CHAPTER 4

Band structure calculations using

FP-LAPW method
The band theory of solids has emerged from the self-consistent field approximation and has proved to be immensely successful, especially in the physics of metals and semiconductors. Several methods have been developed for calculating the band structures of solids\textsuperscript{70,71,72}. The tight binding approximation\textsuperscript{72} deals with the case in which the overlap of atomic wave functions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant. This approximation is most useful for describing the energy bands that arise from the partially filled $d$-shells of transition metal atoms and for describing the electronic structure of insulators. For computing the bands in a muffintin potential two methods namely augmented plane-wave (APW)\textsuperscript{73,74} and Korringa, Kohn and Rostoker (KKR)\textsuperscript{37,38} are widely used. In the APW method, the wavefunction $\psi_k(r)$ is represented as a superposition of a finite number of plane waves in the flat interstitial region, while forcing it to have a more rapid oscillatory atomic behaviour in the core region. This is achieved by expanding the wavefunction in a set of augmented plane waves. In KKR method, Green function’s method is employed. The approximation of the KKR method is to assume that the wavefunction $\psi_k(r)$ will be given to a reasonable degree of accuracy by keeping only a finite number of spherical harmonics. Another method for band structure calculation is the pseudopotential method\textsuperscript{75,76,77}. In this method, the pseudopotential is defined to be the sum of the actual periodic potential $U$ and an operator given by $V^R$. This addition leads to a potential weak enough to do nearly free electron calculations for the so-called pseudo wave function $\phi^*_k$, treating the pseudopotential as a weak perturbation.
The problem with the APW method was that the solutions of the radial part of
the wavefunction $u_1^\alpha$ have to be constructed at the yet unknown eigen energy of the
searched eigenstate. This problem is solved in Linearized Augmented Plane Wave
(LAPW) method\textsuperscript{78,79,80}. In LAPW method, a linearization of the energy dependence is
used by solving the radial Schrödinger equation for fixed linearization energy but
adding an energy derivative of this function. In the full-potential linearized augmented
plane wave (FP-LAPW) method\textsuperscript{81}, both the potential and charge density are expanded
into lattice harmonics and as a Fourier series thereby completing their form. By using
this method, a standard Computer code based on FORTRAN programme called
WIEN2k Code\textsuperscript{82} have been developed by Madsen et al.\textsuperscript{46,47} which is used worldwide.
For our band structure calculations, we are also using the FP-LAPW method
employing the WIEN2k code. In the following we will give the basic theory involved
in FP-LAPW which will be followed by the results and discussions. We have
calculated band structures from Lead salts namely PbS, PbSe and PbTe and also from
metal W.

4.1 Basic Theory of FP-LAPW method:

a) Density functional theory:

The well-established scheme to calculate electronic properties of solids is based
on density functional theory (DFT)\textsuperscript{83,84}. DFT is a universal approach to the quantum
mechanical many-body problem, where the system of interacting electrons is mapped
in a unique manner onto an effective non-interacting system with the same total
density. Hohenberg and Kohn\textsuperscript{45} formulated two theorems which are as follows:

1) There is a one-to-one correspondence between the ground-state density $\rho(\vec{r})$
of a many electron system and the external potential $V_{\text{ext}}$. The immediate
consequence is that the ground state expectation value of any observable $\hat{O}$ is
a unique functional of the exact ground state electron density.

\[ \langle \Psi | \hat{O} | \Psi \rangle = \mathcal{O}[\rho] \quad (4.1) \]

2) For the Hamiltonian $\hat{H}$, the ground state total energy functional
$H[\rho] = E_{\text{v_{ext}}}[\rho]$ is of the form

\[ E_{\text{v_{ext}}}[\rho] = \langle \Psi | \hat{\Pi} + \hat{V} | \Psi \rangle + \langle \Psi | V_{\text{ext}} | \Psi \rangle = F_{\text{HK}}[\rho] + \int \rho(\vec{r})V_{\text{ext}}(\vec{r})d\vec{r} \quad (4.2) \]

where $F_{\text{HK}}[\rho]$ is the Hohenberg-Kohn density functional which is universal
for any many-electron system. $E_{\text{v_{ext}}}[\rho]$ reaches its minimum value for the
ground-state density corresponding to $V_{\text{ext}}$.

b) Kohn-Sham equation:

The equation of Kohn and Sham are a practical procedure to obtain the ground
state density and turn density functional theory into a method of finding energy
bands\textsuperscript{85}. The Hohenberg-Kohn density functional $F_{\text{HK}}[\rho]$ can be written as

\[ F_{\text{HK}}[\rho] = T + V = T_0 + V_{\text{H}} + V_{\text{xc}} \quad (4.3) \]
where $V_{xc} = V_x + V_c$ is the exchange-correlation energy functional, $T_0$ is the functional for the kinetic energy of a non-interacting electron gas, $V_H$ is the Hartree contribution, $V_x$ is the exchange contribution and $V_c$ is the functional for the correlation contribution which is given by $V_c = T - T_0$.

Hence, the energy functional of a non-interacting classical electron gas can be written as

$$E_{v_{\text{ext}}} [\rho] = T_0 [\rho] + V_H [\rho] + V_{xc} + V_{\text{ext}} [\rho] \tag{4.4}$$

This equation shows that the energy $E_{v_{\text{ext}}} [\rho]$ is subjected to two external potentials namely one due to the nuclei and the other due to exchange and correlation effects.

Now, the corresponding Kohn-Sham Hamiltonian is

$$\hat{H}_{\text{KS}} = \hat{T}_0 + \hat{V}_H + \hat{V}_x + \hat{V}_{\text{ext}}$$

$$= -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(r')}{|r-r'|} d\mathbf{r}' + V_{xc} + V_{\text{ext}} \tag{4.5}$$

Therefore, the Kohn-Sham equation is finally given by

$$\hat{H}_{\text{KS}} \phi_i = \varepsilon_i \phi_i$$

$$\left[ -\frac{\hbar^2}{2m_e} \nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0} \int \frac{\rho(r')}{|r-r'|} d\mathbf{r}' + V_{xc} + V_{\text{ext}} \right] \phi_i(\mathbf{r}) = \varepsilon_i \phi_i(\mathbf{r}) \tag{4.6}$$

and the exact ground-state density $\rho(\mathbf{r})$ of an N-electron system is given by

$$\rho(\mathbf{r}) = \sum_{i=1}^{N} [\phi_i(\mathbf{r})]^2 \tag{4.7}$$
The exact functional form of the exchange-correlation functional $V_{xc}$ is not known and thus one needs to make approximations. One of the approximations used is the Local Density Approximation (LDA). This approximation postulates that the exchange-correlation functional has the form

$$E_{xc} = \int \rho(\vec{r}) E_{xc}(\rho(\vec{r})) d\vec{r}$$

(4.8)

In this approximation, the exchange-correlation energy due to a particular density $\rho(\vec{r})$ could be found by dividing the material in infinitesimally small volumes with a constant density. Each such volume contributes to the total exchange correlation energy by an amount equal to the exchange correlation energy of an identical volume filled with a homogeneous electron gas that has the same overall density as the original material has in this volume. To improve the LDA, Generalized Gradient Approximation (GGA) had been developed by Perdew et al. In this approximation, the exchange-correlation contribution of every infinitesimal volume is not only dependent on the local density in that volume, but also on the density in the neighbouring volumes. That is, the gradient of the density is also involved.

To solve the Kohn-Sham equation, we have to find the coefficients needed to express the wavefunction $\phi_m$ in a given basis set $\phi_p^b$,

$$\phi_m = \sum_{p=1}^{P} c_p^m \phi_p^b$$

(4.9)

In our calculations, Eq. (4.9) will be solved by using FP-LAPW which is given below in brief.
c) Full-Potential Linearized Augmented Plane Wave Method (FP-LAPW):

One of the most accurate schemes for solving the Kohn Sham equation given in Eq. (4.6) is the full-potential linearized augmented-plane-wave (FP-LAPW). It is based on the density functional theory for the treatment of exchange and correlation. In LAPW method, a basis set is introduced which is especially adapted to the problem. This adaptation is achieved by dividing the unit cell into two regions, namely (i) non-overlapping atomic spheres (centered at the atomic sites) and (ii) an interstitial region (region II) as shown in Fig. (4.1). For the construction of basis functions, the muffin tin approximation (MTA) is used according to which the potential is assumed to be spherically symmetric within the atomic spheres in which an atomic-like function is used and constant outside in which plane waves are used.

The basis functions for the two regions are:

1) Inside atomic sphere I, of radius $R$, a linear combination of radial functions times spherical harmonics $Y_{lm}(r)$ is used

$$\phi_{kn} = \sum \left[ A_{lm,kn} u_l(r, E_l) + B_{lm,kn} \dot{u}_l(r, E_l) \right] Y_{lm}(r) \quad (4.10)$$

where $u_l(r, E_l)$ is the regular solution of the radial Schroedinger equation for energy $E_l$ and the spherical part of the potential inside sphere I; $\dot{u}_l(r, E_l)$ is the energy derivative of $u_l$ evaluated at the same energy $E_l$. A linear combination of these two functions constitutes the linearization of the radial function. The coefficients $A_{lm}$
Figure (4.1): Partitioning of the unit cell into atomic spheres (I) and an interstitial region (II)
and $B_{lm}$ are functions of $k_n$ determined by requiring that this basis function matches each plane wave (PW) the corresponding basis function of the interstitial region. $u_l$ and $\hat{u}_l$ are obtained by numerical integration of the radial Schrödinger equation on a radial mesh inside the sphere.

(2) In the interstitial region a plane wave expansion is used

$$\phi_{k_n} = \frac{1}{\sqrt{\omega}} e^{i \vec{k}_n \cdot \vec{r}}$$  \hspace{1cm} (4.11)

where $\vec{k}_n = \vec{k} + \vec{K}_n$; $\vec{K}_n$ are the reciprocal lattice vectors and $\vec{k}$ is the wave vector inside the first Brillouin zone. Each plane wave is augmented by an atomic-like function in every atomic sphere.

The solutions to the Kohn-Sham equations are expanded in this combined basis set of LAPW’s according to the linear variation method

$$\psi_k = \sum_n c_n \phi_{k_n}$$  \hspace{1cm} (4.12)

and the coefficients $c_n$ are determined by the Rayleigh-Ritz variational principle.

In order to improve upon the linearization and to make possible a consistent treatment of semicore and valence states in one energy window, adding additional basis functions called ‘local orbitals (LO)’ was suggested by Singh. Local orbitals consists of a linear combination of 2 radial functions at 2 different energies and one energy derivative and is given as

$$\phi^{LO}_{lm} = \left[ A_{lm} u_l(\vec{r}, E_{1,l}) + B_{lm} \hat{u}_l(\vec{r}, E_{1,l}) + C_{lm} u_l(\vec{r}, E_{1,l}) \right] Y_{lm}(\vec{r})$$  \hspace{1cm} (4.13)
In its general form, the FP-LAPW method expands both the potential and the charge density into the lattice harmonics inside each atomic sphere and as a Fourier series in the interstitial region. Thus we have

\[
V(r) = \begin{cases} 
\sum_{LM} V_{LM}(\vec{r})Y_{LM}(\vec{r}) & \text{inside sphere} \\
\sum_{K} V_{\epsilon} e^{i\vec{K} \cdot \vec{r}} & \text{outside sphere}
\end{cases}
\]  

(4.14)

Thus their form is completely general so that such a scheme is termed full-potential calculation. In order to have a small number of LM values in the lattice harmonics expansion a local coordinate system for each atomic sphere is defined according to the point group symmetry of the corresponding atom. This specifies a rotation matrix that relates the local to the global coordinate system of the unit cell.

### 4.2 Results and discussions of band structure calculations:

We have calculated band structures by using FP-LAPW method. FORTRAN programs were written to do band structure and other calculations employing FP-LAPW method and the code so developed is known widely as WIEN2k code. Theoretical values of lattice constant ‘a’ is calculated which is used to obtain the band structures. Band structures are calculated from semiconductors PbS, PbSe and PbTe generally known as lead salts and also from metal W. In our calculation we have used GGA approximation for the exchange-correlation relation.
**Lead Salts:**

The lead salts $\text{PbS}$, $\text{PbSe}$ and $\text{PbTe}$ are IV-VI semiconductors and they exhibit unusual properties. Due to their unusual properties and uses in technology, they have been a subject of intense study for the past few decades. The lead salts are used in infrared detectors, light emitting devices, solar energy panels, thermo electric materials etc. All the three lead salts crystallize in the rock-salt crystal structure. The fundamental space lattice is face-centered cubic. The first Brillouin zone of fcc crystal structure in $k$-space showing the high symmetry points is shown in Fig. (4.2). The experimental values$^{88}$ of the lattice constants $'a'$ of the lead salts at 300K temperature are: for $\text{PbS}$, $a = 5.9362 \text{ Å}$; for $\text{PbSe}$, $a = 6.1243 \text{ Å}$; for $\text{PbTe}$, $a = 6.4603 \text{ Å}$. Using FP-LAPW method, we have calculated volume optimization by using Murnaghan's plot where energy is plotted against volume of the primitive cell. These plots for $\text{PbS}$, $\text{PbSe}$ and $\text{PbTe}$ are given in Figs. (4.3), (4.4) and (4.5) respectively. Then by choosing the volume corresponding to the lowest value of the energy, the lattice constant is obtained. The lattice constants obtained are as follows, for $\text{PbS}$, $a = 5.973 \text{ Å}$; for $\text{PbSe}$, $a = 6.186 \text{ Å}$; for $\text{PbTe}$, $a = 6.50 \text{ Å}$. These theoretical values of the lattice constants obtained are then used in the band structure calculations.

The band structures of $\text{PbS}$, $\text{PbSe}$ and $\text{PbTe}$ along the high symmetry points in the Brillouin zone are shown in Figs. (4.6), (4.7) and (4.8). All the figures show the valence band maximum and the conduction band minimum at the $L$ symmetry point in the Brillouin zone. Hence, the energy gap is found to be a direct gap at the $L$ symmetry point $L_6$. - $L_6$. This common feature of the band structure of lead salts is also observed by others using different methods of theoretical calculations like
Figure (4.2): First Brillouin zone of the face-centered cubic lattice showing symmetry points.
Figure (4.3): Plot of the variation of total energy with respect to the volume for the case of PbS. Theoretical value of lattice constant obtained from the graph is $a = 5.973$ Å.
Figure (4.4): Plot of the variation of total energy with respect to the volume for the case of PbSe. Theoretical value of lattice constant obtained from the graph is $a = 6.186 \ \text{Å}$.
Figure (4.5): Plot of the variation of total energy with respect to the volume for the case of PbTe. Theoretical value of lattice constant obtained from the graph is \( a = 6.50 \, \text{Å} \).
empirical pseudopotential method\textsuperscript{89}, orthogonalized plane wave method\textsuperscript{90}, augmented plane wave method\textsuperscript{91}, linear combination of atomic orbitals\textsuperscript{92}, tight binding method\textsuperscript{93}, and full-potential linear muffin-tin orbital method\textsuperscript{94} as well as from experimental observations\textsuperscript{95,96}. From the figures, the lowest energy bands below the Fermi level at around 10 -12 eV are due to the contribution from the chalcogens that is, S, Se and Te 's' states. The band structures at around 8 eV below the Fermi level are due to the electrons from Pb 6s states and also from chalcogenide s and p states. The energy bands between the Fermi level and 5 eV below the Fermi level consists mostly of chalcogen p states but also to some extend of Pb 6s and 6p states. Just below the Fermi level, the bands are dominated by chalcogen p states, with some contribution coming from the Pb 6p states. Just above the Fermi level, the Pb 6p states dominate. In total, the band structures above the Fermi level are due to the contributions from Pb 6p and 6d states and chalcogen p and s states in about equal amounts.

Our band structure calculations showed that the energy gaps $E_0$ at L symmetry point in the Brillouin zone for the lead salts are found to be: for PbS, $E_0 = 0.4$ eV; for PbSe, $E_0 = 0.3$ eV; for PbTe, $E_0 = 0.5$ eV. The experimental values\textsuperscript{97} of the energy gaps at 376 K temperature are: for PbS, $E_0 = 0.44$ eV; for PbSe, $E_0 = 0.31$ eV; for PbTe, $E_0 = 0.34$ eV. A very interesting observation here is that instead of the usual monotonic decrease of $E_0$ with increase in Z, it is seen that the energy gap for PbTe is larger than that for PbSe. The existence of this anomaly has been noted for many years. It has been proposed\textsuperscript{98} that PbTe is the irregular member of the sequence and that the anomalously large energy gap of PbTe reflects an irregular value of the 5s electron energy of the tellurium atom.
Figure (4.6): Band structure of PbS along symmetry points in the Brillouin zone where lattice constant $a = 5.973 \, \text{Å}$.
Figure (4.7): Band structure of PbSe along symmetry points in the Brillouin zone where lattice constant $a = 6.186 \text{Å}$. 
Figure (4.8): Band structure of PbTe along symmetry points in the Brillouin zone where lattice constant $a = 6.50 \text{ Å}$. 
Figure (4.9): Band structure of PbS calculated by Anna Delin et al.\textsuperscript{94} by using full-potential linear muffin-tin orbital method.
Figure (4.10): Band structure of PbSe calculated by Anna Delin et al.\textsuperscript{94} by using full-potential linear muffin-tin orbital method.
Figure (4.11): Band structure of PbTe calculated by Anna Delin et al.\textsuperscript{94} by using full-potential linear muffin-tin orbital method.
Tungsten:

The experimental value\(^9^9\) of the lattice constant for \(W\) is \(a = 3.16\ \text{Å}\). For the case of \(W\) also, we have done volume optimization by plotting Murnaghan’s plot in which total energy as a function of volume was plotted. The Murnaghan’s plot for \(W\) is shown in Fig. (4.12). Then by using the volume corresponding to the lowest energy, we have calculated the value of lattice constant of \(W\) which comes out to be \(a = 3.1694\ \text{Å}\). By using this value of the lattice constant, we have calculated the band structure of \(W\) along symmetry lines in the Brillouin zone and is shown in Fig. (4.13). One of the notable features in the band structure of \(W\) is the appearance of two small electron lenses along the symmetry line from \(\Gamma\) to \(H\) and from \(H\) to \(N\). Also, the hole ellipsoids around the symmetry point \(N\) exist. Our result is compared to the results obtained using other method like the linearized augmented plane wave method used by Wei and Krakauer\(^{100}\), the relativistic-augmented plane-wave method by Christensen and Feuerbacher\(^{101}\) and also the full-potential linearized augmented-plane wave method used by Jansen and Freeman\(^{102}\). We have found that in our result as well as others mentioned, at least some qualitative features were found similar to the experimental results\(^{103,104}\).

In conclusion we can say that the band structures we have obtained for the lead salts as well as \(W\) using FP-LAPW method are in general agreement on the main features with experimental and calculated results by using various methods.
Figure (4.12): Plot of the variation of total energy with respect to the volume for the case of $W$. Theoretical value of lattice constant obtained from the graph is $a = 3.1694 \, \text{Å}$.
Figure (4.13): Band structure of W along symmetry points in the Brillouin zone where lattice constant $a = 3.1694$ Å.
Figure (4.14): Band structure of scalar-relativistic $W$ obtained by Wei and Krakauer\textsuperscript{100} by using full-potential linearized augmented-plane-wave method
Figure (4.15): Band structure of $W$ obtained by Jansen and Freeman\textsuperscript{101} by using total-energy full-potential linearized augmented-plane-wave method.