CHAPTER 1
INTRODUCTION TO THE ELECTRONIC STRUCTURE OF SOLIDS AND THE LMTO METHOD

1.1 THE ONE ELECTRON SCHRODINGER EQUATION

Most of the physical and chemical properties of condensed matter systems are governed by the conduction electrons. One is often interested in finding the eigen states of these electrons as most of the properties can be well understood from them. As the systems under consideration are highly complex an exact determination of their ground state properties are almost impossible. Thus it became necessary to use approximations for obtaining the ground state. The Born-Oppenheimer approximation is the first and foremost one that simplifies the problem by separating the dynamics of the electrons from the nuclei. The Schrodinger equation that results after the use of Born-Oppenheimer approximation is a N-electron equation and solving this equation is highly impractical and hence it immediately calls for further approximations. An important approximation that reduces the N-electron Schrodinger equation to one electron Schrodinger equation is the so called one electron approximation. The one electron Schrodinger equation (in atomic units) is written as

\[
(-\nabla^2 + V(r)) \psi(r) = E\psi(r)
\]

(1.1)

Here \(V(r)\) is the effective one electron potential and it consists of the field from the nuclei and the field due to the charge cloud of all the other electrons including the exchange the correlation contribution:
The density functional formalism of Kohn and Sham (1965) in the local density approximation is an important scheme for obtaining an appropriate form for the one electron Schrodinger-like equation. The single particle equation obtained from this formalism is written as

$$\left[ -\nabla^2 + \int \frac{2n(r')}{|r-r'|} \, dr' + V_{ne}(r) + V_{xc}(n(r)) \right] \psi_i(k,r) = E_i(k) \psi_i(k,r)$$  \hspace{1cm} (1.2)

where \( n(r) \) is made to satisfy the requirement that

$$n(r) = \sum_{jk}^{occ} |\psi_j(k,r)|^2$$  \hspace{1cm} (1.3)

### 1.2 THE ENERGY BAND STRUCTURE

Having obtained a suitable form of the one-electron Schrodinger equation, the next step is to apply the same for a three dimensional periodic lattice and this constitutes the energy band structure. In other words, the band structure of an infinite crystal is the determination of the eigen values of the one electron Schrodinger equation

$$(-\nabla^2 + V(r)) \psi(k,r) = E_i(k) \psi(k,r)$$  \hspace{1cm} (1.4)

The Bloch sum of \( \psi(r) \) will represent the crystal wavefunction and with the use of the crystal wavefunction, one can obtain the one electron energies.
13. BAND STRUCTURE METHODS

The band structure methods may be classified according to whether they
seek the wavefunctions as an expansion in some set of fixed basis functions (fixed
basis method) or they expand the wavefunction in the set of energy and potential
dependent partial waves (partial wave method).

13.1 Methods using fixed basis-functions

In order to illustrate the fixed basis method, let us consider for example the
Linear Combination of Atomic Orbitals (LCAO) method. In this method, the
wavefunction is expressed as a linear combination of the eigen functions of the
bound states of a free atom $\chi_{ntm}(r)$ which is written as

$$\psi(k, r) = \sum_{R} \sum_{n\ell m} a_{\ell m}^{nt} \chi_{ntm}(r-R) \tag{1.5}$$

By standard variational techniques, one may obtain a set of equations in terms of
the Hamiltonian and overlap matrices as

$$(H - EO)\mathbf{a} = 0 \tag{1.6}$$

which may be solved to get the eigen values $E$ and the expansion coefficients $a$.
The difficulty in this method lies in the choice of a sufficiently small and accurate
basis set and the calculation of a large number of integrals involving potentials and
orbitals centred at two and three different sites.

13.2 Methods using Partial waves

We shall illustrate the partial wave method, by considering the example of
Cellular method of Wigner and Seitz. In this method the wavefunction is expressed as
\[ \psi(k,r) = \sum_{R} c^{*k}_{R} \sum_{\ell m} b^{*}_{\ell m} \theta(r-R) \psi_{\ell}(E, |r-R|) i^{\ell} Y_{\ell m}(r-R) \] (1.7)

where \( \theta \) is unity inside the atomic polyhedron and zero outside. The energy dependent radial part of the partial wave is obtained from numerical solutions of the radial Schrodinger equation. For a given Bloch vector \( k \), the one electron energies \( E_{i}(k) \) are those values of \( E \) for which a set of \( b \) coefficients can be found such that Equation (1.7) is continuous and differentiable across the boundary of the atomic polyhedron. But application of these boundary conditions in a rigorous sense is almost impossible and hence the cellular method is of little use.

The troublesome boundary conditions encountered in the cellular method were avoided in the Augmented Plane Wave (APW) method with the use of the muffin-tin approximation to the potential. In general, however, all the partial wave methods will lead to an equation of the form

\[ M(E).b = 0 \] (1.8)

In contrast to the matrix (1.6) the secular matrix \( M \) has a non-linear energy dependence and hence the one electron energies must be found by tracing the roots of the determinant of \( M \) as a function of \( E \), which requires enormous computational time.

1.3.3 The linear methods

The linear methods which are widely used presently for the band structure calculations employ energy independent basis orbitals. Hence they lead to secular equations linear in energy thereby reducing the computational time substantially. Of the linear methods, the computationally fastest one is the Linear Muffin Tin Orbital Method (LMTO) and it uses a minimal basis. We have used this method for all our calculations and hence we shall present a brief account of this method here.
1.4 THE LINEAR MUFFIN TIN ORBITAL METHOD

The Linear Muffin Tin Orbital method devised by Andersen (1975) is a computationally efficient band structure method. It uses a simple basis set in the form of muffin tin orbitals. It employs the concept of canonical bands and it is that which raises the LMTO method above the level of just being a new method of calculating the band structure. With the use of the canonical bands, the energy band problem may be separated into two parts, one which depends on the crystal structure and the other which depends on the crystal potential.

In the LMTO method, the basis orbitals are the so called muffin tin orbitals and they are constructed from partial waves and their first energy derivatives evaluated at the atomic sphere boundary. We shall therefore just consider the partial waves inside a single muffin-tin well.

1.4.1 Partial waves for a single Muffin-Tin

We shall consider a crystal with one atom per primitive cell and approximate the potential by the muffin-tin form which is expressed as

\[ V_{\text{MT}}(r) = \begin{cases} V(r) - V_{\text{MTZ}} & r \leq S_{\text{MT}} \\ 0 & r \geq S_{\text{MT}} \end{cases} \]  

(1.9)

where \( S_{\text{MT}} \) is the muffin-tin radius and the kinetic energy in the interstitial region is defined as (in atomic Rydberg units)

\[ k^2 = E - V_{\text{MTZ}} \]  

(1.10)

We now seek solutions of the Schrodinger's equation

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

(1.11)
for all the values of \( k^2 \) for an electron moving in the potential from an isolated muffin-tin well embedded in the flat potential \( V_{\text{MTZ}} \). The solution of Equation (1.11) will have the form

\[
\psi_t(E,k,r) = \begin{cases} 
\psi_t(E,r) & r \leq S_{\text{MT}} \\
k[n_t(kr) - \cot(\eta_t) j_t(kr)] & r \geq S_{\text{MT}} 
\end{cases} 
\]  

(1.12)

where \( j_t(kr) \) and \( n_t(kr) \) are the spherical Bessel and Neumann functions. When \( k^2 \) is negative, bound states may be formed and \( n_t \) should be replaced by \( \text{ih}_t \), where \( \text{ih}_t \) is the Hankel function of the first kind. The constant of integration \( \cot(\eta_t) \) is chosen in such a way that the partial wave is everywhere continuous and differentiable. This will lead to the form

\[
cot(\eta_t(E,k)) = \frac{n_t(kr) \quad D_t(E) - krn_t(kr)/n_t(kr)}{j_t(kr) \quad D_t(E) - krj_t(kr)/j_t(kr)} 
\]  

(1.13)

where the logarithmic derivative is defined as

\[
D_t(E) = \frac{S}{n_t} \frac{\partial \psi_t}{\partial r} 
\]  

(1.14)

It can be seen that, solution (1.12) is unbounded and is a delta function normalisable when \( k^2 \) is positive. When \( k^2 \) is negative, it can be normalised only at the eigen values of the single muffin-tin where the constant of integration is zero. For these reasons these partial waves are not well suited as basis functions.

1.4.2 Muffin-Tin Orbitals

In order to obtain suitable basis functions, Andersen (1975) introduced muffin-tin orbitals (MTO) that are reasonably localised, normalisable for all values
of $k^2$ and thus constitute an efficient basis set for first principle electronic structure calculation. The MTO is written as

$$\chi_L(E,k,r) = i^l Y_F(\hat{r}) $$

$$\psi_L(E, r) + k \cot(\eta_L) j_L(kr)$$

$$k n_L(kr)$$

$$r \geq S_{MT}$$

$$r \leq S_{MT}$$

(1.15)

The MTO defined in this fashion are not eigen functions of the muffin-tin potential $V_{MT}(r)$ except at bound states and resonances where the constant of integration is zero. However, the Bloch sum of $\chi_L(E,k,r)$ and $\psi_L(E,k,r)$ are identical because their difference is a Bloch sum of spherical Bessel function which is zero except for the free electron parabola $|K+G|^2 = k^2$.

Now the energy dependent MTO defined in Equation (1.15) may be used in conjunction with the tail cancellation theorem (according to which, inside the muffin-tin sphere at R, the tails coming from all other spheres must interfere destructively) to obtain the secular equation of the form (1.8).

However such a procedure is computationally inefficient and hence it is desirable to develop a method based on the variational principle and a fixed basis set to obtain the computationally efficient eigen value problem

$$|H - EO| \cdot a = 0$$

(1.16)

In order to obtain the fixed basis set, the MTO (1.15) will be made energy independent around an arbitrary energy $E_0$ and the energy independent MTO thus obtained will be used in the eigen value equation (1.16) and the energy dependence of the one, two and three centre integrals and overlap terms resulting from the eigen value equation will be parametrised. This procedure together with the use of atomic spheres instead of muffin-tin spheres will constitute the LMTO method in the atomic sphere approximation.
1.4.3 Energy independent Muffin-Tin Orbitals

The Muffin-tin orbital is now augmented and it will be shown that for a particular choice of the augmented spherical and Neumann functions $J_f(kr)$ and $N_f(kr)$, that the augmented MT orbital

$$\chi_L(E,k,r) = i^L Y_L^m(\mathbf{r}) + \frac{k}{r} \cot(\eta_f(kr)) J_f(kr)$$

may be made energy independent around a fixed energy $E_n$ to first order in $(E-E_n)$. The definition of the augmented spherical Bessel $J_f$ and Neumann $N_f$ functions may be obtained from the condition that the energy derivative of the MTO

$$\chi_L(E,k,r) = \psi_L(E,r) + k \cot(\eta_f(E)) J_f(kr)$$

is zero at $E = E_n$. This leads to the following definition of the augmented spherical Bessel function.

$$J_f(kr) = \begin{cases} \frac{-\psi_f(E_n,r)}{k \cot(\eta_f(E_n))} & r \leq S_{MT} \\ \eta_f(kr) & r \geq S_{MT} \end{cases}$$

As the original Bessel and Neumann functions obey the expansion theorem, it is natural to expect the functions $J_f$ and $N_f$ will also to satisfy the expansion theorem. This leads to the definition of $N_f$ as

$$N_f(k,r-R) = \sum_{L'} \sum_{L''} 4\pi \sum \left( C_{L'L''} J_f(k,r-R') n_{L'} n_{L''} \right)$$

otherwise

$$n_f(k,r-R)$$

$$\left| r-R' \right| \leq S_{MT} \quad \forall R' \neq R$$

$$\left| r-R' \right| > S_{MT}$$

(1.20)
The Bessel function and Neumann functions defined in this fashion has several desirable properties. \( J_l \) is energy independent and everywhere continuous and differentiable. It is orthogonal to the core states of its own muffin-tin well. The function \( N_l \) is orthogonal to the core states of all the muffin-tin wells except at \( R \).

In order to obtain a suitable form of the energy independent muffin-tin orbital and \( J_l \) which will be appropriate for use in the variational procedure, we shall consider a normalised partial wave \( \phi_l \) and a trial function \( \Phi_2 \) inside a sphere of radius \( S \). The normalised partial wave is defined as

\[
\phi_l(E,r) = \sqrt{\psi_l^2(E,r)} \psi_l(E,r)
\] (1.21)

In the LMTO method, attention is focussed on the energy range centred around \( E_0 \); hence for each value of \( l \) we choose an \( E_0 \) and use the energy independent basis set formed by the normalised radial function

\[
\psi_{vl}(r) = \phi_l(E_0,r)
\] (1.22)

its energy derivative

\[
\dot{\phi}_{vl}(r) = \left. \frac{\partial \phi_l(E,r)}{\partial E} \right|_{E_0}
\] (1.23)

The corresponding logarithmic derivatives at the sphere boundary are

\[
D_{vl} = S\dot{\phi}_{vl}(S) / \psi_{vl}(S) = S\dot{\psi}_{vl}(S) / \psi_{vl}(S)
\] (1.24)

\[
\dot{D}_{vl} = S\ddot{\phi}_{vl}(S) / \psi_{vl}(S)
\] (1.25)

The radial trial function of arbitrary logarithmic derivative \( D \) at the sphere boundary is defined by
\[ \Phi(D,r) = \phi_a(r) + \omega(D) \dot{\phi}_n(r) \]  
\hspace{1cm} (1.26)

where \( \omega(D) = - \frac{\phi_v}{\phi_n} \frac{D - D_v}{D - \bar{D}_v} \)  
\hspace{1cm} (1.27)

Using the Equations (1.21), (1.22) and (1.26) the energy derivative \( \psi(E_v, r) \) may be written as

\[ \psi(E_v, r) = <\psi, \hat{\tau}(E_v)>^n \Phi(D(j_s), r) \]  
\hspace{1cm} (1.28)

Finally, the results obtained in this section with the algebraic manipulations will lead to the form of the energy independent MTO as

\[ \chi_t(k, r) = i^t Y(t) \begin{bmatrix} \frac{k n_t(k S)}{\Phi_t(D(n_t), S)} & \Phi_t(D(n_t), r) \quad r \leq S_{MT} \\ k n_t(k r) & r \geq S_{MT} \end{bmatrix} \]  
\hspace{1cm} (1.29)

and the augmented Bessel function as

\[ J_t(k r) = \begin{bmatrix} J_t(k S) & \Phi_t(D(j_t), r) \quad r \leq S_{MT} \\ \Phi_t(D(j_t), S) & r \geq S_{MT} \\ j_t(k r) \end{bmatrix} \]  
\hspace{1cm} (1.30)

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.

1.4.4 One centre expansion and structure constants

The wavefunction for the muffin tin potential \( V_{MT}(r-R) \) centred at site \( R \) of a three dimensional periodic lattice may be written as
\[ \psi(E,r) = \sum_L \alpha_L \chi_L(E,k,r) \]  
(1.31)

where \[ \chi_L(E,k,r) = \sum_R e^{i R} \chi_L(E,k,r-R) \]  
(1.32)

The above multicentre expansion may be rewritten as

\[ \chi_L(E,k,r) = \chi_L(E,k,r) + \sum_{R \neq 0} e^{i R} \chi_L(E,k,r-R) \]  
(1.33)

Recalling that the last term in this Equation (1.33) is the sum of tails coming from all the muffin tin orbitals centred at all sites except at \( R=0 \), the sum may be replaced by

\[ \sum_{R \neq 0} e^{i R} \chi_L(E,k,r-R) = \sum_{R \neq 0} e^{i R} kN_L(k,r-R) \]  
(1.34)

\[ = \sum_L J_L(k,r) B_{LL}^{k}(k) \]  
(1.35)

where \( B_{LL}^{k}(k) \) are the KKR structure constants and are given as

\[ B_{LL}^{k}(k) = 4\pi \sum_{L''} C_{LL'} \sum_{R \neq 0} e^{i R} kN_L^{*}(k,R) \]  
(1.36)

1.4.5 The LCMTO secular matrix

Using the Rayleigh-Ritz variational principle, the secular matrix may be obtained. According to Rayleigh-Ritz variational principle

\[ \delta \langle \psi | H-E | \psi \rangle = 0 \]  
(1.37)

at a solution. The above equation will have solutions whenever
\[
\det\{<\chi_L^\uparrow | H-E | \chi_L^\uparrow>\} = 0 \quad (1.38)
\]

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

\[
N^L<\chi_L^\uparrow | H-E | \chi_L^\uparrow> = \langle \chi_L^\uparrow | H-E | \chi_L^\uparrow> \quad (1.39)
\]

may be obtained, where the integral extends only over the polyhedron at the origin.

The LCMTO secular matrix can be obtained by inserting the one centre expansion (1.33) into the matrix (1.39). We find

\[
<\chi_L^\uparrow | H-E | \chi_L^\uparrow> = <\chi_L^\uparrow | H-E | \chi_L^\uparrow>

+ \sum_L \sum_{L''} B_{LL''}^{\uparrow \uparrow} <J_L | H-E | J_L^\uparrow> \delta_{L''L'}

+ \sum_{L''} <J_L^\uparrow | H-E | J_L^\uparrow> B_{LL''}^{\uparrow \uparrow} \quad (1.40)
\]

The cellular potential used here is spherically symmetric and therefore the cellular integrals in (1.40) becomes diagonal in L and thus

\[
<\chi_L^\uparrow | H-E | \chi_L^\uparrow> = <\chi_L^\uparrow | H-E | \chi_L^\uparrow> \quad (1.41)
\]

The secular matrix then reduces to

\[
<\chi_L^\uparrow | H-E | \chi_L^\uparrow> = <\chi_L^\uparrow | H-E | \chi_L^\uparrow> \delta_{LL'}

+ \{<\chi_L^\uparrow | H-E | J_L^\uparrow> + <J_L^\uparrow | H-E | \chi_L^\uparrow>\} B_{LL'}

+ \sum_{L''} B_{LL''}^{\uparrow \uparrow} <J_L^\uparrow | H-E | J_L^\uparrow> \quad (1.42)
\]
In order to turn this LCMTO equations, into an efficient calculational technique which we shall refer to as the LMTO equations, we shall use the Atomic Spheres instead of the Muffin Tin spheres and parametrise the energy dependence of the one, two and three centre overlap integrals so that it can be transformed in the form of a generalised eigen value problem. In order to see the parametrisation of the energy dependence of the above said integrals, we shall again consider the trial function $\Phi(D,r)$ appearing in Equation (1.26) and find the parametrisation of the function $E_f(D)$ valid around $E_{\nu_f}$.

### 1.4.6 Matrix elements and parameterisation of $E_f(D)$

The trial function having the arbitrary logarithmic derivative $D$ is represented as (along with its angular part)

$$\Phi_{lm}(D, r) = i^l Y^l(r) \Phi_f(D, r)$$

within the basis of this function, the matrix elements of the Hamiltonian in the sphere can be written as

$$<\Phi_{lm}(D') | H - E_{\nu_f} | \Phi_{lm}(D)> = \omega_f(D) \delta_{l'm'}$$

Similarly the overlap matrix elements become

$$<\Phi_{lm}(D') | \Phi_{lm}(D)> = [1 + \omega_f(D') \omega_f(D) \langle \phi_{l'}^2 \rangle] \delta_{l'l} \delta_{m'm}$$

With the above matrix elements, the variational estimate of $E_f(D)$ may be obtained as

$$E_f(D) = E_{\nu_f} + <\Phi_{lm}(D) | H - E_{\nu_f} | \Phi_{lm}(D)> / <\Phi_{lm}^2(D)>$$

$$= E_{\nu_f} + \frac{\omega_f(D)}{[1 + \langle \phi_{l'}^2 \rangle \omega_f(D)]} + o(\epsilon^3)$$

(1.46)
Using these results, the parametrisation of the energy dependence of the integrals in the LCMTO equations can be done which in turn will lead to the LMTO equations.

1.4.7 The LMTO secular matrix and the potential parameters

It may be noted that the LCMTO Equations (1.42) involve seven different integrals and they are respectively

\[
\begin{align*}
\langle \chi_t | H-E_{e-i} | \chi_t \rangle, & \quad \langle \chi_r | H-E_{e-r} | j_r \rangle \\
\langle j_l | H-E_{e-i} | \chi_i \rangle, & \quad \langle j_r | H-E_{e-r} | j_r \rangle \\
\langle \chi_t | \chi_t \rangle, & \quad \langle \chi_r | j_r \rangle \\
\langle j_r | j_r \rangle
\end{align*}
\] (1.47)

These integrals can now be parametrised in terms of the results discussed in the previous section and the secular matrix can be written in the form of a generalised eigen value problem

\[
\Sigma \left( H_{\text{L}} \alpha E^0 \alpha^\dagger \right) = 0
\] (1.48)

where the Hamiltonian matrix is given by

\[
H_{\text{L}} = \begin{bmatrix}
\omega(n) + E_e (1 + \omega^2(n) < \phi^3 >) \\
(S/2) \Phi^2(n)
\end{bmatrix}
\]

\[
+ \begin{bmatrix}
\omega(j) + E_e (1 + \omega(j)\omega(n) < \phi^3 >) \\
\omega(j) - \omega(n)
\end{bmatrix}
\]

\[
\delta_{i,L} + \left[ \right]_{L} \cdot 1
\]

\[
S_{L, k}(k)
\]
while the overlap matrix is

\[ O_{\ell \ell'} = \begin{pmatrix}
1 + \omega'(n)\phi^2
\end{pmatrix}
\]

\[ \frac{1}{(S/2) \Phi^2(n)} \]

\[ + \begin{pmatrix}
1 + \omega'(j)\omega(n)\phi^2
\end{pmatrix}
\]

\[ \frac{1}{\omega(j) - \omega(n)} \]

\[ + \begin{pmatrix}
\delta_{\ell \ell'}
\end{pmatrix}
\]

\[ \frac{1 + w'(j)w(n)\phi^2}{r} \]

\[ \begin{pmatrix}
S_{\ell}(k)
\end{pmatrix} \]

\[ \frac{1 + w'(j)w(n)\phi^2}{r} \]

\[ \begin{pmatrix}
S_{\ell}(k)
\end{pmatrix} \]

\[ \frac{2(D(j) - D(n))^2 S\phi^2(j)}{r} \]

\[ \begin{pmatrix}
S_{\ell}(k)
\end{pmatrix} \]

where the renormalised structure constants matrix is given by

\[ S_{\ell}(k) = \frac{B_{\ell}(k)}{S_{\ell}(k)\kappa(k)/2} \]

In the ASA, we use the approximation \( k^2 = 0 \) and in this approximation, the logarithmic derivatives of the Bessel and Neumann functions become \( \ell \) and \(-\ell-1\) respectively.

Now it is seen that the parametrisation of the energy dependence has been done with the use of the parameters

\[ \omega(-) = \omega(-\ell-1) \]

\[ S\Phi^2(-) = S\Phi^2(-\ell-1) \]
\( \Phi(-)/\Phi(+)=\Phi(-\ell-1)/\Phi(\ell) \)

\( \langle \phi^2 \rangle \)

and hence they are referred to as the standard potential parameters. The + and - signs indicate the boundary conditions \( D=\ell \) and \( D=-\ell -1 \) respectively.

Having obtained a parametrised form of the Hamiltonian and overlap matrices, the generalized eigen value problem can now be solved to get the eigen values \( E^\pm \) and the eigen vectors \( \alpha^\pm \).

The above band structure method is being employed to obtain the electronic energy bands of some of the Laves phase compounds and also for the case of tellurium at high pressure. However, APW method was used for yttrium at high pressure. The band structure results were used to study their superconducting behaviour in addition to the calculation of other electronic properties such as the electronic specific heat coefficient and Pauli paramagnetic susceptibility.