CHAPTER 1

INTRODUCTION

1.1 THE ONE ELECTRON APPROXIMATION

Most of the physical and chemical properties of condensed matter systems are governed by the conduction electrons. One is often interested in finding the eigenstates of these electrons as most of the properties can be understood through them. Electrons are lighter than the nuclei and hence respond much faster. Therefore, for any instantaneous position of the nuclei, the electrons can be considered to be in stationary states. The dynamics of electrons and nuclei can thus be treated independently. This is the Born-Oppenheimer approximation.

Now the problem at hand is the evaluation of the eigenstates of an N-electron system. The Schrodinger equation of an N-electron system is written as

\[ \sum_{i=1}^{N} \left( -\frac{\hbar^2}{2m} \nabla_i^2 + V \right) \psi_i = E \psi_i \]  

(1.1)

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 one electron approximation. The density functional formalism of Kohn and Sham in the local density approximation is an important scheme for obtaining a one electron Schrodinger-like equation. The one electron Schrodinger equation (in atomic units) that results from the formalism is written as
Here $V$ 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 and correlation contribution.

### 1.2 DENSITY FUNCTIONAL FORMALISM

The density functional formalism is due to Hohenberg, Kohn and Sham [1,2] who considered the Hamiltonian of a system of $M$ interacting fermions moving in some fixed external potential $V_{\text{ext}}$ as

$$H = T + U + V$$

Here $T$ is the kinetic energy and $U$ is the electron-electron Coulomb repulsion and $V$ is the interaction with the external potential which includes the interaction with the fixed nuclei. Hohenberg and Kohn showed that the external potential is a unique functional of the electron density $n(r)$ and hence the ground state and the energy functionals are unique functionals of $n(r)$. Further they separated $F[n]$ as

$$F[n] = \frac{1}{2} \int \frac{2n(r)n(r')}{|r - r'|} dr \, dr' + G[n]$$


$$(-\nabla^2 + V)\psi_1 = E_1\psi_1 \quad (1.2)$$

Here $V$ 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 and correlation contribution.

$$F[n] = \langle \phi | H | \phi \rangle = F[n] + \int V_{\text{ext}}(r)n(r)dr \quad (1.4)$$

$$F[n] = \langle \phi | T + U | \phi \rangle \quad (1.5)$$

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where $T_g$ is the kinetic energy of the non-interacting electrons given as

$$ \langle \Phi_s | T | \Phi_s \rangle = \sum_{jk} \int \psi_j^*(k,r) \left( -\nabla^2 \right) \psi_j(k,r) \ dr \quad (1.8) $$

Here $k$ is the Bloch wave vector and $E_{xc}$ is the exchange correlation energy functional which is approximated as

$$ E_{xc}[n] = \int_{\mathbb{R}^3} n(r) \ dr \quad (1.9) $$

This constitutes the famous local density approximation. The exchange correlation energy density $e_{xc}$ is obtained from a homogeneous electron gas of density $n(r)$.

The energy functional $\langle \Phi | H | \Phi \rangle$ can then be written as

$$ \langle \Phi | H | \Phi \rangle = \langle \Phi_s | T | \Phi_s \rangle + \int \left[ \frac{1}{2} \left( \int \frac{2n(r')}{|r-r'|} \ dr' + V_{ext}(r) + V_{xc}(n(r)) \right) n(r) dr \right] \quad (1.10) $$

A minimisation with respect to the density $n(r)$ leads to the effective single particle Schrodinger equation

$$ \left\{ -\nabla^2 + \int \frac{2n(r')}{|r-r'|} \ dr' + V_{ext}(r) + V_{xc}(n(r)) \right\} \psi_j(k,r) = E_j(k) \psi_j(k,r) \quad (1.11) $$

Where $n(r)$ is made to satisfy the requirement that

$$ n(r) = \sum_{jk} |\psi_j(k,r)|^2 \quad (1.12) $$

Thus it has been shown that the density functional formalism leads to an effective one electron Schrodinger equation.
1.3 THE ENERGY BAND STRUCTURE

The energy band structure calculation of an infinite crystal is the determination of the eigen values of the one electron Schrodinger equation

\[ (-\nabla^2 + V(r)) \psi(k,r) = E_j(k) \psi(k,r) \quad (1.13) \]

The Bloch sum of \( \psi(r) \) will represent the crystal wavefunction and with the use of the crystal wavefunction, one may obtain the one electron energies.

1.4 BAND STRUCTURE METHODS

The traditional band structure methods may be classified into two groups as the fixed basis methods and the partial wave methods.

1.4.1 Fixed basis method

In the fixed basis methods, for example in the Linear Combination of Atomic Orbitals (LCAO) method, the wavefunction is expressed as a linear combination of the eigen functions of the bound states of a free atom \( \chi_{n\ell m}(r) \). The wave function is written as

\[ \psi_j(k,r) = \sum_R e^{ik \cdot R} \sum_{n\ell m} a_{n\ell m} \chi_{n\ell m}(r-R) \quad (1.14) \]

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

\[ (H - E_0) \cdot a = 0 \quad (1.15) \]

which may be solved to get the eigen values \( E \) and the expansion coefficients \( a \). Difficulties in this method lie 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.

1.4.2 Partial wave method

In the partial wave approach, for example in the Cellular method of Wigner and Seitz, the wavefunction is expressed as the Bloch sum

$$\psi_i(k, r) = \sum_R e^{ik \cdot R} \sum_{\ell m} b_{\ell m} \Theta(r-R) \psi_{\ell}(E, |r-R|) Y_{\ell m}^*(r-R)$$

(1.16)

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 $E_j(k)$ are those values of $E$ for which a set of $b$ coefficients can be found such that equation (1.16) is continuous and differentiable across the boundary of the atomic polyhedron. But application of these boundary conditions rigorously 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

$$M(E) \cdot b = 0$$

(1.17)

In contrast to the matrix (1.15) 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.

1.5 THE LINEAR METHODS

The linear methods devised by Andersen [3] employ fixed basis functions constructed from the partial waves and their first energy derivatives obtained within the muffin-tin approximation to the potential. Therefore these methods lead to secular equations linear in energy thereby reducing the computational time substantially.

In the Linear Muffin Tin Orbital method [3, 4, 5, 6,], the basis functions are muffin-tin orbitals that are constructed from the partial waves and their first energy derivatives at a fixed energy $E_y$. When the Bloch sum of a linear combination of muffin-tin orbitals is used in a variational procedure, the LMTO secular matrix is obtained. The required eigenvalues can then be obtained from the LMTO secular matrix by a single diagonalisation.

1.6 THE PRESENT WORK

Nowadays the linear methods are widely used in band structure calculations as they are computationally more efficient than the other methods. In particular the LMTO method which uses a minimal basis set is computationally the most efficient method among all the linear methods. Hence for the present work, we have used the LMTO method to calculate the band structures.

In the present work we have done the electronic structure calculations of some of the perovskite oxides of the type $AMO_3$ and chalcogenides of the form $MX$, $MX_2$ and $AX_4$ ($A=$ Sr, La; $M =$ 3d metal and $X =$ S, Se and Te). Using the
results of the calculations some of their properties such as the magnetic properties, superconducting properties etc. were studied. In some of the systems that are magnetic insulators, the one electron picture could not reproduce the semiconducting gap observed in them. The results of our calculations are described in the following chapters along with a brief account of the LMTO method.