2.1 DENSITY FUNCTIONAL THEORY

2.1.1 Many Body Problem

In a quantum mechanical system, wavefunction contains all the basic information. The solution to wavefunction are obtained from the Schroedinger equation. Time independent, non -relativistic Schroedinger equation is written as

\[ H\psi = E\psi \]  \hspace{1cm} (2.1)

where H is the Hamiltonian operator, \( \psi \) is the set of solutions or eigen states of the Hamiltonian. The detailed definition of the Hamiltonian is dependent on the physical system which is described by the Schrodinger equation. The particle in a box or a harmonicoscillator is an example where the Hamiltonian has a simple form and the Schrödinger equation can be solved exactly. But in a many body system where multiple electrons are interacting with multiple nuclei finding the solution is more complicated. The exact many-particle (solids) Hamiltonian is written as

\[
\hat{H} = -\frac{\hbar^2}{2} \sum_i \nabla^2_{R_i} - \frac{\hbar^2}{2} \frac{\nabla^2_{\text{charge}}}{m_e} - \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{e^2 Z_i}{|R_i - R_j|} + \frac{1}{8\pi\varepsilon_0} \sum_{i\neq j} \frac{e^2 Z_i Z_j}{|R_i - R_j|} \] \hspace{1cm} (2.2)
The nucleus has a mass $M_i$ at $R_i$, and the electrons have mass $m_e$ and are at $r_i$. The first two terms describe the kinetic energy operator for the nuclei and the electrons. The last three terms describe the Coulomb interaction between electrons and nuclei, between electrons and other electrons, and between nuclei and other nuclei. The above Hamiltonian form for many-particle includes many interaction terms, so it is very difficult to solve the Schrödinger equation for this kind of a system.

The only viable solution is to replace the many-electron problem to an effective one-electron problem, but this has to be at the expense of introducing certain approximations. Electrons are considered to be lighter than the nuclei and hence their response is much faster. Therefore, for any instantaneous position of the nuclei, the electrons can be considered to be in stationary states. The electrons and nuclei dynamics can thus be treated independently. This method is the Born-Oppenheimer approximation. The other approximation is the one-electron approximation according to which the electrons are assumed to move in the mean field of other electrons and ions. So the Hamiltonian can be reduced to In the above equation, $\hat{T}$ is the kinetic energy of the electron, $\hat{V}$ is the potential energy due to electron-electron interactions and $V_{ext}$ is the potential energy of the electrons in the external potential i.e. potential of nuclei.

$$\hat{H} = \hat{T} + \hat{V} + \hat{V}_{ext}$$

(2.3)

The first self-consistent field approximation (Slater, 1953) was given by Hatree-Fock theory which treats parallel spin electron exchange interactions only by introducing the determinant wave function (Slater determinant) but completely neglects the anti-parallel spin-electrons (electrostatic contribution due to Coulomb correction). The first successful theory which treated both exchange and correlation on the equal footing,
approximately, was the density functional theory (DFT) of Hohenberg-Kohn-Sham.

2.1.2 Wave Functions to Electron Density

The complete field of density functional theory is based on two fundamental mathematical theorems proved by Hohenberg & Kohn (1964). The method used by Hohenberg and Kohn is to formulate density functional theory as an exact theory of many body systems. The formulation applies to any system of interacting particles in an external potential \( V_{\text{ext}}(\vec{r}) \) including any problem of electrons and fixed nuclei. The traditional formulation of the two theorems of Hohenberg and Kohn is as follows:

First theorem: There is a one-to-one correspondence between the ground state density \( \rho(\vec{r}) \) of a many-electron system (atom, molecule, solid) and the external potential \( V_{\text{ext}} \). An immediate consequence is that the ground state expectation value of any observable \( \mathcal{O} \) is a unique function of the exact ground state electron density:

\[
\langle \psi | \mathcal{O} | \psi \rangle = \mathcal{O}[\rho] \quad (2.4)
\]

The first theorem of Hohenberg-Kohn states that the ground state electron density uniquely determines all properties, including the energy and wave function of the ground state.

Second theorem: For \( \mathcal{O} \) being the Hamiltonian, the ground state total energy functional \( H[\rho] \equiv E_{\text{ext}}[\rho] \) is of the form

\[
E_{\text{ext}}[\rho] = \langle \psi | \hat{T} + \hat{V} | \psi \rangle + \langle \psi | V_{\text{ext}} | \psi \rangle = F_{\text{HK}}[\rho] + \rho(\vec{r}) V_{\text{ext}}(\vec{r}) d\vec{r} \quad (2.5)
\]
where the Hohenberg-Kohn density functional \( F_{HK}[\rho] \) is universal for any man electron system i.e it can be used for every atom, molecule or solid which can be imagined. \( E_{V_{ext}}[\rho] \) reaches minimal value (equal to the ground-state total energy) for the ground state density corresponding to \( \tilde{\rho}_{ext} \).

The electronic ground state density and energy can be determined exactly using DFT, provided that \( F_{HK}[\rho] \) is known. DFT is not only useful for calculating the ground state properties of materials, it also useful for excited states calculations.

2.1.3 The Self-Consistent Kohn-Sham Equations

The Kohn-Sham equations (1965) transformed DFT into a practical tool. These equations are a set of practical procedures to obtain the ground state density. The correlation energy is defined as the part of the total energy which is present in the exact solution, which is absent in the Hartree-Fock solution. The total energy functional and corresponding to the exact and Hartree-Fock Hamiltonians respectively are

\[
E_e = T + V
\]

(2.6)

\[
E_{HF} = T_0 + V_H + V_x
\]

(2.7)

where, \( V_H + V_x = V \)

(2.8)

In Equation (2.6), \( T \) and \( V \) are the kinetic and electron-electron potential energy functional, \( T_0 \) is the functional for the kinetic energy of a non-interacting electron gas, \( V_H \) is the Hartree contribution and \( V_x \) stands for the exchange contribution. By subtracting above two equations, the functional for the correlation contribution appears to be

\[
V_c = T - T_0
\]

(2.9)
The exchange contribution to the total energy is defined as that part which is present in the Hartree-Fock solution, but absent in the Hartreesolution. Obviously, with the Hartree functional given by

\[ E_H = T_0 - V_H \]  \hspace{1cm} (2.10)

It can be defined as

\[ V_X = V - V_H (2.11) \]

By using above equations, Hohenberg-Kohn functional is written in the following way

\[ F_{HK} = T_0 + V_H + V_x + V_c \]  \hspace{1cm} (2.12)

Here \( V_c \) is the exchange-correlation energy functional. The energy functional can be written as follows

\[ E_{\text{ext}}[n] = T_0[n] + V_H[n] + V_{xc}[n] + V_{ext}[n] \]  \hspace{1cm} (2.13)

The corresponding Hamiltonian for above equation is called as Kohn-Sham Hamiltonain

\[ \hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext} \]

\[ = - \frac{\hbar^2}{2m_e} \nabla^2_i + \frac{e^2}{4\pi \varepsilon_0} \int \frac{n(r')}{|r-r'|} d\tau + V_{xc} + V_{ext} \]  \hspace{1cm} (2.14)

where the exchange-correlation potential is given by the functionalderivative

\[ \hat{V}_{xc} = \frac{\delta V_{xc}[n]}{\delta n} \]  \hspace{1cm} (2.15)

The theorem of Kohn and Sham can now be formulated as follows
The exact ground-state density $\rho(\vec{r})$ of an N-electron system is

$$n(\vec{r}) = \sum_{i=1}^{N} \psi_i(\vec{r})^* \psi_i(\vec{r}) (2.16)$$

where the single-particle wave functions are the N lowest-energy solutions of the Kohn-Sham equation

$$\hat{H}_{KS} \phi_i = \epsilon_i \phi_i \quad (2.17)$$

Both the terms Hartree operator $V_H$ and the exchange-correlation operator $V_{xc}$ depend on the density $\rho(\vec{r})$, which in turn is found to depend on $\psi_i$ which are being searched. This is a kind of self-consistency problem. Therefore, an iterative procedure is required to solve this problem. Some starting density $\rho_0$ is guessed, and a Hamiltonian $H_{KS}$ is constructed with it. The eigenvalue problem is solved, and results in a set of $\psi$ from which a density $\rho_1$ can be derived. Most probably $\rho_0$ will differ from $\rho_1$. Now $\rho_1$ is used to construct $H_{KS2}$, which will yield $\rho_2$, etc. The procedure can be set up in such a way that this series will converge to a density $\rho_f$ which generates $H_{KS}$ that can yield a solution again $\rho_f$. This density $\rho_f$ would be the final density which is consistent with the Hamiltonian.

2.1.4 The Exchange-Correlation Functional

The major problem to contend with DFT is that the exact function for exchange and correlation is not available. Except in a few simple cases it is impossible to treat exchange-correlation exactly and an approximation is in order. The quality of a DFT calculation is determined by how closer the approximate exchange-correlation comes to the exact value.

2.1.4.1 Local density approximation
The oldest and the most popular of the exchange-correlation functional is said to be the local density approximation (LDA), which assumes a simple form that is a linear functional of the density \[ E_{xc}^{LDA}[n] = \int n(\vec{r}) \varepsilon^{\text{hom}}_{xc}(n(\vec{r})) d\vec{r} \] (2.18)

Here \( \varepsilon^{\text{hom}}_{xc}(n(\vec{r})) \) is the exchange correlation energy density of an interacting homogenous electron gas at the density \( \rho(\vec{r}) \). The expression \( \varepsilon^{\text{hom}}_{xc}(n(\vec{r})) \) was given by Hedin & Lundqvist (1971). In this approximation, the effective potential is based on the chemical potential of a homogeneous interacting electron gas with the local density. For spin-polarized system

\[ E_{xc}^{LDA}[n^+, n^-] = \int n^+(\vec{r}) \varepsilon^{\text{hom}}_{xc}(n^+(\vec{r}), n^-(\vec{r})) d\vec{r} \] (2.19)

Here \( \varepsilon^{\text{hom}}_{xc}(n^+, n^-) \) is the exchange-correlation energy per electron of a homogeneous system with densities \( n^+(\vec{r}) \) and \( n^-(\vec{r}) \) for spin up and spin down respectively. Although LDA is a very crude approximation for systems that are not as homogeneous as an electron gas, it has a big drawback that it does not satisfy the one electron limit. This may be fixed by augmenting it with self interaction correction (SIC). The correction subtracts the error which would be made by the Hartree and exchange-correlation functional in the case of a single electron.

\[ E_{xc}^{LDA,SIC}[n] = E_{xc}^{LDA} - \sum_l (E_H[n_l]) - E_{xc}[n_l] \] (2.20)

### 2.1.4.2 Generalized gradient approximation

LDA is set to treat all available systems as homogeneous. However, the real systems are found to be clearly inhomogeneous with spatially changing electric fields due to nucleus and screening. To consider this, a step is taken beyond the LDA by inclusion of the derivative information of the...
density into the exchange-correlation functional. One way to do away with this is to try to include gradients $|\nabla n(\vec{r})|, |\nabla n(\vec{r})|^2$ into the approximation. However, the one that works better is to seek a more general functional

$$E_{xc}^{GGA}[n] = \int n(\vec{r}) \varepsilon_{xc}^{hom}[n(\vec{r})] d\vec{r} + \int F_{xc}[n(\vec{r}), |\nabla n(\vec{r})|] d\vec{r} \quad (2.21)$$

Such a functional are referred to as generalized gradient approximations, where is dimensionless parameter and is the exchange energy of the un-polarized system for spin polarized system,

$$E_{xc}^{GGA}[n] = \int n(\vec{r}) \varepsilon_{xc}^{hom}[n(\vec{r})] d\vec{r} + \int F_{xc}[n(\vec{r}), |\nabla n(\vec{r})|, |\nabla n(\vec{r})|] d\vec{r} \quad (2.22)$$

There are different varieties of GGA, each one is found to be making a different choice for the function $F_{xc}$. In the present calculation, Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional (Perdew et al. 1992, 1996) has been used. The enhancement factor $F_{xc}$ over the local exchange is defined as

$$E_{xc}^{GGA-PBE}[n] = \int n(\vec{r}) e_{xc}^{LDA}[n(\vec{r})] F_{xc}(n, \zeta, s) d\vec{r} \quad (2.23)$$

where $n$ is the local density, $\zeta$ is the relative spin polarization

$$s = \frac{|\nabla n(\vec{r})|}{2k_F n} \quad (2.24)$$

and $s$ is the dimensionless density gradient.
2.1.5 Solving Kohn-Sham Equations

The Kohn-Sham equations actually provide the framework for finding the exact density and energy of the ground state of a many-body electron problem using the standard independent-particle methods. Irrespective of whether the Hartree, Hartree-Fock is considered or density functional theory is considered, one ends up with an infinite set of one electron equations of the given type:

\[
\left( -\frac{\hbar^2}{2m_e} \frac{e^2}{4\pi\epsilon_0} \int d\vec{r}' \frac{n(\vec{r}')}{|\vec{r} - \vec{r}'|} + V + V_{\text{ext}} \right) \phi_i(\vec{r}) = \varepsilon_i \phi_i(\vec{r})
\]

\(H_{\text{single particle}}^{i}\)

(2.25)

where \(i=1,\ldots,N\).

1. For the Hartree approximation \(V_a\) is equivalent to \(V_{\text{SIC}}\)

2. For the Hartree-Fock approximation, \(V_a\) is the exchange potential, \(\Theta_i\) is the true one electron orbitals of the HF slater determinant. Exchange is treated exactly, but the correlation effects are not included at all

3. For the DFT in the LDA approximation (also LSDA,GGA) \(V_a\) is the exchange correlation operator, \(\Theta_i\) are mathematical single-particle orbitals. Exchange and correlation are treated both approximately. Since formally the HF and KS equations are similar, one can use the same mathematical tools for both the sets of equations have to be solved self consistently. In order to solve the equations, we need to find the expansion coefficients in order to express the crystal wave function in a given basis set.
\[ \phi_i = \sum_{p=1}^{P} c_p \{ \phi_p^{basis} \} \quad (2.26) \]

In principle, the wave function \( \phi_i \) belongs to a function space that has infinite dimensions i.e., \( P \) is infinite. Once a basis has been chosen we come to an eigenvalue problem. The single-particle Equation (2.25), becomes

\[
\begin{bmatrix}
0 \\
0
\end{bmatrix} = \begin{bmatrix}
\langle \phi_n^{basis} | H_{KS} | \phi_m^{basis} \rangle & - \varepsilon_i \langle \phi_n^{basis} | \phi_m^{basis} \rangle
\end{bmatrix} \begin{bmatrix}
c_1^i \\
c_P^i
\end{bmatrix} \quad (2.27)
\]

If the basis set is orthonormal, the overlap matrix \( S_{ij} \) is unity. Diagonalization of Hamiltonian matrix (2.27) leads to \( P \) eigen values and \( P \) sets of expansion coefficients. The larger value of \( P \) is, better is the approximation of the eigenfunctions, but the time consumption is more for the diagonalization of the matrix in equation (2.27). The index \( i \) stands for quantum numbers \((n, \vec{k})\).

If the basis functions are similar to \( \phi_i \), then we only need a few of them to accurately describe wave function, and hence \( P \) and the matrix size are small. Such a basis set is said to be efficient. The art of theoretical condensed matter physics is to find a basis set that is simultaneously efficient and unbiased.

Let us consider a periodic solid. The lattice potential is translationally invariant,

\[ V(\vec{r}) = V(\vec{R} + \vec{T}) \quad (2.28) \]

which implies restrictions on the wave functions of the crystal. These wave functions have to be the basis functions of the irreducible representation of the translation group and are numerated with an index. They are eigenfunctions of the translation operator.
\[ P(\vec{r})\psi_{\vec{k}}(\vec{r}) = \psi_{\vec{k}}(\vec{r} + \vec{T}) = e^{i\vec{kT}\vec{r}}\psi_{\vec{k}}(\vec{r}) \quad (2.29) \]

and the Schroedinger equation

\[ [-\nabla^2 + V(\vec{r})]\psi_{\vec{k}}(\vec{r}) = E(\vec{k})\psi_{\vec{k}}(\vec{r}) \quad (2.30) \]

Wave functions defined in such a way are called Bloch functions. With this definition, we can reduce the problem of determining the electronic structure of a crystal to considering a single unit cell with volume \( \Omega \). \( E(\vec{k}) \) in Equation (2.30) describes the single band structure of the solid. \( \psi_{\vec{k}}(\vec{r}) \) and \( E(\vec{k}) \) possess, as functions of \( \vec{k} \) the translation symmetry of the reciprocal lattice. Therefore, it is sufficient to only consider \( \vec{k} \) vectors in the primitive cell of the reciprocal lattice, i.e., in the Brillouin zone with volume \( \Omega_{BZ} \).

\[ \Omega_{BZ} = \frac{(2\pi)^3}{\Omega^3} \quad (2.31) \]

In this case, the bands \( E_\nu(\vec{k}) \) and wave functions \( \psi_{\vec{k}\nu}(\vec{r}) \) have to be additionally characterized by a band index.

With the knowledge of the band structure, we can calculate other quantities that are relevant for experimental comparison. Among these, the important quantities are the number of states for a given energy, i.e, the density of states per spin,

\[ D_\sigma(E) = \frac{\Omega}{(2\pi)^3} \sum_\nu \int_{BZ} dk \left( E - E_{\nu\sigma}(k) \right) \quad (2.32) \]

The integrated density of states \( N(E) \)

\[ N_\sigma(E) = \int_{-\infty}^{E} D_\sigma(E') dE' \quad (2.33) \]
With $D_\sigma(E)$ and $N_\sigma(E)$ known, we can determine the Fermi energy $E_F$ which separates the occupied from unoccupied states, from the condition that

$$n_\sigma = \int_{-\infty}^{E_F} D_\sigma(E) \, dE \quad (2.34)$$

where $n$ is the number of electrons per spin in the primitive unit cell. There are various methods developed for the purpose of solving the band structure problem.

### 2.2 METHODS OF ELECTRONIC STRUCTURE CALCULATION

The challenge to solve the Kohn-Sham (Equation (2.25)) efficiently for the periodic solids, solids with surfaces and interfaces, cluster and molecules has finally led to a wide spectrum of very successful and efficient electronic structure methods. In treating isolated clusters or molecules, methods based on localized orbitals are frequently selected in parallel with the chemical intuition of the system. With the consideration of methods applicable to periodic solids, frequently algorithms are chosen in such a way that Bloch boundary condition can be included in the basis set. The electronic structure methods are found to depend upon the use of kinetic energy operator $\tilde{V}$, the $1/r$ singularity at the nucleus, exchange correlation potential $V_{xc} n(\tilde{r})$ and Hartree potential $V_H n(\tilde{r})$.

Figure 2.1 shows the schematic outlook of the electronic structure methods that indicates a rich spectrum of methods developed for various purposes, applications, geometries and symmetries, chemical elements and materials requiring different approximations. The plane wave basis is then a very good choice. Thus, by the use of a plane wave basis set, the calculation of the kinetic energy, charge density, and the Hartree potential $V_{xc} n(\tilde{r})$ can be obtained by simple algebraic expressions. The calculation of the can be done
in a best possible way, if the charge density is expressed in the real space. The discrete fast Fourier transformation is capable of providing a fast algorithm to communicate between both spaces. The plane wave basis sets are to be used in the context of a pseudo-potential approximation to the true potential where the potential has been replaced by an appropriate smooth potential.

All-electron methods have to cope with the $1/r$ singularity. The basis functions which are the numerical solution $(-\Delta + V_{\text{eff}} - E_l)\phi = 0$ of the effective (spherical) potential containing the $1/r$ singularity, computed in a sphere around the atom at a given energy parameter $E_l$. These basis functions treat the singularity exactly. The matching of this wave function in such a
sphere to the rest of the crystal outside the sphere divides the all-electron methods with regard to the eigen value dependence of the basis set into two groups:

The non linear methods as for example the Korringa-Kohn-Rostoker (KKR) method and the augmented plane wave method, and the linear methods, of which the most commonly used are the linear muffin-tin orbital method (LMTO) < the augmented spherical and APW-based schemes. In the present work, full potential linearized augmented plane wave method (FP-LAPW) is used.

2.3 LINEAR MUFFIN-TIN ORBITAL METHOD

The linear methods are said to be characterized by using the fixed basis functions constructed from the partial waves and their first order derivatives within the muffin-tin potential approximation. Most of the linear methods are found to make use of minimal basis set and the eigenvalues are obtained by a known single diagonalization. The history and development of the linear methods is given in literatures (Skriver 1984). The first postulation of linear methods including muffin-tin orbitals and the tail cancellation theorem was given by Andersen 1973. In the year 1972, the concept of potential parameters and the atomic sphere approximation was then reported. Later the expression of the LMTO secular matrix, the energy-independent structure constants, canonical bands and the linear combination of muffin-tin-orbital technique were again proposed. It has also the tight binding LMTO and full potential LMTO forms.

For the practical applications, the LMTO and their forms like TB-LMTO and LAPW methods are well suitable and the most convenient. The LMTO method will combine all the desirable features of the traditional methods using fixed basis functions with those of partial waves. Even though
the LMTO method lags behind the LAPW method in terms of accuracy, it is highly efficient, conceptually transparent, and especially well suited for self-consistent calculations. The following section gives the descriptions of this method.

2.3.1 LMTO Formalism

The linear muffin-tin orbital method was devised by Andersen (1975). It is found to use a simple basis set in the form of Muffin-Tin Orbital (MTO). The muffin tin potential is further defined to be spherically symmetric within spheres of radius $S_{MT}$ and to have a constant value $V_{MTZ}$ in the interstitial region between the spheres. Therefore, within a single muffin-tin well the potential is defined be

$$V(r) = \begin{cases} V_{MT}(r), & r \leq S_{MT} \\ V_{MTZ}, & r \geq S_{MT} \end{cases}$$

(2.35)

with this choice of potential once the partial waves is obtained as the solution of equation as

$$\psi_k(E, k, \vec{r}) = i^l Y_l^m(\hat{r}) \left\{ \begin{array}{ll} \psi(E, r) \\ (k n_l(kr) - k \cot(\eta_l) j_l(kr)) \end{array} \right. \begin{array}{ll} r \leq S_{MT} \\ r \geq S_{MT} \end{array}$$

(2.36)

But partial waves can be easily normalized, for negative $K_2$, only at the eigenvalues of the single well and moreover they are found to be energy dependent. This is not advisable for linearizing the problem.

As a partial remedy, MTOs as defined below, can be normalized for all values of $k_2$, is approximately energy independent and reasonably localized.

$$\chi_k(E, k, \vec{r}) = i^l Y_l^m(\hat{r}) \left\{ \begin{array}{ll} \psi(E, r) + k \cot(\eta_l) j_l(kr) \\ (k n_l(kr) r) \end{array} \right. \begin{array}{ll} r \leq S_{MT} \\ r \geq S_{MT} \end{array}$$

(2.37)
Here, $Y_m^l r$ are the well known spherical harmonics, $k^2 = E - V_{MTZ}$ is the kinetic energy in the interstitial region $n_l(kr)$ and $j_l(kr)$ and are the spherical Neumann and Bessel functions, both of which are regular at infinity, while $n_l(kr)$ is singular at the origin and $\psi_l(E, r)$ is the solution of the radial Schrödinger equation,

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

(2.38)

where

$$
cot(\eta_l(E, k)) = \frac{n_l(kr)}{j_l(kr)} \cdot \frac{D_l(E) - kr n_l(kr)/n_l(kr)}{D_l(E) - kr j_l(kr)/j_l(kr)}
$$

(2.39)

Hence, $\eta_l$ is the usual phase shift; the primes denote partial differentiation with respect to $r$. The logarithmic derivative

$$
D_l(E) = \frac{s}{\psi_l(E, s)} \frac{\partial \psi_l(E, r)}{\partial r} \bigg|_r = S_{MT}
$$

(2.40)

Now the electronic wave function can be obtained as the linear combination of the MTO's

$$
\psi(E, \vec{r}) = \sum L \alpha_L K \chi_L^k(E, k, \vec{r})
$$

(2.41)

where $\alpha_L^k$ is the expansion coefficient is the Bloch sum of the MTO's

$$
\chi_L^k(E, k, \vec{r}) = \sum R \exp(i \vec{k} \cdot \vec{r}) \chi_L^k(E, k, \vec{r} - \vec{R})
$$

(2.42)

In order to linearize the problem the energy dependence of the MTO has to be suppressed with a suitable choice of augmentation. Augmentation makes the basis to become energy independent around a fixed energy to first order and also become orthogonal to the core states. These augmented MTOs are,
\[ \chi_L(E, k, \vec{r}) = i^l Y_L^m(\hat{r}) \left\{ \psi_l(E, r) + k\cot(\eta_l) J_l(kr) \right\} \quad r \leq S_{MT} \]
\[ \chi_L(E, k, \vec{r}) = k N_l(kr) \quad r \geq S_{MT} \quad (2.43) \]

where, J and N are augmented spherical Bessel and Neumann functions.

The secular matrix equation can be obtained by using the Rayleigh-Ritz variational principle.

\[ \delta < \langle \psi | H - E | \psi \rangle = 0 \quad (2.44) \]

where E is the Lagrange multiplier. Equation implies that

\[ \text{det} \left\{ < \chi_L^{\vec{k}} | H - E | \chi_L^{\vec{k}} > = 0 \quad (2.45) \right. \]

substitution of in the above equation yields the Linear Combination of the MTO (LCMTO) secular matrix.

\[ \left\langle \chi_L^{\vec{k}} | H - E | \chi_L^{\vec{k}} \right\rangle = \langle \chi_l | H - E | \chi_l \rangle 0 \delta L' L + \{ \langle \chi_l' | H - E | J_{l'} \rangle 0 + \langle J_l | H - E | \chi_l \rangle 0 \} B_{L'' L'}^{k} \]
\[ + \sum_{L''} B_{L'' L'}^{k} + \langle J_{l'} | H - E | J_{l'} \rangle 0 B_{L'' L'}^{k} \quad (2.46) \]

If the cellular potential is spherically symmetric and the cells approximated by spheres, the above integral becomes diagonal in L.

To make the LCMTO method into an efficient calculation technique, atomic sphere approximation has been introduced and the energy dependence of one, two and three centre or overlap integrals appearing in Equation can be parameterized. The resulting procedure constitutes the so-called linear muffin tin orbital method.

The LMTO secular matrix may now be written in the form H-EO which corresponds to the generalized eigenvalue problem.
\[ \sum_{L} \left[ H_{LL}^{\vec{k}} - E_{LL}^{\vec{k}} O_{LL}^{\vec{k}} \right] \alpha_{L}^{\vec{k}} = 0 \quad (2.47) \]

and which may be solved by efficient numerical techniques to give the eigenvalues \( E^{\vec{k}} \) and eigenvectors \( \alpha_{L}^{\vec{k}} \).

The LMTO equations within ASA make the calculations extremely very fast, and it is very easy to reach an accurate minimal basis.

### 2.3.2 Tight Binding LMTO Method

The advantage of LMTO method over other method is that the basis set is fixed, minimal, localized, normalized for all values of \( k^2 \) and energy independent. This method is found to be linear and accurate within an energy scale of 1 Ry. The main drawback of this method is the slow decrease of the muffin-tin orbitals with radius. That means the orbitals that are centered at atomic position at very large distances from the unit cell still contribute non-negligibly to the wave function of its electron. However, the TB-LMTO method solves this problem.

This is due to the fact that the minimal but long-ranged base of muffin-tin orbitals that are frequently used in the first principles band structure calculations are exactly transformed into a TB base. This method has a minimal base, i.e. with at most one \( s \), three \( p \) and five \( d \) orbitals per atom, and in its two centre approximation. The TBMTO have an almost universal decay and with the ASA, further it can be cast in two centre form. The main advantage of this method, it is computationally efficient due to screening. A minimal set of orbitals possesses only one radial function per site, \( \vec{R} \) and angular momentum, \( l m \). Each orbital must therefore be able to approximately satisfy Schrodinger differential equation in the region between the atoms. The formalism of this method is as follows.
A conventional MTO in the interstitial region, the tail is simply the solution of Laplace's equation,

$$\chi_{lm}^0 \propto r^{-l-1} Y_{lm}(\vec{r}) \quad (2.48)$$

This MTO need not satisfy the Laplace equation inside the neighbouring atoms where it will be modified through augmentation. Since the envelope (Equation 2.34) has the form of electrostatic potential from a single $2'$-pole field at $\vec{R}$, we therefore try to localize the MTOs by screening with multipoles added on the neighboring sites. For this, a modified radial function has been defined as,

$$|I_l(r) > = |l^0_l(r) > - |n_l(r) > \quad (2.49)$$

where $l^0_l(r)$ and $K_l(r)$ are the regular and irregular radial solutions of the Laplace equation, $\alpha_l$ is the dimensionless screening constant and $\alpha_l = 0$ for $l > l_a$. The bare $2l$-pole field at $\vec{R}_j$ is denoted by $|n_l^0 >$ and it equals $|n_l >$ inside its own sphere i.e., $n_l^0(r) > = |n_j(r) >$ for $i=j$ site. Inside at any other site it may be expanded in terms of regular Laplace solution of $|l^0_l >$ as

$$|K_l^0 > = \sum_{ij} (|K_l > \alpha_{ij} - |l^0_i > S_{ij}^0) \quad (2.50)$$

The expansion coefficient $S_{ij}^0$, which is dimensionless is the so-called canonical structure matrix and $S_{ij}^0 = 0$ when $i=j$ and it decays as $(\omega/d)^n$ where $n = l_i + l_j + 1$. $d = |\vec{R}_i - \vec{R}_j|$. In analogy with Equation (2.50) the screened field is defined as

$$|K^\alpha > \equiv |K > - |J^\alpha > S^\alpha \quad (2.51)$$

and
of bare fields, and that the relation between the bare and screened structure matrices is

\[ S^\alpha = S^0 (1 - \alpha S^0)^{-1} \] (2.53)

where \( \alpha \) is now regarded as a diagonal matrix with elements \( \alpha_{Ri} \). As a function of \( d/w \) the decay of \( S^\alpha \) must be exponential for sufficiently small but positive \( \alpha \) values because the spectrum of \( S'' \) which is the essentially the so-called canonical bands is upwards bound.

Thus, \( \alpha \) is chosen in such a way that \( S'' \) has the shortest possible range. For an assumed lattice and \( \alpha \), the behaviour of \( S'' \) is found to be. (i) The range of \( S'' \) is essentially limited to first and second nearest neighbours, (ii) The corresponding \( \alpha \) is independent of the structure provided that \( w \) is taken with as the average Wigner-Seitz radius, and hence measures the density of multipoles,(iii) \( S^\alpha \) is almost universal.

In the one-centre expansions Equation(2.51) we substitute for each radial function \( f_l^\alpha \) by some regular function, \( \bar{f}_l^\alpha \) and each radial function \( K_l \) by a linear combination of \( \bar{f}_l^\alpha \) and the regular solution \( \Phi_{Rl}(E) \), at energy \( E \) of the radial Schroedigner equation for the potential spherically averaged around site \( \bar{R} \). Continuity and differentiability conditions for the functions lead to the expressions.

\[ |K\rangle = |\phi(E)\rangle N^\alpha(E) + |f^\alpha\rangle P^\alpha(E) \] (2.54)

at near the sphere surface and the elements of the diagonal matrices \( P \) and \( N \) are
\[
P^\alpha(E) = \frac{[\phi(E),K]}{[\phi(E),J]} = \frac{p^0(E)}{1-\alpha p^0(E)} \quad (2.55)
\]
\[
N^\alpha(E) = \frac{[J_{\alpha,K}]}{[J_{\alpha,\phi(E)}]} = (w/2)^{1/2} p^\alpha(E)^{1/2} \quad (2.56)
\]

for the so called normalization factor

The set of energy dependent MTO's \( |\chi^\alpha(E)\rangle \) in the interstitial region and in the spheres.

\[
|\phi(E)\rangle N^\alpha(E) + |J^\alpha\rangle [P^\alpha(E) - S^\alpha] \quad (2.57)
\]

The set \( |\chi^\alpha(E)\rangle \) is complete to first order in \( E - E_0 \) and can yield variational energy estimates correct to third order. With this new screened basis, the linear combination \( |\chi^\alpha(E)\rangle u^\alpha \) will be a solution of the Schordinger's equation at energy \( E \), provided that \([P^\alpha(E)-S^\alpha]u^\alpha=0\) where \( u^\alpha \) is a column vector. This is the generalization of the so-called tail cancellation of KKR condition.

The secular matrix \( P^\alpha(E)-S^\alpha \) depends on the potential only through the potential functions along the diagonal and, for the most localized set; it has the TB two centre form with \( S^\alpha \) playing the role of the transfer integrals. The potential function \( P^\alpha(E) \) can be parameterized as

\[
\alpha + P^\alpha(E)^{-1} \equiv P^0(E)^{-1} \approx \gamma \Delta/(E - C) \quad (2.58)
\]

where \( C_{Ri} \) and \( \gamma_{Ri} \) are the well known conventional potential parameters describing, respectively, the position, width and shape of the Ri band. The KKR equations have the form of an eigenvalue problem if \( P^\alpha \) is a linear function of \( E \). This is true if \( \alpha = \gamma \), then the effective two centers Hamiltonian is seen to be
\[
H_{ij}^\gamma = C_i \delta_{ij} + (\sqrt{A_i}) S_{ij}^\gamma (\sqrt{A_i}) \quad (2.59)
\]

This turns out to be the MT or AS Hamiltonian in a base, \( |\chi^\alpha > \) of energy-independent, nearly orthogonal MTO's.

In order to obtain an energy eigen value problem also when \( \alpha \neq \gamma \), energy-independent orbitals are needed. Now, \( |\chi^\alpha(E) > \) is independent of E in the interstitial region and the spheres, its first energy derivative will vanish at \( E = E_v \) if we choose \( J^\alpha \) proportional to the energy derivative function

\[
|\phi^\alpha > = \{ \partial |\phi(E) > N^\alpha(E)/ \partial (E) \} | N^\alpha = |\phi^\gamma > + |\phi > N^\alpha \equiv |\phi^\gamma > + |\phi > O^\alpha
\]

(2.60)

where \( \phi = \partial \Phi / \partial E \). The overlap \( \langle \phi \phi^\alpha \rangle = O^\alpha \) is the potential parameter. The set \( |\chi^\alpha > \) is this complete to first order in \( E - E_v \) and therefore can yield variational energy estimates correct to third order

If we normalize \( |\chi^\alpha > \) equal to \( |K^\alpha > N^\alpha \) in the third interstitial region, then

\[
|\chi^\alpha > = |\phi > + |\phi^\alpha > h^\alpha \quad (2.61)
\]

\[
h^\alpha = -(P^\alpha / P^\alpha) + (P^\alpha)^{-1/2} S^\alpha (P^\alpha)^{-1/2} \quad (2.62)
\]

in the spheres. In this base the MT or AS parts of the overlap and Hamiltonian matrices are

\[
\langle \chi | \chi \rangle = (1 + ho)(1 + oh) + hph \quad (2.63)
\]

\[
\langle \chi | H - E_v | \chi \rangle = h(1 + oh) \quad (2.64)
\]
because where $(H - E) |\phi(E)\rangle = 0$, where $p \equiv \langle \phi^\dagger \phi \rangle$.

Since all-energy independent MTO sets are obtained by substitution of each radial $(K, J^0)$ Hilbert space by the $(\phi, \phi^\dagger)$ space; all MTO sets span the same Hilbert space and transform into each other according to Equations (2.38) and (2.42). This method has been applied to semiconductors, amorphous alloys and surfaces of solids.

### 2.4 FULL POTENTIAL LINEARIZED AUGMENTED PLANE WAVE METHOD

In any practical implementation the computational effort increases significantly with the number of electrons that have to be taken into account. The observation that the chemical binding is determined almost entirely by the valence electrons, while the influence of the core electrons is negligible, has given rise to the idea to replace the core electrons by an effective potential, so they don't have to be taken explicitly into account. This is done in pseudopotential plane wave method, and the plane wave method has been applied with a great success to understand and predict the solid-state properties especially for semiconductors, as well as metals. On the other hand, there are reasons to why alternative methods are attractive. For some elements there is a significant interaction between core and valence electrons, or one may be interested in properties due to the core electrons. Thus different basis set should be designed to expand the wave functions.

Koelling & Arbamna developed the linear augmented plane wave (LAPW) method that is applied to Cu. However, Takeda & Kubler(1979) have proposed a more general formalism of the LAPW method. In this method, the basis function is represented as a combination of solutions of the radial Schrodinger equation for a set of $N$ energies, which are selected from the condition of self consistency. Now, the basis function becomes ($N$-
times differentiable on the muffin-tin sphere surface. The Augmented Spherical Wave (ASW) method is a modification of the LMTO method.

The basis function of this method is expanded into a series in terms of energy independent augmented spherical waves. The ASW function in the muffin-tin region is the solution of the Helmholtz equation. This improves the convergence. Linear KKR method has been realized on the basis of the KKR method. In this method, the energy dependence of matrix element is ensured by transformation of the KKR method. It may be called the linearization methods with mixed basis sets.

The linear augmented Slater orbitals method has been used for calculating the electronic structure, total energy and cohesive energy of the 5d metals in the scalar relativistic approximation. The results obtained show good agreement with computations by the APW method. An important feature of all these methods is their high efficiency and it allows a significant reduction in the computer time with no loss in accuracy.

2.4.1 Augmented Plane Wave Method

In the year 1937, Slater introduced augmented plane waves as basis functions for solving the one electron equations, which now correspond to the Kohn-Sham equations within DFT. Considering the characteristics of electrons in the space, when electrons are far away from the nuclei, they show the behaviour of the free electrons, and are then suitably characterized by plane waves. While close to the nuclei, electrons will bind strongly to their nuclei, their behaviour will be as in a free atom and they are described more efficiently by atomic like functions. Therefore, the whole space is technically divided into two regions: one being nonoverlapping atomic spheres called muffin tin MT regions and other is the interstitial region as shown in Figure 2.2. Accordingly, the potential in the whole space is defined as
\[ V(r) = \begin{cases} V(r), & (r \leq MT) \\ \text{constant}, & (r \geq I) \end{cases} \quad (2.65) \]

![Figure 2.2 Schematic division of space into atomic sphereregion (MT) and interstitial region(I)](image)

In this case two types of basis sets are used in the two different regions.

\[ \phi^\text{APW}_k(r, \varepsilon_l) = \begin{cases} \sum_{lm} A_{lm,k} U_l(r, \varepsilon_l) Y_{lm}(\hat{r}), & (r \leq MT) \\ \frac{1}{\Omega} e^{ikr}, & (r \geq I) \end{cases} \quad (2.66) \]

In the atomic spheres the wave functions are expanded by radial functions times spherical harmonics, \( u_l \) is the solution of the radial Schroedinger equation for a spherical potential \([V(r)]\) for energy \( \varepsilon_l \).

\[ -\frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{du_l}{dr} \right] + \left[ \frac{l(l+1)}{r^2} + V(r) - \varepsilon_l \right] r u_l = 0 \quad (2.67) \]

In the interstitial region plane waves are instead used to build the wave function.

The coefficients \( A_{lm} \) in the atomic sphere approximation are determined by requiring that the wave functions in the MT and the interstitial regions match each other at the MT boundary. Thus, each plane wave is
augmented by an atomic like function in every atomic sphere and constitutes thus the basis set used to expand the wave function,

$$\Psi(r) = \sum_n C_n \phi_k(r)$$  \hspace{1cm} (2.66)

The biggest disadvantage in the APW method is that it cannot get the eigen values from a single diagonalization due to the unknown parameter $\varepsilon_i$ in Equation (2.67). The exact $\varepsilon_i$ value, which is what we want to know is needed to describe the eigen state accurately. Since this energy depends on the function

$$V(\vec{r}) = \left\{ \begin{array}{ll}
\sum_{lm} V_{lm} Y_{lm}(\vec{r}) , \\
\sum_k V e^{ik\cdot r} ,
\end{array} \right.$$  

the resulting eigen value problem is no linear in energy. One has to set a trial energy $\varepsilon_i$ for solve equation 2.68 to obtain the APW basis, set up the matrix elements and compute the determinant $|H - ES|$. If the eigenergy does not equal $\varepsilon_i$, another trial energy must be chosen until the eigne energy equals $\varepsilon_i$. This makes the APW method extremely inefficient.

### 2.4.2 LAPW Method

In an effort to overcome the non linearity problem in the APW method, Andersen developed this linearized augmented plane wave method (LAPW). In this idea, the radial function $u_i$ is expanded by a Taylor expansion around $\varepsilon_i$,

$$u_i(r, \varepsilon_i) = u_i(r, \varepsilon_i^0) + (\varepsilon_i - \varepsilon_i^0)u_i(r, \varepsilon_i^0) + O((\varepsilon_i - \varepsilon_i^0)^2)$$ \hspace{1cm} (2.69)
In this case, the radial function error is second order and the energy error is of fourth order. When $\varepsilon_i^1$ is set near $\varepsilon_i$, the radial function and energy errors are negligible. Substituting Equation (2.69) into equation (2.66), we get the formulation of LAPW basis set.

$$\phi_k^{LAPW}(r) = \begin{cases} \sum_{lm} [A_{lm,k}u_l(r, \varepsilon_i^1) + B_{lm,k}\tilde{u}_l(r, \varepsilon_i^1)]Y_{lm}(\hat{r}), (r \leq MT) \\ \frac{1}{\sqrt{\Omega}} e^{i k r}, (r \geq l) \end{cases} \quad (2.70)$$

In the interstitial region, the basis set is the same as in the APW method, but in the MT sphere, the basis functions not only depend on $u_l$, but also on its energy derivative $\tilde{u}_l$. It is very clear that LAPW method is thus more flexible than the APW in the MT spheres.

To know the exact real value for $\varepsilon_i$ as in the case of APW is no longer a requirement any longer. For a fixed value of $\varepsilon_i^1$ the modified basis functions (Equation 2.69) provide the extra flexibility to cover a large energy region around this linearization energy. In order to arrive at both $A_{lm,k}$ and $B_{lm,k}$, the functions in the MT spheres are required to match the plane wave function in value and in slope at the sphere boundary. However, the continuous derivatives require higher plane wave cut offs to achieve a given level of convergence.

### 2.4.3 Local Orbital with LAPW

It is based on whether or not electrons in the atom participate in the chemical bonding with other atoms, that the electrons can be classified into two types.

One class of electrons are core electrons, which are extremely bound to their nucleus and are hence entirely localized in the MT sphere. Then those states are called core states. The other type of electrons is valence
electrons, which are leaking out of the MT sphere and bond with other atoms. However, for many elements in the periodic table, the electrons cannot be clearly distinguished like that. But, some states are neither contained in the core states, nor lie in the valence states and are correspondingly termed semi-core states. They have the same angular quantum number \( l \) as the valence states but with lower principal quantum number \( n \). When it comes to applying LAPW on these states, it is thus hard to use one \( \varepsilon_l^1 \) to determine the two same \( l \) in Equation (2.70). The dilemma is solved by introducing local orbitals (LO) which are defined as

\[
\phi^LO_k(r) = \begin{cases} 
\sum_{lm} \left[ A_{lm,k} u_l(r, \varepsilon_l^1) + B_{lm,k} \hat{u}_l(r, \varepsilon_l^1) + C_{lm,k} u_l(r, \varepsilon_l^2) \right] Y_{lm}(\hat{r}), & (r \leq MT) \\
0, & (r \geq l)
\end{cases}
\]

(2.72)

Each local orbital is taken as zero in the interstitial region and other atoms’ MT sphere. The three coefficients \( A_{lm}, B_{lm}, \) and \( C_{lm} \) can be determined by requiring the LO to have both zero value and zero slope at the MT boundary and be normalized.

The DFT’s overwhelming success for the description of the groundstate properties of large systems including semiconductors, insulators, semimetals, half metals, simple metals, transition metals and rare earths in bulk, at surfaces and as nanostructures makes it the unchallenged basis of any modern electronic structure theory. The wide applicability coupled with the predictive power of the approach turned it to the standard model in material science. In principle, the real inputs required for the theory are the atomic numbers of the main atoms of a system, all other properties follow as a direct result of the density functional equations.
In reality, the definition is to be modified since one is always limited to some set of model systems. These limitations can include system size, crystal structure, neglect of disorder, low or zero temperature, or any number of other boundaries on the phase space to probe. While these restrictions and limitations are troublesome, the aim of calculations is not merely to obtain numbers, but rather to get an insight. In the density functional theory many objectives have been done in an effective one-particle picture: the wave functions are solutions of the Kohn-Sham equations and the interaction of the particles is mainly taken into account by a self-consistent field which depends on the density of the particles.

2.4.4 FP-LAPW Method

The muffin tin approximation was actually frequently used in the 1970s and it works reasonably well in arena of highly coordinated systems such as face centred cubic (fcc) metals. However, for covalently bonded solids, open or layered structures, muffin tin approximation is meant to be a poor approximation and can lead to serious discrepancies with the experiments. In all these cases a treatment without any shape approximation is completely essential. Both, the potential and the charge density, are expanded into lattice harmonics inside each atomic sphere and as a Fourier series in the interstitial region.

\[
V(\vec{r}) = \left\{ \begin{array}{ll}
\sum_{lm} V_{lm} Y_{lm}(\vec{r}), & (r \leq MT) \\
\sum_k V e^{ikr}, & (r \geq l)
\end{array} \right. \quad (2.73)
\]

Thus the expansion form is completely general so that such a scheme is termed to be full-potential calculation. The choice of radii of the sphere is not very critical in full-potential calculations in comparison with muffin tin approximation in which one has to obtain different radii as optimum choice depending on whether one looks at the potential maximum
between two adjacent atoms or the charge density minimum between two adjacent atoms. Therefore, in muffin tin approximation one has to make a compromise but in full potential calculations one can efficiently handle this problem. The program used in this present work is WIEN2k based on the Full Potential Linearized Augmented Plane Wave (FP-LAPW) method.

2.4.5 WIEN2k Code

The WIEN2k code (Blaha et al. 1990) is fully based on the FP-APW+lo method. The code is to be applied to systems with periodic boundary conditions and it is mainly used for crystal calculations. The WIEN2k code has two main parts as shown in Figure 2.3. One is about the initialization; it includes the running a series of small auxiliary programs, which can generate the inputs for the main program that is for the self consistency.

It is used to check if MT spheres overlap, generate a new structure file according to its space group, detect its symmetry operations, generate a k-mesh in the irreducible part of the BZ, and get the input trial density by making superposition of atomic densities. The other one is the self consistency cycle. It calculates the potential used in the KS equation, diagonalises the Hamiltonian and overlap matrices and generates eigen values and eigen vectors, integrates all valence states and obtains the valence electron density ($\rho_{val}$) solves the atomic calculation and gets the core electron density ($\rho_{core}$); mixes the two electron densities with the old total electron density ($\rho_{old}$) and gets the new total electron density ($\rho_{new}$). Thereafter, it checks if the properties ($\rho_{new}$ or $E_{tot}$ or Force) of the system are converged, and either stops the self consistency cycle or starts anew. Apart from two the main parts, WIEN2k have lots of additional packages to evaluate a variety of system properties. This comprises geometry optimization, plotting the density
of states, band structure, electron density, X-ray structure factors, X-ray spectra elastic properties for cubic systems etc.

There are two types of parallelization modes which are implemented in the WIEN2k code to increase the efficiency of calculation. One of them is k-point parallelization, which distributes the computations for the different irreducible k-points over several processors. This method can be only useful for small calculations and a low communication bandwidth across the processors. If there is a big system with few k points, then fine grained parallelization can be additionally applied. It can diagonalize the Hamiltonian and overlap matrices for each k-point on different processors.

Figure 2.3 Flow of program in WIEN2k
The speed of this method greatly depends on the communication between the processors, and on the number of the processors and on the matrix size. To run the WIEN2k code more efficiently, one has to do the parallelizing of \( k \) points on different block of processors and the fine grained parallelization on each block of processors.