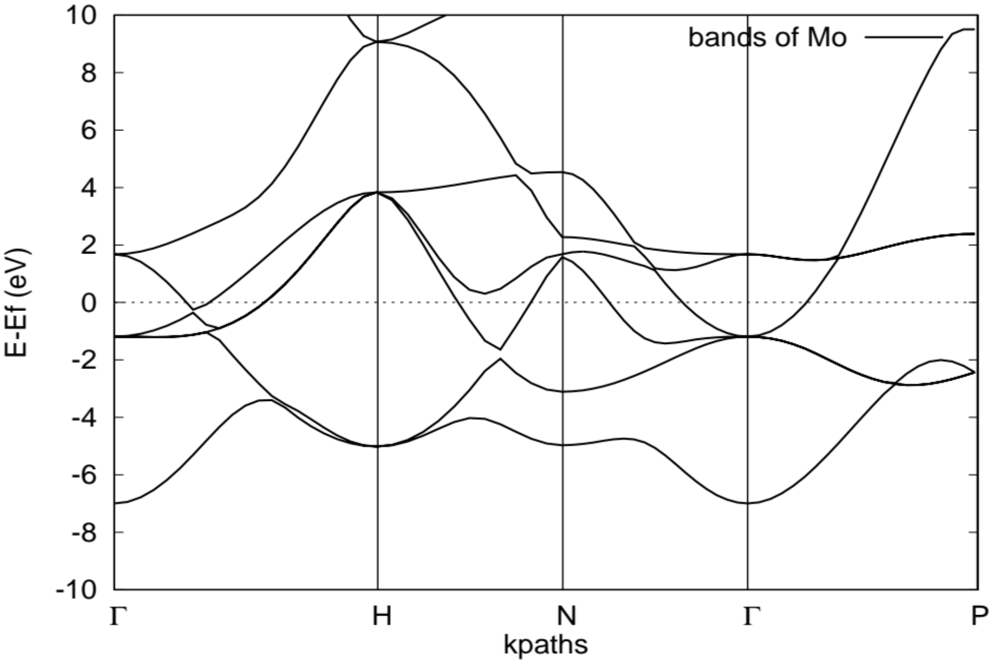


Figure4.10: the plot of energy gap between conduction and valence band of Mo.

5.4 Density of States

The density of states (DOS) is defined as the number of states per unit energy range available for the particles to be occupied. In other words, the density of states refers to the number of quantum states per unit energy range and it indicates how density packed quantum states in a particular system. In solid state and condense matter physics, the density of states is of immense important as it can be used to calculate the various parameters that give the insight of the different electronic, magnetic and transport properties. For example, Specific heat and paramagnetic susceptibility of a substance, mobility of charge carriers, diffusion properties and so on can be readily computed with the knowledge's of density of states (DOS). Moreover, the density of states provides numerical information on the states that are available at each energy level. The value of zero density of states indicates that there are no available states for occupation in an energetic level The density of sates is calculated by pseudopotential and plane wave basis set method within the Density functional theory (DFT), treating exchange- correlation functional with generalized gradient approximation (GGA) in the form of PredewBerke- Erzndof (PBE) functional. All pseudopotential used in the calculations were norm- conserving scalar relativistic and full relativistic pseudopotentials. All calculation was performed within the Quantum- ESPRESSO package, plane wave kinetic energy cut-off was set at 85 Ry for both Cr and Mo.

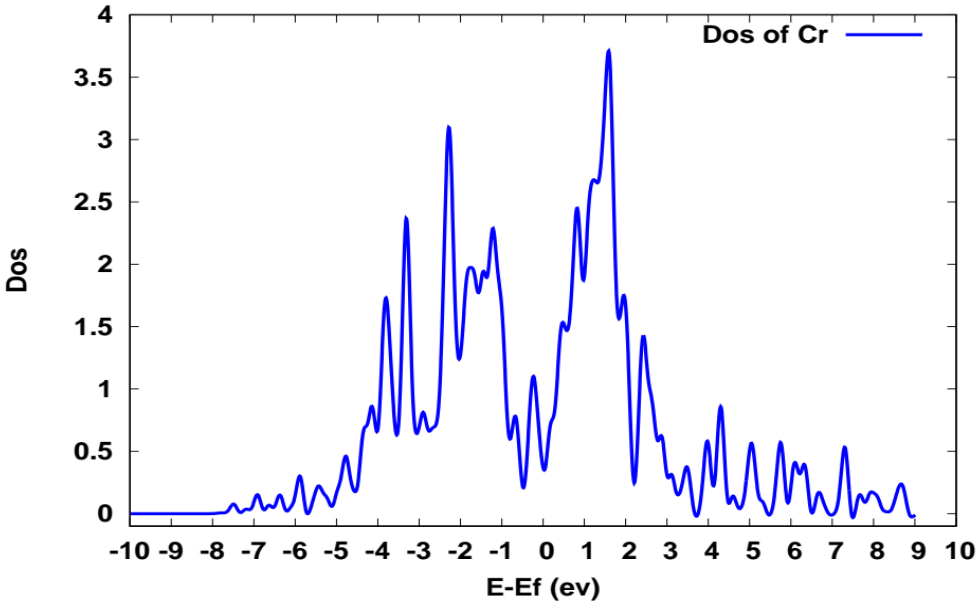


Figure4.11: The plot of DOS of Cr.

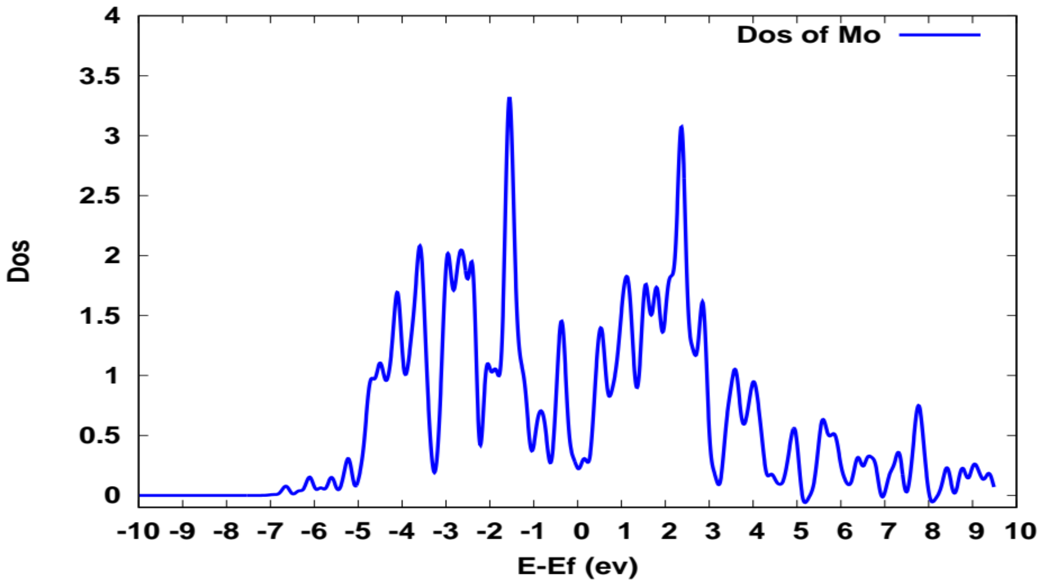


Figure 4.12: The plot of DOS of Mo.

The results of density of Cr and Mo help to further elaborate the nature of the band gap as shown in above Fig. 4.11 and Fig. 4.12, Where density of states DeltE=0.01, shows the respective states of crystal which clarify the nature of the element. For the comparative study of the band structures and density of states, we have merge the figure of band structures and density of states of transition metal of Cr and Mo in suitable scale which is shown in Fig.4.13 and Fig.4.14 respectively.

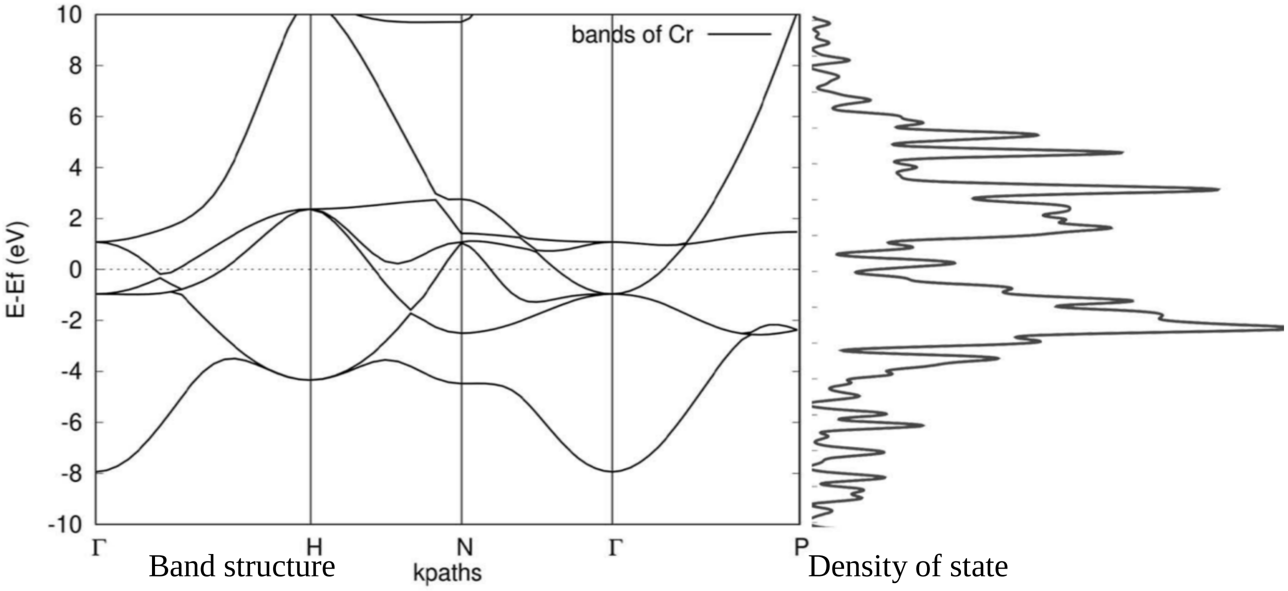
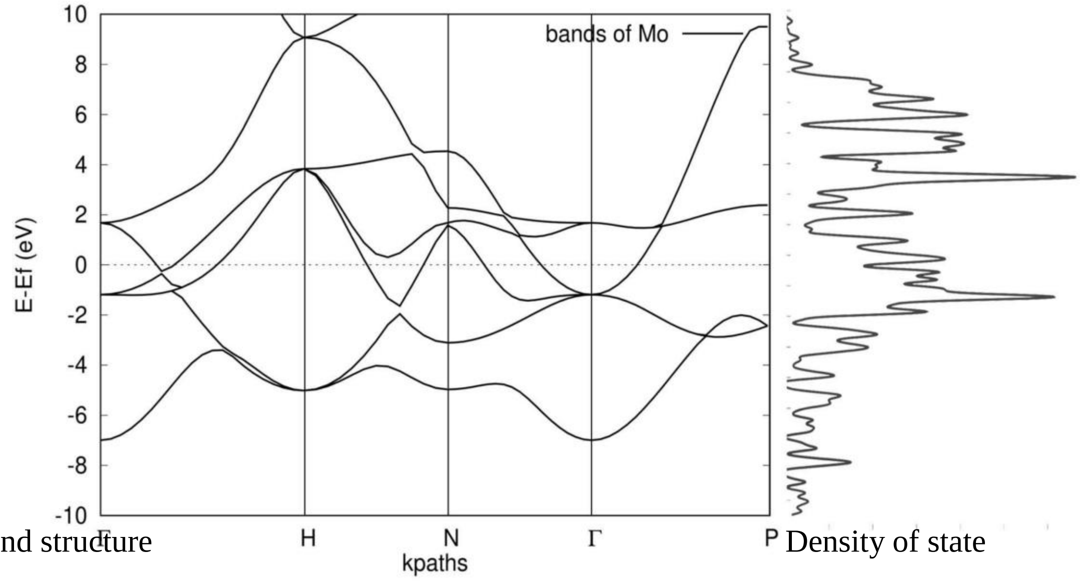


Figure4.13: comparative study of the band structures and density of states of Cr.



Band structure

Density of state

Figure4.14: comparative study of the band structures and density of states of Mo.

5.5 Partial Density of States

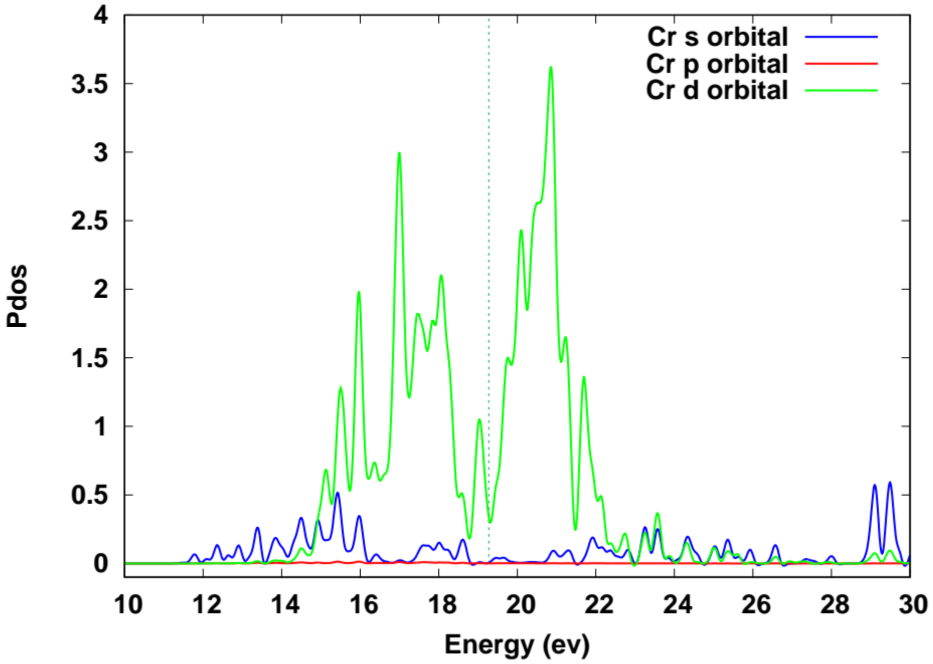


Figure 4.15: PDOS curve of Cr

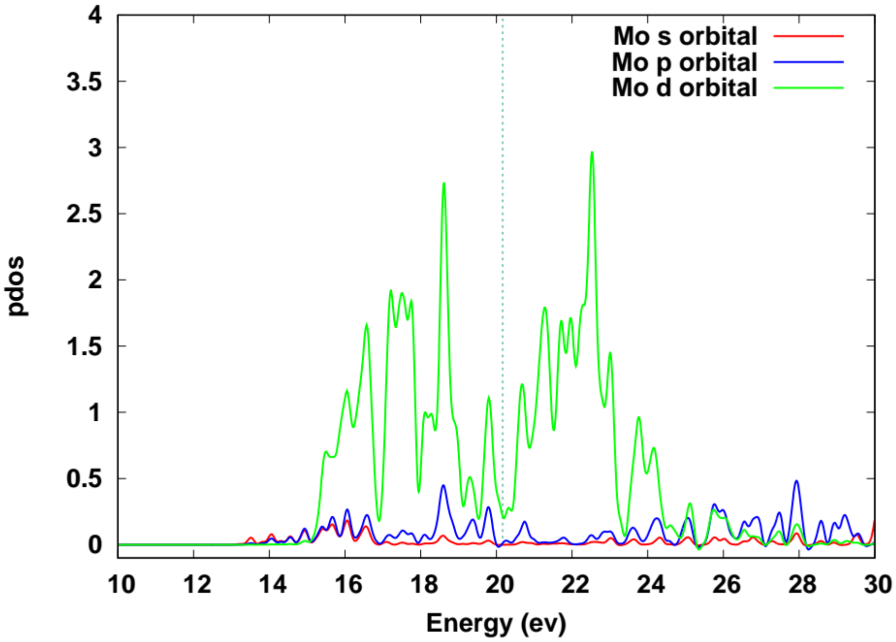


Figure 4.16: PDOS curve of Mo

The results of partial densities of states (PDOS) of Cr and Mo help to further elaborate the nature of band gap as shown in Fig. 4.15 and Fig.4.16. The partial density of states gives information about the origin of bands.

CHAPTER 6

CONCLUSION AND CONCLUDING REMARKS

This thesis has successfully employed to examine the structural properties of transition element Cr and Mo with the help of DFT, GGA, implemented with Quantum ESPRESSO code. At first we have constructed optimized structure of unit cell of BCC structure of both Cr and Mo. During optimization, the kinetic energy (cut-off energy) is found to be 85 Ry having k-point grid 8×8×8 for Cr. Then we estimate the lattice Parameter is found to be 5.4 Bohr for Cr which is very near with experimental results as well as previous calculated data. Which is only 1.81% deviated from experimental result and previous data. Thus the lattice parameter of Cr estimated with GGA method is in close agreement with experimental values. Then we have study the band structure, density of states and partial density of states of Cr using GGA method in QE package.

Similarly, optimization, the kinetic energy (cut-off energy) is found to be 85 Ry having k-point grid $8 \times 8 \times 8$ for Mo. Then we estimate the lattice Parameter is found to be 6.04 Bohr for Mo which is very near with experimental results as well as previous calculated data. Which is only 1.51% deviated from experimental result and previous data. Thus the lattice parameter of Mo estimated with GGA method is in close agreement with experimental values. Then we have study the band structure, density of states and partial density of states of Mo using GGA method in QE package.

This shows that Quantum ESPRESSO code using the plane-wave pseudopotential method can be used to perform first-principles calculations to study the electronic and other system which is more complex of transition element. We belive code can be used to study correlated systems for interest to current research to amble technological potential they support. All our study method which we have performs in this work can be used standard frame work to calculate the electronic, magnetic, and structural properties of materials in the elements and other related materials for which experimental data are not available.

6.1 Further Enhancement

The following studies can be done as further enhancement in our present study.

- Similar study from metal at least few more candidates, possibly adding optical and phonon properties can be done in future.
- We also can study the effect of doping of other suitable atom, which would give rise to alloy of different properties.
- We also study same from other different method suitable for these elements.

Thus we are now willing to extend our work to study the magnetic properties and phonon calculation, thermal expansion, optical properties which may have many potential applications in modern electronics.

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APPENDIX

[A]. LIST OF TABLES:

Cut-off kinetic energy and its corresponding total energy of Cr

Cut-off energy (Ry)	Total energy (Ry)
40	-248.1978629
45	-248.2133532
50	-248.2133532
55	-248.2168952
60	-248.2181238
65	-248.2195165
70	-248.2207115
75	-248.2215002
80	-248.2219531
85	-248.2221682
90	-248.2222616
95	-248.2221848
100	-248.2223664

Ccut-off kinetic energy and its corresponding total energy of Mo

Cut-off energy (Ry)	Total energy (Ry)
40	-363.906369
45	-363.9082616
50	-363.9091567
55	-363.9094294
60	-363.9095015
65	-363.9095922
70	-363.9097264
75	-363.9098492
80	-363.9099229
85	-363.9099534
90	-363.9099643
95	-363.9099726
100	-363.9099863

Variation of total energy with k-point grid of Cr

K-point	Total energy (Ry)
2	-248.0750938
4	-248.2333677
6	-248.2204456
8	-248.2221682
10	-248.2227714
12	-248.2222479
14	-248.2226355
16	-248.2222075
18	-248.2226225

Variation of total energy with k-point grid of Mo

K-point	Total energy (Ry)
2	-363.7095622
4	-363.9242953
6	-363.9078283
8	-363.9099229
10	-363.9113418
12	-363.9097207
14	-363.9107836
16	-363.9099972
18	-363.9106311

Variation of total energy with lattice constant of Cr

Lattice constant (Bohr)	Total energy (Ry)
5.0	-248.1743698
5.1	-248.1939968
5.2	-248.2067243
5.3	-248.2135691
5.4	-248.2154515
5.5	-248.2130944
5.6	-248.2072489
5.7	-248.1982853
5.8	-248.187511
5.9	-248.1754811
6.0	-248.1601537

The Variation of total energy with lattice constant of Mo

Lattice constant (Bohr)	Total energy (Ry)
5.54	-363.845305
5.64	-363.8727492
5.74	-363.8916195
5.84	-363.9032158
5.94	-363.9086598
6.04	-363.9088973
6.14	-363.9047329
6.24	-363.8968473
6.34	-363.8858576
6.44	-363.8723229

Variation of total energy with degauss of Cr

Degauss	Total energy (Ry)
0.001	-248.2220886
0.01	-248.2221682
0.02	-248.2224395
0.03	-248.2230632
0.04	-248.2234158
0.05	-248.2225862
0.06	-248.2208614

Variation of total energy with degauss of Mo

degauss	Total energy (Ry)
0.001	-363.9098915
0.01	-363.9099229
0.02	-363.9102481
0.03	-363.9108676
0.04	-363.9115105
0.05	-363.9116624
0.06	-363.9109134

B]. Different input Files:

List 1: Input script for scf final

Cr

```
&control
                 calculation = 'scf'
                restart_mode = 'from_scratch',
                  pseudo_dir = '/home/amrit/qe-6.5/pseudo/',
                      outdir = './' ,
                      prefix = 'Cr'
                     tstress = .TRUE.
                     tprnfor = .TRUE.
 &system
                       ibrav = 3,
                   celldm(1) = 5.40,
                         nat = 1,
                        ntyp = 1,
                 occupations = 'smearing' ,
                    smearing = 'mv' ,
                     degauss = 0.01 ,
                     ecutwfc = 85.0 ,
                     ecutrho = 680.0 ,
 /
 &electrons
                 conv_thr = 1.0d-6,
                 mixing_beta = 0.7 ,
```

```
 /
ATOMIC_SPECIES
  Cr   51.9961  Cr.pbe-spn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
  Cr 0.00 0.00 0.00
  Cr 0.5 0.5 0.5
K_POINTS automatic
 8 8 8  1 1 1
```

Mo

```
&control
         calculation = 'scf'
        restart_mode = 'from_scratch',
          pseudo_dir = '/home/amrit/qe-6.5/pseudo/',
            outdir = './' ,
            prefix = 'Mo' ,
           tstress = .TRUE.
           tprnfor = .TRUE.
 /
 &system
            ibrav = 3,
          celldm(1) = 6.04,
             nat = 1,
             ntyp = 1,
         occupations = 'smearing' ,
           smearing = 'mv' ,
```

```
              degauss = 0.06 ,
              ecutwfc = 85.0 ,
              ecutrho = 680.0 ,
 /
 &electrons
            conv_thr = 1.0d-6,
            mixing_beta = 0.7 ,
 /
ATOMIC_SPECIES
  Mo  95.95   Mo.pbe-spn-kjpaw_psl.0.2.UPF
ATOMIC_POSITIONS (alat)
  Mo 0.00 0.00 0.00
 K_POINTS automatic
 8 8 8  1 1 1
```

List 2: Input script for nscf calculation of Band

Cr

```
&control
            calculation = 'nscf'
           restart_mode = 'from_scratch',
             pseudo_dir = '/home/amrit/qe-6.5/pseudo/',
                outdir = './' ,
                prefix = 'Cr'
              tstress = .TRUE.
              tprnfor = .TRUE.
 /
```

```
 &system
                ibrav = 3,
             celldm(1) = 5.40,
                 nat = 1,
                ntyp = 1,
           occupations = 'smearing' ,
              smearing = 'mv' ,
              degauss = 0.01 ,
              ecutwfc = 85.0 ,
              ecutrho = 680.0 ,
 /
 &electrons
           conv_thr = 1.0d-6,
           mixing_beta = 0.7 ,
 /
ATOMIC_SPECIES
  Cr   51.9961  Cr.pbe-spn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
  Cr 0.00 0.00 0.00
  Cr 0.5 0.5 0.5
K_POINTS automatic
 12 12 12  0 0 0
```

Mo

```
&control
           calculation = 'nscf'
```

```
        restart_mode = 'from_scratch',
         pseudo_dir = '/home/amrit/qe-6.5/pseudo/',
           outdir = './' ,
           prefix = 'Mo' ,
           tstress = .TRUE.
           tprnfor = .TRUE.
/
&system
            ibrav = 3,
          celldm(1) = 6.04,
             nat = 1,
            ntyp = 1,
         occupations = 'smearing' ,
          smearing = 'mv' ,
           degauss = 0.06 ,
           ecutwfc = 85.0 ,
           ecutrho = 680.0 ,
/
&electrons
         conv_thr = 1.0d-6,
         mixing_beta = 0.7 ,
/
```

```
ATOMIC_SPECIES
   Mo  95.95   Mo.pbe-spn-kjpaw_psl.0.2.UPF
ATOMIC_POSITIONS (alat)
   Mo 0.00 0.00 0.00
  K_POINTS automatic
  12 12 12  0 0 0
```

List 3: Input script for Bands.in

Cr

```
&control
                 calculation = 'bands'
                restart_mode = 'from_scratch',
                  pseudo_dir = '/home/amrit/qe-6.5/pseudo/',
                      outdir = './' ,
                      prefix = 'Cr'
 /
 &system
                       ibrav = 3,
                   celldm(1) = 5.40,
                         nat = 1,
                        ntyp = 1,
                 occupations = 'smearing' ,
                    smearing = 'mv' ,
                     degauss = 0.01 ,
                     ecutwfc = 85.0 ,
```

```
                    ecutrho = 680.0 ,
 /
 &electrons
                conv_thr = 1.0d-6,
                mixing_beta = 0.7 ,
 /
ATOMIC_SPECIES
   Cr   51.9961  Cr.pbe-spn-kjpaw_psl.1.0.0.UPF
ATOMIC_POSITIONS (alat)
   Cr 0.00 0.00 0.00
K_POINTS crystal_b
5
0.0 0.0 0.0 20 | Gm
0.5 0.5 -0.5 12 | H
0.5 0.0 -0.5 18 | N
0.0 0.0 0.0 20 | Gm
0.75 0.25 -0.25 10 | P
```

Mo

```
&control
                calculation = 'bands'
               restart_mode = 'from_scratch',
                 pseudo_dir = '/home/amrit/qe-6.5/pseudo/',
                     outdir = './' ,
                     prefix = 'Mo' ,
```

```
/
 &system
             ibrav = 3,
           celldm(1) = 6.04,
               nat = 1,
              ntyp = 1,
          occupations = 'smearing' ,
            smearing = 'mv' ,
            degauss = 0.06 ,
            ecutwfc = 85.0 ,
            ecutrho = 680.0 ,
 /
 &electrons
          conv_thr = 1.0d-6,
          mixing_beta = 0.7 ,
 /
ATOMIC_SPECIES
  Mo  95.95   Mo.pbe-spn-kjpaw_psl.0.2.UPF
ATOMIC_POSITIONS (alat)
  Mo 0.00 0.00 0.00
K_POINTS crystal_b
5
0.0 0.0 0.0 20 | Gm
0.5 0.5 -0.5 12 | H
0.5 0.0 -0.5 18 | N
```

```
0.0 0.0 0.0 20 | Gm
0.75 0.25 -0.25 10 | P
```

List 4: Input script for DOS.in

Cr

```
&dos
    prefix='Cr'
    outdir='./'
    ngauss=-1
    degauss=0.01
    DeltaE=0.01
    fildos='Cr.dos.dat'
/
```

Mo

```
&dos
    prefix='Mo'
    outdir='./'
    ngauss=-1
    degauss=0.01
    DeltaE=0.01
    fildos='Mo.dos.dat'
/
```

List 5: Input script for PDOS.in

Cr

```
&projwfc
   prefix='Cr'
   outdir='./'
   ngauss=-1
   degauss=0.01
   DeltaE=0.01
   filpdos='Cr.pdos.dat'
/
```

Mo

```
&projwfc
   prefix='Mo'
   outdir='./'
   ngauss=-1
   degauss=0.01
   DeltaE=0.01
   filpdos='Mo.pdos.dat'
/
```

List 7: Input script for

```
set term postscript enhanced color 'Helvetica-Bold' 20
set output 'Cr.ecut.ps'
set autoscale
unset log
unset label
```

```
set xtic 40,5
#set ytic 0,0.2
set xlabel "Cut-off energy (Ry)"
set ylabel "Total Energy (Ry)"
set xr [40:100]

plot  "Cr.ecut.dat" using 1:2 title 'Cut-off energy (Ry) of Cr' w lp lw 3 lt 1 lc rgb
"blue",\

set output
 ! ps2pdf Cr.ecut.ps
 ! rm Cr.ecut.ps
pause -1 "hit any key to continue\n"
```

List 7: Input script for bands plot

```
set terminal postscript enhanced color "Helvetica" 20
set output "Cr.band.ps"
set autoscale
unset log
set xzeroaxis lw 2 lc -1
unset xtics
set ytics -10,2
set bmargin 3
set xlabel "kpaths" offset 0,-1,0
set ylabel "E-Ef (eV)"
set label "{/Symbol G}" at -0.02,-10.9
```

```
set label "{/Symbol G}" at 2.39559,-10.9

set label "H" at 0.98094,-10.9

set label "N" at 1.68536,-10.9

set label "P" at 3.26301,-10.9

set arrow from 1.00405, graph 0 to 1.00405, graph 1 nohead

set arrow from 1.70960, graph 0 to 1.70960, graph 1 nohead

set arrow from 2.41414, graph 0 to 2.41414, graph 1 nohead

set arrow from 3.28954, graph 0 to 3.28954, graph 1 nohead

#set key 0.01,100

set xr [0.0:3.29154]

set yr [-10:10]

ef=19.3783

plot "Cr.bands.dat.gnu" using 1:($2-ef) title 'bands of Cr' w l lw 3 lt 4 lc rgb "black"

set output

! ps2pdf Cr.band.ps

! rm Cr.band.ps

pause -1 "Hit any key to continue\n"
```

List 8: Input script for plot dos

```
set term postscript enhanced color 'Helvetica-Bold' 20

set output 'Mo.dos.ps'

set autoscale

unset log

unset label

set xtic -10,1
```

```
set ytic auto
set xlabel "E-Ef (ev)"
set ylabel "Dos"
#set key 0.01,100
set xr [-10:10]
set yr [0:4]
ef= 20.1642
plot "Mo.dos.dat" using ($1-ef):2 title 'Dos of Mo'  w l lw 5 lt 5 lc rgb "blue"
set output
! ps2pdf Mo.dos.ps
! rm Mo.dos.ps
pause -1 "Hit any key to continue\n"
```

List 8: Input script for plot pdos

```
 set term postscript enhanced color 'Helvetica-Bold' 20
set output 'Cr.pdos.ps'
set autoscale
unset log
unset label
set xtic 10,2
set ytic auto
set xlabel "Energy (ev)"
set ylabel "Pdos"
set xr [10:30]
set yr [-0.1:4]
set arrow from 19.2746,0.0 to 19.2746,4, 2 nohead ls 10 dt 2
```

```
plot  "Cr.pdos.dat.pdos_atm#1(Cr)_wfc#2(s)" using 1:2 title 'Cr s orbital' w l lw 3 lt 1 lc rgb "blue",\
     "Cr.pdos.dat.pdos_atm#1(Cr)_wfc#3(p)" using 1:2 title 'Cr p orbital' w l lw 3 lt 1 lc rgb "red",\
     "Cr.pdos.dat.pdos_atm#1(Cr)_wfc#4(d)" using 1:2 title 'Cr d orbital' w l lw 3 lt 1 lc rgb "green"

set output
 ! ps2pdf Cr.pdos.ps
 ! rm Cr.pdos.ps
pause -1 "hit any key to continue\n"
```