CHAPTER - I

THEORY OF TB-LMTO AND FP-LMTO METHODS

1.1 INTRODUCTION

The study on structural changes and phase stability of crystalline materials play a basic role in Theoretical and Computational Chemistry, because the better understanding of the various Chemical properties of solids mainly depend upon their structure [1]. Currently there is lot of interest in the study of structural changes and phase stability of materials under pressure [2]. The Chemical properties of materials undergo a variety of changes when they are subjected to pressure [3]. The proposed work will be focused on the details of the theoretical investigation of the electronic band structure, density of states, structural changes, phase stability and superconductivity of some transition metals Ti(Titanium), Zr(Zirconium), Hf(Hafnium), V(Vanadium), Nb(Niobium), Ta(Tantalum), Ni(Nickel), Pd(Palladium), Pt(Platinum), Cu(Copper), Ag (Silver) and Au(Gold) under pressure. The band structures of the above transition metals corresponding to various pressures are obtained using the full potential linear muffin-tin orbital (FP-LMTO) method [4]. The understanding of various properties of materials under high pressure has significantly improved due to the availability of accurate band structure methods in the past few decades [5]. Materials are always an integral part of human culture and civilization. They exist in four states viz. solid, liquid, gas and plasma. Consequently, their properties depend on their internal structure, which influences their performance in different conditions [6]. From the macroscopic point of view, the existence of substances in different phases is generally related to (i) temperature (ii) pressure and...
(iii) volume. It is a fact that the solid state of matter exists at low temperature and volume, the gaseous when the temperature and volume are very high and the liquid state when the temperature and volume have their intermediate values. The plasma state occurs at extreme high pressure and temperature conditions. Microscopically their existence depends on their internal structure [7]. It has a large overlap with Chemistry, statistical physics, materials science, fluid and solid mechanics, nanotechnology and engineering. These involve different types of research on thousands of different materials, in both pure and applied fields. This science of condensed phase of matter begins with the crystal, its single most important structural idea [8]. The two broad subareas of solids and liquids are paid much attention in this regard. Solids can be broadly classified as either crystalline or amorphous (noncrystalline) phase. The crystalline phases are characterized by ordered or regular arrangements of their basis (ions, atoms or molecules) [9].

The arrangement of atoms in crystalline materials is responsible for most of their characteristics. By knowing the arrangement of atoms in a unit cell of a crystal, the entire structure may be described by repeating process in a periodic manner. But this is not true for the amorphous materials because of their disordered or irregular structure. An amorphous solid is a solid in which there is no long range order of the positions of the atoms. A perfect crystal is a completely ordered material while a deviation in structure and properties creates the disorderliness. A material at absolute temperature may be considered as highly ordered system while rise in temperature, pressure and volume creates disordered states. Also an impurity in a pure material develops defects in their structure and thus develops disorderliness. Glasses, alloys, liquid crystals, plasmas, gels, dense gasses and superfluids etc. are disordered
materials [2]. With relevant theoretical models, one can get results from computational simulations which are comparable to the experiments which makes a valuable complement to experiment and push the development of science. Virtually all of the properties of metals are determined by the valence electrons. Most of the calculations of the physical and chemical properties of a metal require the knowledge of the band electrons and interactions among the ion cores. The total lattice potential could be calculated in principle, by solving the Schrödinger equation for a system of interacting nuclei and electrons that form the crystal. Thus, this is a many body problem and is difficult to solve exactly. Hence it requires some unavoidable approximations like adiabatic or one–electron approximation. In the last century, along with the development of computers, many computational methods were developed for various fields of science [3]. In computational chemistry, among these methods, methods based on quantum mechanics i.e. muffin-tin, pseudopotential and density functional theory (DFT) are well accepted and admired methods[4]. A major breakthrough happened in the electronic band structure calculation with the introduction of tight binding linear muffin-tin orbital (TB-LMTO) method by Andersen [2]. It reduced the computational time to a large extend [3]. Within the various theories, the tight-binding theory allows very direct interpretation and is simple enough to allow much more realistic treatment [3]. It is based on the idea that one electron states of solids can be written as combinations of a small number of states of the constituent atoms. Also the crystal potential is approximated by a series of non-overlapping atomic like spherically symmetric potentials and a constant potential between the spheres. This method has the advantage that the theory and the result are very easy to understand. For this reason most results of the electronic structures computed are interpreted in the light of tight-binding theory [4].
In this thesis, the band structure and total energy calculations are performed using FP-LMTO method within local density approximation (LDA) and atomic sphere approximation (ASA) [4]. This chapter describes briefly the theory of TB-LMTO and FP-LMTO methods [6].

1.2 THE TB-LMTO METHOD

The complete description of tight binding linear muffin-tin orbital method was given by Andersen [3]. In this linear method, functions constructed from partial waves and their first energy derivatives obtained within the muffin-tin approximation are used as fixed basis. The chemical content of this technique acts as a guide to the non-specialist who wants to perform band structure calculations of his own. The problem of electronic structure involves the computation of eigen states for an infinite number of interacting electrons. This leads to the estimation called one electron approximation, which describes each electron as an independent particle moving in the mean field of the other electrons plus the field of the nuclei [2]. In this context, one can solve the one electron Schrödinger equation

\[ [-\nabla^2 + V(\mathbf{r})] \psi_j(\mathbf{k}, \mathbf{r}) = E_j(\mathbf{k}) \psi_j(\mathbf{k}, \mathbf{r}) \]  \hspace{1cm} (1.1)

where \( V(\mathbf{r}) \) is the crystal potential, which is usually referred to as the effective one electron potential and it consists of the electrostatic field from the nuclei and the charge clouds of all the electrons plus corrections for exchange and correlation. Here \( \psi_j \) and \( E_j \) are the one-electron wave functions and energies respectively.

Throughout the calculation we use atomic units (\( h = m = \frac{e^2}{2} = 1 \)) in which one unit
of energy is 1 Ry (13.604 eV) and one unit of length is 1 Bohr radius (0.529 Å). This potential is determined in a self-consistent manner by solving Poisson’s equation

$$\nabla^2 u(\mathbf{r}) = -8\pi n(\mathbf{r})$$

where

$$n(\mathbf{r}) = \sum_{j} \left| \psi_j \right|^2$$

The calculation is repeated using iterative procedure until self consistency is achieved. When a self consistent solution is obtained the total electronic energy may be estimated from the one electron energies and wave functions.

**Tight Binding Method for Energy Bands**

2 neutral $H$ atoms

Ground state of $H_2$

Excited state of $H_2$

1s band of 20 $H$ atoms ring.
1.2.1 The Energy Band Problem

An energy band structure consists of the eigen values of the one electron Schrödinger equation (1.1) for a single electron moving in the local potential \( V(\mathbf{r}) \).

In an infinite crystal, the potential is invariant under lattice translations. Hence one may introduce Bloch’s theorem,

\[
T_{\mathbf{R}} \psi(\mathbf{r}) = \psi(\mathbf{r} + \mathbf{R}) = e^{i \mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r})
\]  

(1.4)

Here \( \mathbf{R} \) is the lattice vector of real space, which is written as the integer linear combinations of translational vectors \( \{ \mathbf{a}_i \} \). i.e,

\[
\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3
\]  

(1.5)

In \( \mathbf{k} \) space, the reciprocal lattice vector \( \mathbf{G} \) is expressed in the form of integer linear combination

\[
\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3
\]  

(1.6)

Where the set of translational vectors \( \{ \mathbf{b}_j \} \) satisfy

\[
\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \, \delta_{ij}
\]  

(1.7)

The energy bands and wave functions have the translational symmetry of the reciprocal lattice. i.e,

\[
E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G}) \quad \text{and} \quad \psi(\mathbf{k}, \mathbf{r}) = \psi(\mathbf{k} + \mathbf{G}, \mathbf{r})
\]  

(1.8)
The complete description of the electronic states in a crystal requires a band index \( j \), which may be defined such that

\[
E_j(\mathbf{k}) \leq E_{j+1}(\mathbf{k})
\]

(1.9)

The wave function of electron in the solid is expressed in terms of the Bloch sums of linear combination of atomic orbitals.

\[
\psi_j(\mathbf{k}, \mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \sum_{n/m} a_{n/m}^{jk} \chi_{n/m}(\mathbf{r} - \mathbf{R})
\]

(1.10)

where \( \chi_{n/m} \) is the eigen functions of the bound state of the free atom. By standard variational technique one can obtain a set of linear equations,

\[
(H - EO) \cdot \mathbf{a} = 0
\]

(1.11)

in terms of the Hamiltonian \( H \) and overlap \( O \) matrices to determine the eigenvalues \( E \) and the expansion coefficients \( \mathbf{a} \). Here the one electron energies are found by a single diagonalisation of the secular matrix \( (H - EO) \).

1.2.2 Partial waves for a single Muffin-Tin

The muffin-tin potential is defined to be spherically symmetric within the sphere of radius \( S_{MT} \) and to have a constant value \( V_{MTZ} \), the muffin-tin zero in the interstitial region between the spheres. Consider a crystal with one atom per primitive cell and with in a single muffin-tin well, and define the potential as,
where \( V(r) \) is the spherically symmetric part of the crystal potential. Now it is found the solution of Schrödinger equation

\[
[-\nabla^2 + V_{\text{MT}}(r) - k^2] \psi_{l,m}(E,r) = 0
\]

(1.13)

for all values of \( k^2 \). Inside the muffin-tin well the radial part \( \psi_l(E,r) \) must be regular at the origin in order to be normalizable. It is obtained by numerical integration of the radial Schrödinger equation

\[
\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_{\text{MT}}(r) - k^2 \right] r \psi_l(E,r) = 0
\]

(1.14)

In the region of constant potential the solutions of (1.13) are spherical waves with wave number \( k \), and their radial parts satisfy (1.14) with \( V_{\text{MT}}(r) = 0 \). i.e,

\[
\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - k^2 \right] r \psi_l(kr) = 0
\]

(1.15)

This is the well-known Helmholtz wave equation and it has two linearly independent solutions which may be written in terms of spherical Bessel \( j_l(kr) \) and Neumann \( n_l(kr) \) functions. It follows that only \( j_l(kr) \) is regular at the origin while both \( j_l(kr) \) and \( n_l(kr) \) are regular at infinity. Here and in the following we write expressions explicitly for the case of positive kinetic energy \( k^2 \). This is the range of
unbounded continuum states. The bound states may be formed when the kinetic energy in the interstitial region is negative. i.e.

\[ k = |k| = i \sqrt{V_{MTZ} - E} \]  

(1.16)

Hence the solution of \(-\nabla^2 + V_{MT} (r) - k^2 \) \(\psi_{l,m}(E, r) = 0\) will have the form,

\[ \psi_{l,m}(E, k, r) = i^l Y_l^m (\hat{r}) \left[ \psi_l (E, r) \left[ k [n_l (kr) - \cot(\eta_l) j_l (kr)] \right] \right] \]

\[ r \leq S_{MT} \]  

(1.17)

\[ r \geq S_{MT} \]

The constant of integration \(\cot(\eta_l)\) is taken in such a way that the partial wave is everywhere continuous and differentiable. i.e,

\[ \cot(\eta_l) = \frac{n_l (kr) D_l (E) - kr n_l' (kr) / n_l (kr)}{j_l (kr) D_l (E) - kr j_l' (kr) / j_l (kr)} \big|_{r = S_{MT}} \]

(1.18)

where \(D_l(E)\) is the logarithmic derivative which is defined as,

\[ D_l (E) = \frac{S}{\psi_l (E, r)} \frac{\partial \psi_l (E, r)}{\partial r} \big|_{r = S_{MT}} \]

(1.19)

This is monotonically decreasing function of energy except at its singularities. Another function called potential function \(P_l (E)\) (which is an increasing function of energy) is introduced as,

\[ P_l (E) = \frac{2(2l + 1)(D_l (E) + l + 1)}{(D_l - 1)} \]

(1.20)

Solution (1.17) is unbounded and is normalisable when \(k^2\) is positive. If \(k^2\) is negative then (1.17) can be normalized only at the eigen values of the single well, where the
constant of integration is zero. For this reason these partial waves are not well suited as basis functions.

1.2.3 The Muffin-Tin Orbitals

The muffin-tin orbitals (MTO) were introduced to obtain the suitable basis functions which are approximately independent of energy, reasonably localized and normalisable for all values of \( k^2 \). This is partially accomplished by adding a spherical Bessel function that cancels the divergent part of \( \psi_j(E, \mathbf{r}) \) and simultaneously reduces the energy and potential dependence of the tails. The MTO is written as,

\[
\chi_j(E, \mathbf{k}, \mathbf{r}) = i^j Y_j^m(\hat{\mathbf{r}}) \left( \psi_j(E, \mathbf{r}) + k \cot(\eta_j) j_j(kr) \right) \begin{cases} 
\mathbf{k} n_j(kr) & r \leq \mathbf{S}_{MT} \\
 & r \geq \mathbf{S}_{MT}
\end{cases} \tag{1.21}
\]

The important feature of this definition is that the functions inside the well are regular at the origin, while the tail \( \mathbf{k} n_j(kr) \) is regular at infinity.

1.2.4 Expansion theorem for Muffin-Tin Tails

One reason for choosing the MTO as solution of the translationally invariant Helmholtz wave equation (1.15) is the extremely simple expansion theorem, where

\[
n_L(k, |\mathbf{r} - \mathbf{R}|) = 4\pi \sum_{L'} \sum_{L''} C_{LL'L''} J_{L'}(k, |\mathbf{r} - \mathbf{R}'|) n^*_L(k, |\mathbf{R} - \mathbf{R}'|) \tag{1.22}
\]

are the Gaunt coefficients. The expansion in (1.22) is valid inside the sphere centered at \( \mathbf{R}' \) and passing through \( \mathbf{R} \). This expansion theorem means that the tails of the
MTO positioned at \( \mathbf{R} \) may be expanded in terms of spherical Bessel functions centered at \( \mathbf{R}' \). The reason is that the Neumann function centered at \( \mathbf{R} \) is regular at the origin and therefore is expanded only in terms of the regular solutions of the wave equation. Consequently, inside the muffin-tin sphere the tails from the other spheres will have the same functional form as term proportional to \( \cot(\eta_f) \). Expression (1.22) is analogous to the linear combinations of Bessel and Neumann functions provided \( n \) is substituted by the linear combination.

### 1.2.5 Energy independent Muffin-Tin orbitals

If MTO is used in a variational procedure then it should be energy independent. In order to achieve this, the MTO will be augmented. The augmented MTO will be made energy independent around a fixed energy \( E_v \), to first order in \((E-E_v)\) for a particular choice of the augmented spherical Bessel function \( J_l(kr) \) and Neumann function \( N_l(kr) \). The augmented MTO may be written as,

\[
\chi_l(E, k, r) = i^l Y_l^m (i) \begin{cases} 
\psi_l(E, r) + k \cot(\eta_l) J_l(kr) \\
kN_l(kr)
\end{cases} \quad \begin{array}{ll}
r \leq S_{MT} \\
r \geq S_{MT}
\end{array} \quad (1.24)
\]

At the same time MTO becomes orthogonal to the core states and ensuring that LMTO method does not converge to core eigen values. In order to obtain suitable spherical Bessel \( J_l(kr) \) and Neumann \( N_l(kr) \) functions, we have fixed \( k \) and the energy derivative of the MTO be zero at \( E = E_v \).

\[
\dot{\chi}_l(E, k, r) = \psi_l(E, r) + k \cot(\eta_l(E)) J_l(kr) \quad \begin{array}{ll}
r \leq S_{MT}
\end{array} \quad (1.25)
\]
This leads to the following possible definition of the augmented spherical Bessel function $J_l(kr)$. i.e,

$$J_l(kr) = \begin{cases} \frac{-\psi_l(E_v, r)}{k \cot (\eta_l(E_v))} & r \leq S_{MT} \\ j_l(kr) & r \geq S_{MT} \end{cases} \quad (1.26)$$

which will make the MTO (1.24) energy independent. i.e, $\dot{\chi}_l(E_v, k, r) = 0$, to first order in $(E - E_v)$. From the continuity and differentiability of the MTO (1.21), it follows that

$$n_l(kr) = \psi_l(E, r) + k \cot (\eta_l(E)) j_l(kr) \quad (1.27)$$

near the sphere boundary. Therefore

$$0 = \psi_l(E_v, r) + k \cot (\eta_l(E_v)) j_l(kr) \quad (1.28)$$

holds first order in $(r - S_{MT})$, showing that (1.26) is continuous and differentiable at $r = S_{MT}$.

### 1.2.6 One-center expansion and structure constants

A wave function for a MT potential of a set of non-overlapping array of MT wells $V_{MT}(|r - R|)$ centred at sites $R$ of a three dimensional periodic lattice may be written as the linear combination of MTO’s as

$$\psi(E, r) = \sum_L \alpha_L^k \chi_L^k(E, k, r) \quad (1.29)$$

where the Bloch sum $\chi_L^k(E, k, r)$ is
The wave function may be written in terms of one centre expansion of the form

\[ \chi_k^L(E, k, r) = \sum_R e^{i k \cdot R} \chi_{k}^L(E, k, r - R) \]  

(1.30)

The wave function may be written in terms of one centre expansion of the form

\[ \chi_k^L(E, k, r) = \chi_L^L(E, k, r) + \sum_{L'} J_{L'}(k, r) B_{LL'}^k(k) \]  

(1.31)

where \( B_{LL'}^k(k) \) is the KKR structure constants, which is defined by,

\[ B_{LL'}^k(k) = 4\pi \sum_{L''} C_{LL''L'} \sum_{R \neq 0} e^{i k \cdot R} \mathbf{k} n^*_L(k, R) \]  

(1.32)

which play the role of coefficients in the one-centre expansion of the MTO tails.

1.2.7 The Secular Matrix

The LMTO method is a fixed basis method based upon the variational principle. According to the Rayleigh - Ritz variational principle, one varies \( \psi \) to make the energy functional stationary, i.e,

\[ \delta < \psi | H - E | \psi > = 0 \]  

(1.32)

The above equation has solutions whenever

\[ \det \{ < \chi_k^L | H - E | \chi_k^k > \} = 0 \]  

(1.33)

Since the MTO is everywhere continuous and differentiable, we may evaluate the integral over all space in (1.32) as a sum of integrals over all atomic polyhedra. After repeated use of the Bloch condition (1.30) and rearrangement of the lattice sums, we obtain the well-known result
\[ \frac{1}{N} < \chi^k_L | H - E | \chi^k_L > = < \chi^k_L | H - E | \chi^k_L >_0 \]  

(1.34)

where the integral on the right side extends only over the polyhedron at the origin.

The LCMTO secular matrix is now simply obtained by inserting the one-centre expansion (1.31) into the matrix (1.34). i.e., The secular matrix reduces to

\[ < \chi^k_L | H - E | \chi^k_L > = < \chi^k_L | H - E | \chi^k_L >_0 \delta_{LL} \]
\[ + \{ < \chi^k_L | H - E | \chi^k_L >_0 + < J^I_L | H - E | \chi^k_L >_0 \} B^k_{LL} \]
\[ + \sum_{L'} B^k_{LL'} < J^I_{L'} | H - E | J^I_L >_0 B^k_{L'L} \]  

(1.35)

In the above equation, the one-centre term is zeroth order in \( B \), the two-centre term is first order in \( B \), and the three-centre or crystal field term is second order in \( B \). To turn the LCMTO method into an efficient calculational technique, one can introduce the atomic sphere approximation and parameterise the energy dependence of the integrals appearing in (1.35). The resulting procedure constitutes the TB-LMTO method. The TB-LMTO secular matrix is written in the form of the generalized eigenvalue problem,

\[ \sum_L \left( H^k_{LL} - E^{jk} O^k_{LL} \right) \alpha^{jk}_L = 0 \]  

(1.36)

where \( H^k_{LL} \) is the Hamiltonian matrix element and \( O^k_{LL} \) is the overlap matrix elements which may be solved by efficient numerical techniques to give the eigenvalues \( E^{jk} \) and eigen vectors \( \alpha^{jk}_L \).
1.3 THE FULL POTENTIAL - LMTO METHOD

A muffin-tin orbital (MTO), which is centered about the site $\mathbf{R}$ has the long range behavior and takes longer time for convergence. Andersen and Jepsen [4,5] succeeded in transforming the minimal but long ranged base of MT orbitals used in the TB-LMTO method into a full potential basis which are screened and short ranged. To curtail its long range behavior, it is subjected to screening by the charges located at the neighbouring sites. These neighbouring charges are represented by multipoles of order $2^l$. So effectively the MT orbitals are screened and hence short ranged by the multipoles situated at the neighbouring sites. The FP-LMTO method could reproduce exactly all the results obtained in the TB-LMTO method with faster convergence. Each orbital must satisfy Schrödinger equation in the region between the atoms. The regular and irregular radial laplace solutions are given as,

$$J^0_l(r) = \left[2(2l + 1)\right]^{-1} \left(\frac{r}{w}\right)^l$$

and

$$K^0_l(r) = \left(\frac{r}{w}\right)^{-l-1}.$$ Here $K^0_l$ has the form of the electrostatic potential from a single $2^l$ pole at $\mathbf{R}$. It is regular except at $\mathbf{R}$, and it may be expanded about any other site in terms of $J^0_l(r)$. The modified function is written as,

$$J^\alpha_l(r) = J^0_l(r) - \alpha_l K^0_l(r)$$

(1.37)

where $w$ is the length scale introduced to make the functions and the screening constants $\alpha$ dimensionless. In equation (1.37), the form of $J^\alpha$ is independent of the orbital and its site. It is obvious that the screened field,
\[ |K^\alpha\rangle = |K^0\rangle - |J^\alpha\rangle S^\alpha \] (1.38)

must be a superposition of conventional envelope functions \( |K^0\rangle \) placed at all sites where the corresponding matrix elements of \( \alpha S^\alpha \) do not vanish and hence \( |K^\alpha\rangle \) has the same form as the electrostatic potential from a 2\(^l\) pole at \( \mathbf{R} \) screened by multipoles at all sites. If we insert the equation (1.37) in (1.38) we obtain

\[ |K^\alpha\rangle = |K^0\rangle (1 + \alpha S^\alpha) - |J^0\rangle S^\alpha \] (1.39)

The relation between bare \((S^0)\) or canonical structure matrix and screened structure constant \(S^\alpha\) matrices is,

\[ S^\alpha = S^0 (1 - \alpha S^0)^{-1} \]

The screened field (1.39) is given by the superposition of bare fields as,

\[ |K^\alpha\rangle = |K^0\rangle (1 + \alpha S^\alpha) = |K^0\rangle (1 - \alpha S^0)^{-1} \] (1.40)

where \( \alpha \) is now regarded as a diagonal matrix with elements \( \alpha_{ij} \). From equation (1.40) it is identified that \( \alpha S^\alpha \) as the screening charge. That means \( \alpha_{ij} S^\alpha_{ij} \) is the relative strength of the 2\(^i\) pole at \( \mathbf{R}_i \) which screened the 2\(^j\) pole at \( \mathbf{R}_j \). We now determine \( \alpha \) such that \( S^\alpha \) has the shortest possible range. For including \( s, p \) and \( d \) MT orbitals in the superposition of (1.40), let’s choose \( \alpha = 0 \) for \( l > 2 \).
Let us consider periodic structures in which we the same on all lattice sites and are left with three parameters, \( \alpha_s, \alpha_p, \) and \( \alpha_d \) which we determine numerically by trial and error. For an assumed lattice and \( \alpha, \) we invert the small Hermitian matrix, \( \alpha^{-1} - S^0(k) \), as a function of Bloch vector \( \mathbf{k} \). Subsequent Fourier transformation then yields \( S^\alpha \) in \( \mathbb{R} \) space. The range of the corresponding TB structure matrix is essentially limited to the second nearest neighbors and it behaves approximately as \( e^{-4d/w} \). Here \( w \) is taken as the average Wigner-Seitz (WS) radius and hence measures the density of multipoles and \( d \) is the inter atomic distance. For more open structures, TB structure matrix extends to the third nearest neighbors. In order to construct the set of FP-LMTOs, first define the conventional set of TB-LMTOs \( \left| \chi^0 \right\rangle \), by augmentation of \( \left| K^0 \right\rangle \) inside the MT (or WS) sphere and then use the superposition given in equation (1.40).

In the MTO set the one-electron potential is treated as follows, inside each WS cell the potential is spherically averaged and the corresponding radial Schrödinger equations are solved as functions of the one-electron energy \( \varepsilon \) yielding the regular radial functions \( \phi_{R^j}(\varepsilon, r) \). If these are normalized to unity in the MT sphere of radius \( S_{MT} \), then

\[
\int_0^{S_{MT}} \phi_{R^j}^2(\varepsilon, r) \, r^2 \, dr = 1 \tag{1.41}
\]

The partial waves are given as,
\[
\left| \phi^\alpha (\varepsilon) \right| \equiv \left| \phi (\varepsilon) \right| \frac{N^\alpha (\varepsilon)}{N^\alpha (\varepsilon_v)} \quad (1.42)
\]

where \( \varepsilon_v \) is an arbitrary energy near the center of interest. The continuous and differential matching leads to the expression for potential function \( P^\alpha (\varepsilon) \) and normalization function \( N^\alpha (\varepsilon) \), i.e,

\[
P^\alpha (\varepsilon) = \frac{P^0 (\varepsilon)}{1 - \alpha P^0 (\varepsilon)} \quad (1.43)
\]

\[
N^\alpha (\varepsilon) = \left[ \left( \frac{w}{2} \right) \hat{P}^\alpha (\varepsilon) \right]^{1/2} \quad (1.44)
\]

where \( P^0 (\varepsilon) = 2(2l + 1) \left( \frac{w}{2} \right)^{2l+1} \left( \frac{D(\varepsilon) + l + 1}{D(\varepsilon) - l} \right) \quad (1.45) \]

with \( D(\varepsilon) = \frac{S \phi'(\varepsilon, s)}{\phi(\varepsilon, s)} \) is the conventional potential function and energy derivative.

\[
\left[ \hat{P}^\alpha (\varepsilon) \right]^{1/2} \equiv \left[ \frac{\partial}{\partial \varepsilon} P^\alpha (\varepsilon) \right]^{1/2} \quad (1.46)
\]

Now, the tight-binding MTO turns out to be the full potential base as,

\[
\left| \chi^\alpha (\varepsilon) \right| = \begin{cases} 
\left| \phi (\varepsilon) \right| N^\alpha (\varepsilon) + \left| j^\alpha \right| P^\alpha (\varepsilon) & \text{r} \leq w \\
\left| K^\alpha \right| & \text{r} \geq w
\end{cases} \quad (1.47)
\]
The Schrödinger equation for the crystal is solved as in FP-LMTO method, using the new screened base in equation (1.47). This leads to the tail cancellation or Korringa-Kohn - Rostoker (KKR) condition as,

$$\left[ P^\alpha (\varepsilon) - S^\alpha \right] U^\alpha = 0 \quad (1.48)$$

The secular matrix $P^\alpha (\varepsilon) - S^\alpha$ depends on the potential only through the potential functions along the diagonal. Equation (1.48) is in the form of an eigen value problem if $P^\alpha$ is a linear function of $\varepsilon$. The FP-LMTOs $\chi^\alpha (\varepsilon)$ will be independent of $\varepsilon$ in the spheres as well as in the interstitial region. Also its first derivative at $\varepsilon_0$ will vanish. The normalized $\chi^\alpha (\varepsilon)$ is written as,

$$\chi^\alpha = \phi^\alpha + \phi^\alpha \ h^\alpha \quad (1.49)$$

where

$$h^\alpha = \left( \frac{P^\alpha}{\hat{P}^\alpha} \right) + \left( \frac{\hat{P}^\alpha}{\hat{S}^\alpha \hat{P}^\alpha} \right)^{1/2} \quad (1.50)$$

is the effective two-centre Hamiltonian. The overlap and Hamiltonian matrices are given by,

$$\langle \chi^\alpha | \chi^\alpha \rangle = (1 + h^\alpha O^\alpha)(O^\alpha h^\alpha + 1) + h^\alpha P^\alpha h^\alpha \quad (1.51)$$

and

$$\langle \chi^\alpha | H - \varepsilon_0 | \chi^\alpha \rangle = h^\alpha (1 + h^\alpha O^\alpha) \quad (1.52)$$
where overlap, $O^{\alpha} = \langle \phi^{\alpha} \phi^{\alpha} \rangle$. The set of \( |\chi^{\alpha} \rangle \) is thus complete to first order in \((\varepsilon - \varepsilon_{\nu})\) and it can yield energy estimates correct to third order.

Theoretical studies of cohesive, structural and vibrational properties of transition metals under pressure are now routinely being performed by means of ab-initio calculations [1]. The accuracy of total energies obtained within the full potential theory, often even using the local density approximation (LDA), is in many cases sufficient to predict which structure, at a given pressure, has the lowest free energy. Whereas conventional structural optimizations are performed by comparing the free energies of various guessed crystal structures, new ab-initio full potential muffin tin orbital methods allow a better determination of the structures and understanding of transformation mechanisms. Transition metals exhibit a multitude of structural transformations when pressure is applied, and the study of the various high-pressure phases has become a central field in theoretical and experimental solid state Chemistry[9]. Although a large amount of structures has been resolved over the last two decades, essential parts still need revisions in transition metals [10].

1.4 SUPERCONDUCTING TRANSITION TEMPERATURE
CALCULATION


The electron –phonon mass enhancement factor, $\lambda$

$$
\lambda = \frac{N(E_F)(I^2)}{M\langle \omega^2 \rangle}
$$

(1.53)
where \( M \) is the atomic mass, \( \langle \omega^2 \rangle \) is an average of the phonon frequency square and \( \langle I^2 \rangle \) is an average (over the Fermi energy) of the electron–phonon matrix element square[13].

\[
\langle I^2 \rangle \text{(in Rydbergs)} \text{ can be written as [14]}
\]

\[
\begin{align*}
\langle I^2 \rangle &= 2 \sum \frac{(l + 1)}{(2l + 1)(2l + 3)} M^2_{l,l+1} \frac{N_l(E_F)N_{l+1}(E_F)}{N(E_F)N(E_F)} \\
&= \phi_l \phi_{l+1} [(D_l(E_F)-1)(D_{l+1}(E_F)+l+2) + (E_{F}-V(S))S^2]
\end{align*}
\]

where \( M_{l,l+1} = -\phi_l \phi_{l+1} [(D_l(E_F)-1)(D_{l+1}(E_F)+l+2) + (E_{F}-V(S))S^2] \) and in this,

\( \phi_l \) is the radial wave function at the muffin-tin sphere radius corresponding to the Fermi energy.

\( D_l \) is the logarithmic derivative of the radial wave function at the sphere boundary.

\( V(S) \) is the muffin-tin potential at the sphere boundary.

\( S \) is the radius of the muffin-tin sphere.

The above quantities are taken from the band structure results [13]. The average of the phonon frequency square is

\[
\langle \omega^2 \rangle = \frac{1}{2} \theta^2_D
\]

The variation of Debye temperature with pressure \( \theta_D(P) \) is given by [15],

\[
\theta_D(P) = \frac{\sqrt{E_F}}{\sqrt{E_F^0}} \frac{\alpha_o}{\alpha} \theta^0_D
\]
where \( \theta_D^0 \), \( a_o \) and \( E_F^0 \) are normal pressure quantities.

The McMillan’s formula used for \( T_c \) calculation [12],

\[
T_c = \frac{\theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right]
\]  

(1.57)

gives the good estimate of the \( T_c \) value. Here \( \mu^* \) is the electron-electron interaction parameter which is estimated using the relation [16],

\[
\mu^* = \frac{0.26 N(E_F)}{1 + N(E_F)}
\]  

(1.58)

where \( N(E_F) \) is the density of levels per atom per eV at \( E_F \).

The calculated total energies are fitted to the Murnaghan’s equation of state to determine the ground state properties and phase transition [17]. The pressure dependence of lattice constant is given by the relation,

\[
a = a_0 \left[ \frac{V}{V_0} \right]^{1/3}
\]

where,

\( a \) is the Lattice constant after applying pressure

\( a_0 \) is the normal pressure Lattice constant

\([V/V_0]\) is the Reduced Volume

\( V_0 \) is the volume at normal pressure

\( V \) is the Volume at different Pressure
The Murnaghan’s equation of state is given by

\[ P = 1.5B_0 \left[ (V_o/V)^{7/3} - (V_o/V)^{5/3} \right] \left[ 1 + 0.75 \left( B_0^{-1} - 4 \right) \left( (V_o/V)^{2/3} - 1 \right) \right] \] (1.59)

Where \( P \) is the pressure at any given volume \( V \),

\( V_o \) is the equilibrium volume,

\( B_0 \) is the bulk modulus at normal pressure

\( B_0' \) is the pressure derivative of bulk modulus

The enthalpy relation is given by

\[ H(P) = E_{\text{tot}}(P) + PV(P) \] (1.60)

and the transition pressure corresponding to the phase transition from structures bcc to fcc is obtained from the relation

\[ H_{\text{BCC}}(P) = H_{\text{FCC}}(P) \] (1.61)

Similarly we can predict the other structures also [17].

With the results obtained from the self-consistent calculation, we have computed \( \theta_D, \lambda, \mu^* \) and \( T_c \) as a function of pressure using Equations.(1.53-1.57)

The bulk modulus is a property of the material which defines its resistance to volume change when compressed. Both theoretical and experimental results suggest that the bulk modulus is a critical single material property for including hardness especially for cubic crystals; Bulk modulus of the solid is given by,

\[ B_0 = -V \left( \frac{\partial^2 P}{\partial V^2} \right)_T \] The above equation shows the relation between Bulk modulus and volume change [16]. The cause for phase transition and the relation between phase transition pressure and atomic radii are deduced from band structure
investigation. In addition to that, the band structure results are used to arrive at the pressure dependence of $T_c$. Calculation of electron-phonon interaction parameter, $\lambda$, evaluation of related interaction matrix element and estimation of $T_c$ using Mcmillan’s formula [12] are some of the important steps in the calculation of superconducting transition temperature. Necessary programs are developed for this purpose. With the developed FP-LMTO code in working condition for band structure calculation. The Chemical properties of materials undergo a variety of changes when they are subjected to pressure. The proposed work will be focused on the details of the theoretical investigation of the electronic band structure, density of states, structural changes, phase stability and superconductivity of some transition metals Ti(Titanium), Zr(Zirconium), Hf(Hafnium), V(Vanadium), Nb(Niobium), Ta(Tantalum), Ni(Nickel), Pd(Palladium), Pt(Platinum), Cu(Copper), Ag (Silver) and Au(Gold) under pressure (groups IVb, Vb, VIII and Ib in the periodic table).
The band structures of the above transition metals corresponding to various pressures are obtained using the full potential linear muffin-tin orbital (FP-LMTO) method. In this process the total energy also will also calculated. The calculated total energies will be analyzed and fitted to Murnaghan’s equation of state [17] to obtain the equilibrium lattice constant, bulk modulus and its pressure derivative. In order to study the structural phase transition of materials under pressure, the enthalpy calculation is performed for various competing crystal structures. From enthalpy results, we can find out the ground state and high pressure phase stability of these materials. From the normal and high pressure band structures and density of states results, we have obtained the definite conclusions regarding the band broadenings, valence band widths, band crossings at Fermi energy, electronic $s \rightarrow d$ transitions, electronic charge distributions, phase stability, superconducting transition and its variation with pressure. Reasons for choosing particularly the above metals in our investigation are that, recently numerous diamond anvil cell experiments and computational Chemistry calculations have been carried out on these metals and many observed phenomena like structural changes, phase stability and superconductivity under pressure still lack a theoretical explanation.

In particular, transition metals exhibit interesting and exciting superconducting behavior under pressure. In the proposed work, the route to high temperature superconductivity in transition metals will be discussed, with reference to the number of valence electrons, increasing of delocalized anion $d$-electron number using the band structure and other superconductivity results. These metals will be identified
as pressure-induced electron-phonon mediated superconductors. It may be found out
the highest superconducting transition temperature value depends more on the ground
state structure rather than the high pressure structure. As per the previous works, this
method predicts the ground state and high pressure band structures and total energies
of all the transition and noble metals including hcp metals.

In the case of Ti(Titanium), Zr(Zirconium) and Hf(Hafnium) we found hcp to
bcc phase transition. In V(Vanadium), Nb(Niobium) and Ta(Tantalum) we found
bcc to fcc phase transition. Ni(Nickel), Pd(Palladium), Pt(Platinum), Cu(Copper), Ag
(Silver) and Au(Gold) undergo structural phase transition from fcc to hcp structure.
The structures and brillouin zone of hcp, bcc and fcc lattices are given below.

1.5 STRUCTURES AND BRILLOUIN ZONE OF hcp, bcc AND fcc
LATTICES

(i) Structure of hcp crystal
(ii) Structure of bcc crystal

(iii) Structure of fcc crystal
(iv) Brillouin zone of hcp crystal
(v) Brillouin zone of bcc crystal

![Brillouin zone of bcc crystal]

(vi) Brillouin zone of fcc crystal

![Brillouin zone of fcc crystal]