CHAPTER 2

INTRODUCTION TO THE ELECTRONIC STRUCTURE OF SOLIDS AND THE LMTO METHOD

2.1 INTRODUCTION

To understand the behaviour of the solid state materials, such as metals, semiconductors or insulators, thinfilms, etc., a good knowledge of the electronic band structure of these compounds is needed. Most of the physical properties such as transport properties, optical phenomena, study of Fermi surface, lattice dynamics, cohesions, alloying, magnetism, superconductivity, nuclear magnetic resonance, mossbäuer spectra, positron annihilation, etc., are directly dependent on the electronic structure. The direct computation of the electronic states or their investigation by inference from experiment, is therefore one of the major works of the solid state physics.

2.2 THE ONE-ELECTRON SCHröDINGER EQUATION

The electronic structure of a solid consists in finding the eigenstates for a large number of (N) interacting electron system in the background of the lattice. Since the electrons are light particles compared to the much heavier nuclei, the dynamics of the electrons and the nuclei can be treated separately, using the procedure known as Born-Oppenhiemer approximation. Yet the problem is complex, which needs further approximation. The most important approximation is the one-electron approximation which describes each electron as an independent particle.
moving in the mean field of the other electrons, plus the field due to the nucleus. Now one is led to solve the one-electron Schrödinger equation

\[-V^2 + V(r)\] \[\psi_j(r) = E_j \psi_j(r)\] \hspace{1cm} (2.1)

where \(V(r)\) is the effective one-electron potential, which consists of the electrostatic field from the nuclei and the charge clouds of all the other electrons plus corrections for exchange and correlation and \(\psi_j(r)\) are the eigenstates. (Here and throughout we use atomic Rydberg units \(\hbar = 2m = e^2/2 = 1\)). Having solved the Schrödinger equation, the charge density \(n(r)\) has been obtained using

\[n(r) = \sum_{\text{occ.}} \Sigma_j |\psi_j(r)|^2\] \hspace{1cm} (2.2)

The potential \(V(r)\) has been calculated from the Poisson's equation for the Hartree part and the Kohn Sham's density functional description for the exchange correlation part. With this new \(V(r)\), again calculate \(n(r)\) and hence \(V(r)\) till self-consistency is reached. The total energy of the electrons has been calculated finally and hence the pressure, stresses and interatomic forces.

2.3 BAND STRUCTURE METHODS

Band structure is basically a plot between the energy (E) and the wave vector (k). Band structure methods may be classified according to whether they seek the wave functions as an expansion in some set of fixed basis functions, like atomic orbitals, plane waves, Gaussians, etc., or they expand the wave functions in the set of energy and potential dependent partial waves.
2.3.1 Methods using fixed basis-functions

The linear combination of atomic orbitals (LCAO) method is a typical fixed basis method. In this method the wave functions are expressed as a linear combination of the eigenfunctions of the free atom.

By the use of standard variational principle, a set of eigenvalue equations can be obtained with Hamiltonian and overlap matrices, which is

\[(H - EO).a = 0\]  \hspace{1cm} (2.3)

This equation can be solved to get energy eigenvalues \(E\) and the overlap matrices \(O\). The most important advantage of fixed basis method is that it reduces to an algebraic eigenvalue problem, which can be solved straightforwardly in most cases. The essential disadvantage of this method is that, the basis-sets should be large in order to be reasonably complete.

2.3.2 Methods using partial waves

In the partial wave method of Wigner and Seitz (or cellular) the potential inside the atom is taken to be spherically symmetric and this is extended all the way to the boundaries of an atomic polyhedron. The wave functions in the solid can be expressed as bloch sum of partial waves such that the wave functions and hence their first derivatives are continuous and differentiable across the boundary of the atomic polyhedron. The main disadvantage of the Wigner-Seitz cellular method is that it is almost impossible to apply the boundary conditions.

To avoid the troublesome boundary conditions, muffin-tin approximation has been used (APW method). In this form the spherically symmetric part of the potential is retained only inside the so called muffin-tin spheres centered on each atomic site. The potential in the interstitial
region between the spheres where it is slowly varying is taken to be flat. Now it becomes possible to solve the Schrödinger equation exactly in terms of the energy dependent partial waves inside the spheres and plane wave expansion for the interstitial region.

In this APW method, the partial wave is taken to vanish outside its own sphere and the interstitial function is taken to vanish outside the interstitial region.

On the other hand, in the KKR method, inside the muffin-tin spheres, partial wave expansion similar to cellular or APW method is used and in the interstitial region, the wave functions are expanded in terms of phase-shifted spherical waves, so that the boundary condition can be expressed as the condition for self-consistent multiple scattering between the muffin-tin spheres.

In general all the partial wave methods will lead to a set of linear, homogenous equations of the form

\[ \mathbf{M}(E) \cdot \mathbf{b} = 0 \quad (2.4) \]

The secular matrix \( \mathbf{M} \) has a nonlinear energy dependence and hence the one-electron energies must be found by tracing the roots of determinant of \( \mathbf{M} \) as a function of \( E \), which requires enormous computational time. Therefore, linear methods were proposed.

### 2.4 THE LINEAR METHODS

The linear methods which are widely used at present for the band structure calculations employ energy-independent basis-functions derived from the partial waves. They lead to eigenvalue equations of the form (2.3) thereby reducing the computational time substantially. Of the linear
methods, the computationally fastest one is the linear muffin-tin orbital method (LMTO) which uses minimal basis. The LMTO method has been used in the present work. A brief discussion of this method is presented below, whose detailed version can be found in the "The LMTO method" by Skriver (1984).

2.5 THE LMTO METHOD

In the linear muffin-tin orbital method, devised by Andersen (1975), the energy band problem may be separated into two parts, with the use of canonical bands, one which depends only on the crystal structure and the other which depends solely on the potential inside the atomic sphere.

In the LMTO method, the basis-orbitals are the so called muffin-tin orbitals and they are constructed from the partial waves.

2.5.1 Partial waves for a single muffin-tin

In the LMTO method, the crystal potential $V(r)$ appearing in the Schrödinger equation is approximated by the so called muffin-tin potential which is defined to be spherically symmetric within spheres of radius $S_{MT}$ and to have a constant value $V_{MTZ}$ in the interstitial region between spheres. i.e. within a single muffin-tin well the potential is defined to be

$$V_{MT}(r) = \begin{cases} 
V(r) - V_{MTZ} & r \leq S_{MT} \\
0 & r \geq S_{MT}
\end{cases}$$  \hspace{1cm} (2.5)

where $S_{MT}$ is the muffin-tin sphere radius. $V(r)$ is the spherically symmetric part of the crystal potential. We now seek solutions of Schrödinger's equation for both in the interstitial region and inside the spheres

$$[-\nabla^2 + V_{MT}(r) - \kappa^2] \psi_L(E,r) = 0$$  \hspace{1cm} (2.6)
where \( \kappa^2 = E - V_{MTZ} \), the kinetic energy in the interstitial region for all values of \( \kappa^2 \) both in the continuum and in the bound state region for an electron moving in an isolated muffin-tin well embedded in the flat potential \( V_{MTZ} \).

For the region inside the sphere, the wave functions are

\[
\psi_L(E,r) = i^l Y_l^m(r) \psi_L(E,r) \tag{2.7}
\]

where \( \psi_L(E,r) \) is the radial solution and \( Y_l^m(r) \) is the spherical harmonics. In the region of constant potential, where \( V_{MT}(r) = 0 \), the solutions are linear combinations of spherical Bessel \( j_l(\kappa r) \) and Neumann \( n_l(\kappa r) \) functions respectively.

Now the solution of equation (2.6) will have the form.

\[
\psi_L(E,\kappa r) = i^l Y_l^m(r) \begin{cases} \psi_L(E,r) & r \leq S_{MT} \\ \kappa [n_L(\kappa r) - \cot(\eta_l) j_l(\kappa r)] & r \geq S_{MT} \end{cases} \tag{2.8}
\]

The constant of integration \( \cot(\eta_l) \) are chosen in such a way that the partial wave is everywhere continuous and differentiable. This requires that

\[
cot(\eta_l(E,\kappa)) = \left. \frac{n_l(\kappa r)}{j_l(\kappa r)} \cdot \frac{D_j(E) - \kappa n_j'(\kappa r)/n_j(\kappa)}{D_l(E) - \kappa n_l'(\kappa r)/n_l(\kappa)} \right|_{r=S_{MT}} \tag{2.9}
\]

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

\[
D_j(E) = \left. \frac{S}{\psi_j(E,S)} \frac{\partial \psi_j(E,r)}{\partial r} \right|_{r=S_{MT}} \tag{2.10}
\]
The solution (2.8) is unbounded but delta function normalisable for positive values of $\kappa^2$. When $\kappa^2$ is negative it can be normalised only at the eigenvalues of the single well. For these reasons the partial waves are not well suited as basis functions.

2.5.2 Muffin-tin orbitals

The problem of normalisation has been mitigated with the introduction of MTO's which are reasonably localised can be made energy-independent and normalisable for all values of $\kappa^2$ and thus constitute an efficient basis set for the first principle electronic structure calculations. The MTO is defined as

$$\chi_L(E, \kappa, r) = i^l Y_l^m(r) \begin{cases} \psi_l(E, r) + \kappa \cot(\eta_l) j_l(\kappa r) & r \leq S_{MT} \\ \kappa n_l(\kappa r) & r \geq S_{MT} \end{cases} \quad (2.11)$$

Now the energy-dependent MTO's defined in equation (2.11) may be used in conjunction with tail cancellation theorem to obtain secular equation of the form (2.4).

However, such a procedure is inefficient and it is desirable to develop a method based on the variational principle and a fixed basis set to obtain the computationally efficient eigenvalue problem (2.3).

2.5.3 Energy-independent MTO's

In order to obtain the fixed basis set, the MTO's will be made energy-independent around an arbitrary energy $E_v$ and the energy-independent MTO's thus obtained will be used in the eigenvalue equation (2.3) and the energy dependence of one, two and three centre integrals and overlap terms resulting from the eigenvalue equation will be parametrised. The energy-independent MTO around a fixed energy $E_v$ can be obtained by augmenting equation (2.11) with a particular choice of augmented spherical
Bessel $J_j(kt)$ and Neumann $N_j(kt)$ functions. The augmented MTO is everywhere continuous and differentiable and is orthogonal to the core states of all the muffin-tins. Hence these orbitals are well suited for use in connection with the variational principle.

2.5.4 The LCMTO secular matrix

Using the Rayleigh-Ritz variational principle, the secular matrix (2.4) can be obtained. According to the Rayleigh-Ritz variational principle

$$\delta \langle \psi | H - E | \psi \rangle = 0$$

(2.12)

where $E$ is the Lagrange multiplier needed to ensure the normalisation of $\psi$. The above equation has the solution, whenever

$$\det \langle \chi_L^k | H - E | \chi_L^k \rangle = 0$$

(2.13)

The integral may be evaluated over all space as a sum of integrals over all atomic polyhedra. After repeated use of the Bloch condition one obtains the well known result

$$N^{-1} \langle \chi_L^k | H - E | \chi_L^k \rangle = \langle \chi_L^k | H - E | \chi_L^k \rangle_0$$

(2.14)

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

One can obtain the LCMTO secular matrix, by inserting the one centre expansion for the Neumann function given below

$$\chi_L^k(E, \kappa, \mathbf{r}) = \chi_L^k(E, \kappa, \mathbf{r}) + \sum_{\mathbf{R} \neq \mathbf{0}} e^{i \mathbf{k} \cdot \mathbf{R}} \chi_L^k(E, \kappa, \mathbf{r} - \mathbf{R})$$

(2.15)
into the matrix (2.14), leads to the following equation
\[ \langle \chi_{L,k} | H - E | \chi_{L,k} \rangle_0 = \langle \chi_{1,k} | H - E | \chi_{1,k} \rangle_0 \delta_{L,L} \]
\[ + \sum_{L'} B_{L,L'}^{k} \langle J_{1,k} | H - E | J_{1,k} \rangle_0 B_{L,L'}^{k} \]
\[ + \sum_{L''} B_{L,L''}^{k} \langle J_{1,k} | H - E | J_{1,k} \rangle_0 B_{L,L''}^{k} \]  \hspace{1cm} (2.16)

where \( B_{L,L'}^{k} \) are the KKR structure constants and are given as
\[ B_{L,L'}^{k} = 4\pi \sum_{L''} \frac{C_{L,L''}^{k}}{R=0} \sum_{\kappa} e^{i\kappa} \n_{L''}^{\kappa} (\kappa, R) \]  \hspace{1cm} (2.17)

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

\subsection{2.5.5 The LMTO method}

To make the LCMTO method into an efficient calculational technique, atomic sphere approximation has been introduced and the energy dependence of one, two and three centre or overlap integrals appearing in equation (2.16) can be parametrised. The resulting procedure constitutes the so-called linear muffin-tin orbital method.

The LMTO secular matrix may now be written in the form \( H-EQ \), which corresponds to the generalised eigenvalue problem.
\[ \sum_{L} (H_{L,L}^{k} - E^{k} O_{L,L}^{k}) \alpha_{L}^{jk} = 0 \]  \hspace{1cm} (2.18)

and which may be solved by efficient numerical techniques to give the eigenvalues \( E^{k} \) and eigenvectors \( \alpha_{L}^{jk} \). The Hamiltonian matrix is given by
\[
H_{LL}^k = \left[ \frac{\omega(n) + E_0(1 + \omega^2[n])\phi^2}{(S/2)\phi^2[n]} \right] \delta_{LL} + \\
\left\{ \frac{\omega[j] + E_0(1 + \omega[j][n])\phi^2}{\omega[j] - \omega[n]} \right\}_j^{[..]_1} + \frac{1}{2} S_{LL}^k(x)
\]

while the overlap matrix is

\[
O_{LL}^k = \left[ \frac{1 + \omega^2[n]\phi^2}{(S/2)\phi^2[n]} \right] \delta_{LL} + \\
\left\{ \frac{1 + \omega[j][n]\phi^2}{\omega[j] - \omega[n]} \right\}_j^{[..]_1} + \frac{1}{2} S_{LL}^k(x) + \\
+ \sum_L S_{LL}^k(x) \left[ \frac{1 + \omega^2[j]\phi^2}{2(D[j] - D[n])^2\phi^2[j]} \right] S_{LL}^k(x)
\]

where \( S_{LL}^k(x) \) are the structure constants which is given by

\[
S_{LL}^k(x) = \frac{B_{LL}^k(x)}{S\chi_{1} \cdot (\kappa S)\chi_{1} (\kappa S)/2}
\]
where \( D(n) - D(j) = \frac{1}{K_S n(K_S) j(K_S)} \) (2.22)

\[ S \phi(n) \phi(j) = \frac{\omega(n) - \omega(j)}{D(n) - D(j)} \] (2.23)

where \( \omega(n), \omega(j), \phi(n), \phi(j) \) are the potential parameters. These expressions are used in the LMTO program.

2.5.6 Atomic sphere approximation (ASA)

ASA (Andersen 1975, Andersen et al. 1979) is essentially a combination of two approximations, one being that, the atomic polyhedron of Wigner and Seitz may be approximated by an atomic sphere with radius \( S \), so that the volume of the atomic sphere is equal to that of Wigner-Seitz polyhedron \( 4/3 \pi S^3 = \Omega \). All integrals over the cell are replaced by integrals over the atomic sphere, where by the contribution from the region between the muffin-tin and the atomic sphere will be taken exactly into account.

The second one is that we include only \( s, p, d \) (and \( f \)) orbitals, neglecting all higher waves, for \( k^2 \) at zero and integrate the radial Schrödinger equation out to the boundary of the atomic sphere.

2.5.7 The combined correction terms (cc)

In the ASA, the Hamiltonian and the overlap matrices are given by equations (2.19) and (2.20) with \( k^2 = 0 \) and truncated at \( l = 2 \) or 3. Then the LMTO eigenvalues will have small order of errors. Although the errors introduced by the ASA are unimportant for many applications, eg. self consistency procedures, there are case where energy bands of high accuracy are needed. In such cases some extra terms are added to the LMTO
matrices which accounts to first order for the differences between the atomic sphere and the atomic polyhedron, reestablishes the correct kinetic energy in the region between the sphere and the polyhedron and corrects for the neglect of higher partial waves. The extra terms which accomplish these corrections are the so-called combined correction terms. The form of which is

\[ \langle \chi_{L'}^{l'}|\Delta V|\chi_{L}^{k}\rangle = (V_{MTZ} - E + \kappa^2) \langle \chi_{L'}^{l'}|\chi_{L}^{k}\rangle_C - (V_{MTZ} - E + \kappa^2) \langle \chi_{L'}^{l'}|\chi_{L}^{k}\rangle_S \]  

(2.24)

2.6 LINEAR MUFFIN-TIN ORBITAL IN TIGHT-BINDING REPRESENTATION (TB-LMTO)

The MTO's used in the LMTO method can form an efficient basis set for the first principles electronic structure calculation of solids. It has got several advantages.

1. It is transparent in the sense that it is applicable to materials composed of atoms from any part of the periodic table.

2. It is minimal, i.e. it consists of one s orbital, three p orbitals, five d orbitals and for f-band materials seven f orbitals per site.

3. Its energy dependence may be retained in the Green's function calculations and neglected in band-structure calculations.

4. The MTO's may be expanded about other sites in terms of numerical, radial functions, spherical harmonics and canonical structure constants. This together with the ASA, according to which the Wigner-Seitz polyhedron are replaced by overlapping "Space-filling" atomic sphere, leads to the factorization of the matrix elements of nearly any operator into products of structure constants and radial integrals.
The basic disadvantage of the conventional solid state MTO's is their infinite range. This has limited its applications to those cases where the structure constant can be summed by the sites from a periodic lattice. Also with orbitals of infinite range, the electronic wave function in a given cell has contributions from orbitals throughout the solid.

Therefore the long ranged MTO's are exactly transformed into tight-binding (TB) or screened basis which are short ranged (Andersen and Jepsen 1984, Andersen et al (1986)). The TB-MTO's have an almost universal decay and with atomic sphere approximation (ASA), this method can be cast into two center form. The main advantage of this scheme is that it is computationally effective due to screening.

As mentioned in section (2.5.1) for an LMTO in its ASA belonging to the conventional set, the envelope function or the tail is simply the solution of the Laplace equation

\[ \chi_{lm} \propto r^{-1} Y_{lm}(r) \quad (2.25) \]

This tail need not satisfy the Laplace equation inside the neighbouring site, where it will be modified through augmentation. Since the envelope (2.25) has the form of electrostatic potential from a single 21-pole at \( R \), we therefore try to localize the MTO's by screening with multipoles added on the neighbouring sites.

For this a modified radial function has been defined as,

\[ |J_l(r)> = |J_l(r)> - \alpha |n_l(r)> \quad (2.26) \]

(Note : For convenience hereafter ket and bra notations has been used to denote the functions)
where \(| J^0_i(r) \rangle\) and \(| n_i(r) \rangle\) are the regular and irregular radial solutions of the Laplace equation. \(\alpha_l\) is the dimensionless screening constant and \(\alpha_l = 0\) for \(l > l_\alpha \leq 2\). The bare \(2^l_j\) pole at \(R_j\) is denoted by \(| n_j^0 \rangle\) and it equals \(| n_j \rangle\) inside its own sphere i.e., \(| n_j^0(r) \rangle = | n_j(r) \rangle\) for \(i=j\) site.

Inside at any other site it may be expanded in terms of regular solutions of \(| J^0_i \rangle\) as

\[
| n_j^0 \rangle = \sum_i \delta_{ij} - | J^0_j \rangle S^0_{jj} (2.27)
\]

The expansion coefficient \(S^0_{jj}\), which is dimensionless is the so-called canonical structure matrix and \(S^0_{jj} = 0\) when \(i=j\) and it decays as \((w/d)^m\), where \(m = l_i + l_j + 1\), \(d = | R_i - R_j |\) and \(w\) is the average Wigner-Seitz radius.

In analogy with equation (2.27) the screened field has been defined as

\[
| n^\alpha \rangle = | n \rangle - | J^\alpha \rangle S^\alpha (2.28)
\]

substituting for \(| J^\alpha \rangle\) we get

\[
| n^\alpha \rangle = | n \rangle (1 + \alpha S^\alpha) - | J^0 \rangle S^\alpha (2.29)
\]

The screened structure constant \(S^\alpha\) is given by

\[
S^\alpha = S^0 (1 - \alpha S^0)^{-1} (2.30)
\]

Substituting for \(S^\alpha\) and \(| n \rangle\) in equation (2.29) we get

\[
| n^\alpha \rangle = | n^0 \rangle (1 + \alpha S^\alpha) = | n^0 \rangle (1 - \alpha S^0)^{-1} (2.31)
\]
In electrostatic analogue, $\alpha S^\alpha$ is identified as the "screened charge" and with this, the decay of $S^\alpha$ must be an exponential function of $d/w$ for small but positive values of $\alpha$, since the spectrum of $S^0$ is upwards bound.

Thus $\alpha$ is chosen in such a way that $S^\alpha$ has the shortest possible range. For an assumed lattice and $\alpha$, the behaviour of $S^\alpha$ is found to be

1. The range of $S^\alpha$ is essentially limited to first and second nearest neighbours.
2. $\alpha$ is independent of the structure provided that w is taken as the average Wigner-Seitz radius which is the measure of the site density.
3. $S^\alpha$ depends almost only on $d/w$ and hardly on the structure i.e. $S^\alpha$ is almost universal.

For constructing a set of TB-LMTO's $|\chi^\alpha>$, a set of conventional LMTO's $|\chi^0>$ were formed by augmentation of the envelope set $|n^\alpha>$ inside the Wigner-Seitz sphere i.e. in equation (2.28) we substitute for each radial function $|J^\alpha>$ by some regular function $|J^\text{Ri}\alpha>$ and each radial function $|n>$ by a linear combination of $|J^\text{Ri}\alpha>$ and the regular solution $|\phi\text{R}(E)>$, at energy $E$ of the radial Schrödinger equation for spherically averaged potential around the site $R$.

\[ |J^\alpha> = |J^\text{Ri}\alpha> \] \hspace{1cm} (2.32)

\[ |n> = |\phi(E)>N^\alpha(E) + |J^\alpha>P^\alpha(E) \] \hspace{1cm} (2.33)

Continuity and differentiability conditions for the functions leads to the expressions

\[ P^\alpha (E) = P^0(E) \left[ 1 - \alpha P^0(E) \right]^{-1} \] \hspace{1cm} (2.34)
for the potential function and

\[ N^\alpha(E) = \left( \frac{w}{2} P^\alpha(E) \right)^{\frac{1}{2}} \]  

(2.35)

for the so-called normalization factor.

The conventional (bare) potential function with their augmentation, the MTO's turn out to be the TB base as

\[ |\chi^\alpha(E)> = \begin{cases} |\phi(E)> N^\alpha(E) + |J^\alpha>[P^\alpha(E) - S^\alpha] & r \leq w \\ |n^\alpha> & r \geq w \end{cases} \]  

(2.36)

The set \(|\chi^\alpha>\) is complete to first order in \((E-E_u)\) and can yield variational energy estimates correct to third order.

With this new screened basis, the linear combination \(|\chi^\alpha(E)>u^\alpha\) will be a solution of the Schrödinger's equation at \(E\), provided that \(|P^\alpha(E)-S^\alpha|u^\alpha = 0\) where \(u^\alpha\) is a column vector.

This is the so called tail cancellation or KKR-ASA equation. The potential function \(P^\alpha(E)\) can be parameterized as

\[ \alpha + [P^\alpha(E)]^{-1} = [P^0(E)]^{-1} = \frac{\Delta}{E - C} + \gamma \]  

(2.37)

where \(\gamma\), \(\Delta\) and \(C\) are the well known conventional potential parameters.

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 center Hamiltonian is seen to be

\[ H^Y_{ij} = C_i \delta_{ij} + (\sqrt{\Delta}) S_{ij} (\sqrt{\Delta}) \]  

(2.38)
This turns out to be the MT or AS Hamiltonian in a base $|\chi^\gamma\rangle$, of energy-independent, nearly orthogonal MTO's.

In order to obtain an energy eigenvalue problem also when $\alpha \neq \gamma$, energy independent orbitals are needed. Now $|\chi^\alpha(E)\rangle$ is independent of $E$ in the interstitial region and inside the spheres its first energy derivative will vanish at $E = E_0$ if we choose $|J^\alpha\rangle \propto |\dot{\phi}^\alpha\rangle$ where

$$|\dot{\phi}^\alpha\rangle = |\dot{\phi}^\gamma\rangle + |\phi\rangle \dot{N}^\alpha/N^\alpha = |\dot{\phi}^\gamma\rangle + |\phi\rangle O^\alpha$$

where $\dot{\phi} = \partial \phi / \partial E$ (2.39)

The overlap $\langle \phi^\gamma | \dot{\phi}^\alpha \rangle = O^\alpha$ is the potential parameter. Thus the set $|\chi^\alpha\rangle$ is complete to first order in $E - E_0$ and therefore can yield variational energy estimates correct to third order.

If we normalize $|\chi^\alpha\rangle$ equal to $|n^\alpha\rangle N^\alpha$ in the third interstitial region, then

$$|\chi^\alpha\rangle = |\phi\rangle + |\dot{\phi}^\alpha\rangle h^\alpha$$

$$h^\alpha = -P^\alpha \dot{P}^\alpha + (\dot{P}^\alpha)^{1/2} S^\alpha (\dot{P}^\alpha)^{-1/2}$$

in the spheres.

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

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

and

$$\langle \chi^\alpha | H - E_0 | \chi^\alpha \rangle = h^\alpha (1 + O^\alpha h^\alpha)$$

where $P = \langle \phi^\gamma | \dot{\phi}^\gamma \rangle$ (2.42)

Moreover, since all energy independent MTO sets are obtained by substitution of each radial $(n,\ell^0)$ Hilbert space by the $(\phi, \dot{\phi})$ space, all MTO
sets span the same Hilbert space and transform into each other according to equations (2.31) and (2.35).

2.7 DENSITY FUNCTIONAL THEORY (DFT)

Density functional theory is the basis for most of the band structure methods to calculate the ground state properties of crystalline solids and is based on the Hohenberg-Kohn (1964) theorem. According to which the external potential is an unique functional of the electron density, i.e. \( V(n(\mathbf{r})) \leftrightarrow n(\mathbf{r}) \).

The Hamiltonian of a system of \( N \) interacting electrons can be written as

\[
H = T + U + V = \sum_{i=1}^{N} \left( \frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} + \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i) \right)
\]  

(2.44)

Here \( T \) is the kinetic energy of the electrons, \( U \) is the electron - electron coulomb repulsion and \( V \) is the electrostatic interaction with the fixed nuclei, where \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \). As the external potential \( V_{\text{ext}}(\mathbf{r}) \) is an unique functional of the electron density \( n(\mathbf{r}) \), hence that the ground state \( \langle \phi \rangle \) and the energy functionals

\[
\langle \phi | H | \phi \rangle = F[n] + \int V_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) \, d\mathbf{r}
\]  

(2.45)

\[
F[n] = \langle \phi | T + U | \phi \rangle
\]

are unique functionals of \( n(\mathbf{r}) \).

where \( F[n] = 1/2 \int \frac{2n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r} d\mathbf{r}' + G[n] \)  

(2.46)
Here the first term is the classical Hartree contribution. Hohenberg and Kohn showed that for a given external potential the correct ground state charge density $n(r)$ minimises the energy functional equation 2.45 which is an unique functional of $n(r)$. If the functional $F[n]$ or $G[n]$ which are universal were known then the variational principle can be used to determine the ground state energy. Unfortunately the functional is not known. This theory is exact in two limiting cases (i) for slowly varying $n(r)$ which leads to Thomas-Fermi approximation (ii) for a density which is an average over a fluctuation, which leads to Hartree-Fock theory.

In this situation Kohn and Sham (1965) made an approximation according to which the ground state density of a real interacting electron system is assumed to be the same as that of a non-interacting system.

$G[n]$ is written in the form

$$G[n] = T_S[n] + E_{xc}[n]$$

(2.47)

where

$$T_S[n] = \langle \phi_S | T | \phi_S \rangle = \sum_{jk} \int \psi_j^*(r) (-\nabla^2) \psi_j(r) \, dr$$

(2.48)

is the kinetic energy of the non-interacting electrons of density $n(r)$ which is assumed to be that of the interacting system. $E_{xc}[n]$ is the so-called exchange correlation energy functional which describes the difference between the true kinetic energy and that of the non-interacting system plus the difference between the true interaction energy and that included by Hartree contribution. $E_{xc}[n]$ can be written within the local density approximation (LDA) (Hedin and Lundqvist 1971, Gunnarsson and Lundqvist 1976) as

$$E_{xc}[n] = \int n(r) \epsilon_{xc}(n(r)) \, dr$$

(2.49)
which is exact in the limit of slowly varying as well as high density. The exchange correlation energy density $\varepsilon_{xc}(n)$ is calculated from the homogeneous electron gas of density $n$.

Following Kohn and Sham, now the total energy functional can be written as,

$$\langle \phi | H | \phi \rangle = \langle \phi_S | T | \phi_S \rangle + \int \left\{ \frac{2n(r')}{|r-r'|} dr' + V_{\text{ext}}(r) + \varepsilon_{xc}(n(r)) n(r) \right\} dr$$

Minimisation of the total energy functional with respect to charge density $n(r)$, leads to the one-electron Schrödinger's equation

$$[-V^2 + \int \frac{2n(r')}{|r-r'|} dr' - \frac{2Z}{|r_1-R|} + V_{xc}(r)] \psi_i(r) = \varepsilon_i \psi_i(r)$$

The exchange correlation potential $V_{xc}(r)$ is given by

$$V_{xc}(r) = \frac{d\ln \varepsilon_{xc}(n)}{dn} = \mu_{xc}[n(r)]$$

where $\mu_{xc}$ is the exchange correlation part of the chemical potential in a homogenous electron gas of density $n(r)$. In general the exchange only part of this potential is proportional to $n(r)$. There are different schemes for calculating $\mu_{xc}[n(r)]$.

In our calculation Barth and Hedin (1972) exchange scheme has been used. Using equation (2.50) the ground state properties of the interacting system can be calculated.