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Chapter 2

Determination of Energy Bands of
Solids

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In this Chapter we discuss few conventional approaches like, Wigner-Seitz Cellular Method, Nearly Free Electron Theory, Tight Binding Approximation, Kronig-Penney Model, Green Function Method, Density Functional Theory, Muffin-tin Approximation used for determining the energy bands of solids.

2.1   Wigner-Seitz Cellular Method:

This is the first band structure determination cellular method proposed by Wigner and Seitz (1934). They considered the unit cell as truncated polyhedron and wrote the crystalline wave function as a linear combination of atomic functions. The unit cells are latter called as **Wigner-Seitz** cells. They assumed the potential inside the polyhedron as spherically symmetric even though it is perturbed by the neighbouring atoms.

In this method, the crystalline wave function is written as

$$\psi(\boldsymbol{k},\boldsymbol{r}) = \sum_{l,m} A_{lm}(\boldsymbol{k}) Y_{lm}(\theta,\phi) R_l(E,\boldsymbol{r}) \qquad (2.01)$$

where $l = 0,\ 1,\ 2.....$ and m varies from $-l$ to $+l$. A_{lm} is the expansions coefficients and $R_l(E,\boldsymbol{r})$ is the radial solution of the Schrödinger equation

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$$\frac{d^2 R_l}{dr^2} = \left[V(r) + \frac{l(l+1)}{r^2} - E \right] r R_l(r) .$$

$V(r)$ is the spherically symmetric potential inside the Wigner-Seitz cell.

At the surface of the polyhedron, the following boundary conditions are to be imposed on the wave function

$$\psi(\boldsymbol{k}, \boldsymbol{r}_2) = e^{i\boldsymbol{k}.t} \psi(\boldsymbol{k}, \boldsymbol{r}_1)$$

and
$$\boldsymbol{n}.\nabla \psi(\boldsymbol{k}, \boldsymbol{r}_2) = e^{i\boldsymbol{k}.t} \boldsymbol{n}.\nabla \psi(\boldsymbol{k}, \boldsymbol{r}_1)$$

where $\boldsymbol{n}$ is the unit vector normal to the faces of the unit cell and $\boldsymbol{t}$ is the lattice translation vector.

The maximum l value is taken as 2 in the expression (2.01) so as to include the d states. This leads to only a finite number of expansion coefficients and one has to apply the boundary conditions only for that many set of points on the surface of the cell. The imposition of this finite set of boundary conditions leads to a set of homogeneous equations which in turn determines the order of the secular determinant. One has to search for the zeros of the determinant to find the eigen values for a given $\boldsymbol{k}$ point and this has to be repeated for different $\boldsymbol{k}$ points in the Brillouin zone to get the band structure.

In this method the potential employed is that due to a single ion and it does not take into account the interactions arising from the neighbours. It has a discontinuous derivative across the boundary between the cells. But in reality, it is continuous and flat in the region across the cell boundary. The second difficulty is the arbitrary selection of points in the cell boundary and the enormous amount of labour involved in matching the boundary conditions.

2.2   Nearly Free Electron Theory:

The nearly-free electron theory is a modification of the free-electron gas model (Ashcroft and Mermin, 1975; Dekker, 1957; Elliot and Gibson, 1974; Kittel,

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1971). It includes a weak periodic perturbation meant to model the interaction between the conduction electrons and the ions in a crystalline solid. This model, like the free-electron model, does not take into account electron-electron interactions; that is, the independent-electron approximation is still in effect. In this model, the crystal potential is assumed to be very weak as compared to the electronic kinetic energy so that the electrons behave essentially like free particles. The weak periodic potential introduces only a small amount of perturbing effect on the free electrons in the solid. So this model demands the application of very elementary perturbation theory. In the following, the one dimensional case is discussed.

Let $V(x)$ denote the potential energy of an electron in a linear lattice of lattice constant 'a'. The Schrödinger equation to be solved is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E-V)\psi = 0 \tag{2.02}$$

If $V = 0$, it describes a free electron with wave function (unperturbed) $\phi_k(x)$ and the free energy $E^0(k)$ given by

$$\phi_k(x) = \frac{1}{\sqrt{Na}}\exp(ikx) \tag{2.03}$$

$$E^0(k) = \frac{\hbar^2 k^2}{2m} \tag{2.04}$$

Here, the wave function is normalised over a crystal containing N atoms. In this case all values of k are allowed.

Now, as in the free electron theory a very weak periodic potential is introduced, this will perturb the free electron wave function and the energy. Therefore the real wave function and the energy can be calculated by using the perturbation theory.

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As the potential is periodic, it can be expressed as a Fourier series of the form:

$$V(x) = \sum_{n=0} V_n \exp(-i\frac{2\pi}{a}nx) \qquad (2.05)$$

The perturbed wave function (upto first order) becomes

$$\psi_k(x) = \phi_k(x) + \sum_{k\neq k'} \frac{\langle k'|V|k\rangle}{E^0(k) - E^0(k')} \phi_{k'}, \text{ where } \langle k'|V|k\rangle = \int \phi_k^* V \phi_k dx$$

$$\Rightarrow \psi_k(x) = \frac{1}{\sqrt{L}}\left[e^{ikx} + \sum_{k\neq k'} \frac{\langle k'|V|k\rangle}{E(k) - E^0(k')} e^{ik'x} \right] \qquad (2.06)$$

where $L = Na$

The perturbed energy, correct to second order is

$$E(k) = E^0(k) + \sum_{k\neq k'} \frac{|\langle k'|V|k\rangle|^2}{E^0(k) - E^0(k')} e^{ik'x} \qquad (2.07)$$

Now,

$$\langle k'|V|k\rangle = \int \phi_k^* V \phi_k \ dx = \int_0^L \frac{1}{\sqrt{L}} e^{(-ik'x)} \left(\sum_{n=0} V_n e^{-i\frac{2\pi n}{a}x} \right) \frac{1}{\sqrt{L}} e^{(ikx)} dx$$

$$\Rightarrow \langle k'|V|k\rangle = \int \phi_k^* V \phi_k \ dx = \sum_{n=0} \frac{V_n}{L} \int_0^L \frac{1}{\sqrt{L}} e^{i(k-k')x} e^{-i\frac{2\pi n}{a}x} dx$$

$$\Rightarrow \langle k'|V|k\rangle = \int \phi_k^* V \phi_k \ dx = V_n \quad \text{If } k - k' = \frac{2\pi n}{a}$$

$$= 0, \quad \text{otherwise}$$

Consequently the wave function and energy becomes

$$\psi_k(x) = \frac{1}{\sqrt{L}} e^{ikx}\left[1 + \sum_{n\neq 0} \frac{V_n}{E^0(k) - E^0(k - \frac{2\pi n}{a})} e^{-i\frac{2\pi n}{a}x} \right] \qquad (2.08)$$

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and
$$E(k) = E^0(k) + \sum_{n \neq 0} \frac{|V_n|^2}{E^0(k) - E^0(k - n\frac{2\pi}{a})} \qquad (2.09)$$

This expression of $E(k)$ is satisfactory if

    i) V_n tends to zero rapidly as n increases.

    ii) The denominator i.e. $E^0(k) - E^0(k - n\frac{2\pi}{a})$ is not very small

Now, $E^0(k) - E^0(k - n\frac{2\pi}{a}) = \frac{\hbar^2}{2m}\left[k^2 - \left(k - n\frac{2\pi}{a} \right)^2 \right]$ becomes very small when

$$E^0(k) \simeq E^0\left(k - n\frac{2\pi}{a} \right)$$

$$\Rightarrow k^2 \simeq \left(k - n\frac{2\pi}{a} \right)^2$$

and this happens for $k = \pm\frac{n\pi}{a}$, these k values are near to zone boundary.

      It can be concluded that the plane wave function given by Eq. (2.08) can not be considered at near to zone boundary and hence the energy is given by Eq. (2.09).

      The wave function in this case must arise from a superposition of an incident wave propagating along +ve X direction and a reflected wave in the opposite direction. In this situation the electron wave is reflected at $k = \pm\frac{n\pi}{a}$. We may therefore write the wave function as

$$\psi_k(x) = e^{ikx}\left[A_0 + A_n\, e^{-i\frac{2\pi n}{a}x} \right]$$

$$\Rightarrow \psi_k(x) = A_0\, e^{ikx} + A_n\, e^{i(k - \frac{2\pi n}{a})x} \qquad (2.10)$$

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Here, A_0 and A_n are constants referred to incident and reflected waves respectively.

Now, using this value of ψ as given by Eq. (2.10) and V_x as given by Eq. (2.05) in Eq. (2.02), we get

$$-\frac{\hbar^2}{2m}\left[-A_0\,k^2 e^{ikx} - A_n\left(k-\frac{2\pi n}{a}\right)^2 e^{i\left(k-\frac{2\pi n}{a}\right)x}\right] + \sum_{n'\neq 0} V_{n'}\, e^{-i\frac{2\pi n'}{a}x}\left(A_0\,e^{ikx} + A_n\,e^{i\left(k-\frac{2\pi n}{a}\right)x}\right)$$

$$= E(k)\left[A_0\,e^{ikx} + A_n\,e^{i\left(k-\frac{2\pi n}{a}\right)x}\right]$$

Putting $E^0(k) = \dfrac{\hbar^2 k^2}{2m}$ and $E^0(k') = \dfrac{\hbar^2}{2m}\left(k-\dfrac{2\pi n}{a}\right)^2$ in above equation and rearranging the terms we get,

$$A_0\left[E^0(k) - E(k)\right]e^{ikx} + A_n\left[E^0(k') - E(k)\right]e^{i\left(k-\frac{2\pi n}{a}\right)x} + A_0\sum_{n'\neq 0} V_{n'}e^{-i\frac{2\pi n'}{a}x}e^{ikx}$$

$$+A_n\sum_{n'\neq 0} V_{n'}e^{i\left(k-\frac{2\pi n}{a}-\frac{2\pi n'}{a}\right)x} = 0 \qquad (2.11)$$

Multiplying both sides of Eq. (2.11) by e^{ikx} and integrating over $x=0$ and $x=a$, we get,

$$A_0\left[E^0(k) - E(k)\right] + A_n V_n^* = 0 \qquad (2.12)$$

where, $V_{-n} = V_n^*$

Similarly multiplying both sides of Eq. (2.11) by $e^{-ik'x}$ and integrating over $x=0$ and $x=a$, we get

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$$A_0 V_n + A_n \left[E^{0}(k') - E(k) \right] = 0 \tag{2.13}$$

For a non trivial solution, the determinant of the coefficients must vanish. The resulting quadratic equation has two solutions:

$$E(k) = \frac{1}{2} \left[\left\{ \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{2m} \left(k - \frac{2\pi n}{a} \right)^2 \right\} \pm \left\{ \sqrt{ \frac{\hbar^2 k^2}{2m} - \frac{\hbar^2}{2m} \left(k - \frac{2\pi n}{a} \right)^2 + 4|V_n|^2 } \right\} \right] \tag{2.14}$$

Therefore, at the zone boundary i.e. at $k = \pm\dfrac{n\pi}{a}$, there are two energies viz.,

$$E(k) = E^{0}(k) \pm |V_n|$$
$$\Rightarrow E(k) = E^{0}(\frac{n\pi}{a}) \pm |V_n| \tag{2.15}$$

Here, the first term in the R. H. S. of Eq. (2.15) represents the free particle energy associated with the zone boundary. At the zone boundary $k = \pm\dfrac{n\pi}{a}$, standing waves having different energies are formed. Since difference of their energies represents an energy gap in the E vs K curve, the width of the gap is $2|V_n|$, where $|V_n|$ is the nth Fourier coefficient in the Fourier series expansion of periodic potential. Thus in every zone points there is a gap in the energy of width $2|V_n|$ centred around the energy value $\dfrac{\hbar^2}{2m} \left(\dfrac{n\pi}{a} \right)^2$ and at other values of k, the energy is continous.

2.3   Tight Binding Approximation:

Tight binding approximation (TBA) is a convenient model for the description of electronic structure in molecules and solids. It provides the basis for construction of many body theories. Slater and Koster called it the tight binding or "Bloch" method (Slater and Koster, 1954). "Slater–Koster" table is used to formulate Hamiltonians for tight bound cases. The TBA model does not require to approximate the crystal periodic potential as a sequence of square wells and

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barriers. The TBA describes situations for which the atomic potential is quite large and the wave function for an electron belonging to an atom forming part of a crystal remaining localized about the atomic core -- hence the name "tight binding." The outer-electron wave functions slightly overlap between neighbouring atoms. Further this model provides a way of evaluating the allowed energy values of an electron in a solid, starting from the energy levels of neutral atoms. It accounts the energy changes in the level because the charge distribution of the adjacent atoms overlap when atoms are brought together to form a solid.

Let us consider that the potential function associated with an isolated atom is $V_0(r)$. Then the Schrödinger equation is written as,

$$\nabla^2 \psi + \frac{2m}{\hbar^2}[E - V_0(r)]\psi(r) = 0$$

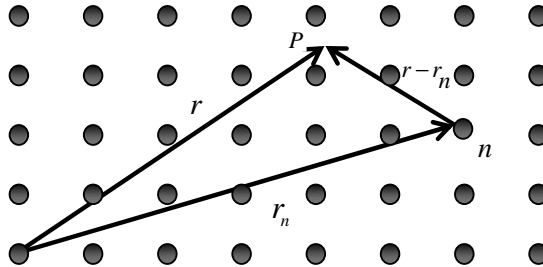Let ψ_0 be the non degenerate ground state wave function corresponding to the ground state energy E_0.

Figure 2.1: Two dimensional arrangements of atoms at lattice sites

Let r and r_n be the position vector of an electron (at P) and n[th] atom of the crystal as shown in figure 2.1 above.

As in the tight binding model, it is assumed that only nearest neighbour atoms have overlapping electron wave functions, the electron wave function near the nth atom is approximately independent of the other atoms and is approximately

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given by $\psi_0(\boldsymbol{r} - \boldsymbol{r}_n)$.   The crystal wave function can be written as a linear superposition of atomic wave functions of the form:

$$\psi_k(\boldsymbol{r}) = \sum_n a_n \psi_0(\boldsymbol{r} - \boldsymbol{r}_n) \tag{2.16}$$

As electrons have the form of Bloch wave function, the coefficients a_n must describe a progressive wave within the crystal lattice, i.e. $a_n = e^{i\boldsymbol{k}.\boldsymbol{r}_n}$. Thus we have,

$$\psi_k(\boldsymbol{r}) = \sum_n e^{i\boldsymbol{k}.\boldsymbol{r}_n} \psi_0(\boldsymbol{r} - \boldsymbol{r}_n) \tag{2.17}$$

With this wave function, the Schrödinger equation for the crystal wave function becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \psi_k(\boldsymbol{r}) = E\psi_k(\boldsymbol{r})$$

$$\Rightarrow \left[-\frac{\hbar^2}{2m} \nabla^2 + V_0(\boldsymbol{r} - \boldsymbol{r}_n) + V(r) - V_0(\boldsymbol{r} - \boldsymbol{r}_n) \right] \psi_k(\boldsymbol{r}) = E\psi_k(\boldsymbol{r})$$

$$\Rightarrow \left[H_0 + H_1 \right] \psi_k(\boldsymbol{r}) = E\psi_k(\boldsymbol{r})$$

$$\Rightarrow H\psi_k(\boldsymbol{r}) = E\psi_k(\boldsymbol{r}) \tag{2.18}$$

where, $H_0 = -\dfrac{\hbar^2}{2m} \nabla^2 + V_0(\boldsymbol{r} - \boldsymbol{r}_n)$, $H_1 = V(r) - V_0(\boldsymbol{r} - \boldsymbol{r}_n)$ and $H = H_0 + H_1$

The quantity H_1 represents the potential energy of the electron in the crystal at the point P (due to all the atoms) minus the potential energy of the electron at the same point when there is only a single atom located at n. But $H_o \psi_o = E_o \psi_o$, so

$$H_o \psi_k(\boldsymbol{r}) = H_o \sum_n e^{i\boldsymbol{k}.\boldsymbol{r}_n} \psi_o(\boldsymbol{r} - \boldsymbol{r}_n) = E_o \sum_n e^{i\boldsymbol{k}.\boldsymbol{r}_n} \psi_o(\boldsymbol{r} - \boldsymbol{r}_n) \tag{2.19}$$

The energy of the electron in the crystal $E(k)$ can be found by evaluating the expectation value of the Hamiltonian operator as

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$$E(k) = \frac{\int \psi_k^*(r)[H_o + H_1]\psi_k(r)dr}{\int \psi_k^*(r)\psi_k(r)dr} = E_0 + \frac{\int \psi_k^*(r)H_1\psi_k(r)dr}{\int \psi_k^*(r)\psi_k(r)dr}$$

Here $\int \psi_k^*(r)\psi_k(r)dr = \sum_m \sum_n \int e^{ik(r_n - r_m)}\psi_0^*(r - r_m)\psi_0(r - r_n)dr$

At $m = n$, $\int \psi_k^*(r)\psi_k(r)dr = \sum_n \int \psi_0^*(r - r_n)\psi_0(r - r_n)dr = N$. N is the total

number of electrons (atoms) in the crystal. So

$$E(k) = E_0 + \frac{1}{N}\sum_n \left[\sum_m e^{ik(r_n - r_m)} \int \psi_0^*(r - r_m)[V(r) - V_0(r - r_n)]\psi_0(r - r_n)dr \right]$$

Since all the terms in the summation over n are identical because of the periodicity
of the lattice potential, we need to consider only one term and multiply the result
by N which is the number of terms in the sum. If we take $n = 0$, then

$$E(k) = E_0 + \sum_m e^{-ik.r_m} \int \psi_0^*(r - r_m)[V(r) - V_0(r)]\psi_0(r)dr \qquad (2.20)$$

To simplify further, we write a term for $m = 0$ (i.e. m^{th} atom is at the origin and
hence $r_m = 0$) and the other terms in the summation for $m \neq 0$ i.e.

$$\begin{aligned} E(k) = E_0 &+ \int \psi_0^*(r)[V(r) - V_0(r)]\psi_0(r)dr \\ &+ \sum_{m \neq 0} e^{-ik.r_m} \int \psi_0^*(r - r_m)[V(r) - V_0(r)]\psi_0(r)dr \end{aligned} \qquad (2.21)$$

For $m = 0$, the integral in above equation gives

$$\int \psi_0^*(r)[V(r) - V_0(r)]\psi_0(r)dr = -\alpha$$

and for the nearest neighbour atoms

$$\int \psi_0^*(r - r_m)[V(r) - V_0(r)]\psi_0(r)dr = -\beta$$

where α and β are known as overlap integrals. Since $[V(r) - V_0(r)]$ is negative
therefore α and β are positive. Consequently the Eq. (2.21) can be written in a
simplified form as

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$$E(k) = E_0 - \alpha - \beta \sum_m e^{-ik \cdot r_m} \qquad\qquad (2.22)$$

where the summation is to be carried out over the nearest neighbours only. It is observed that the Eq. (2.22) consists of a constant term $E_0 - \alpha$ together with the term dependent on k. It is the latter term that transforms the discrete atomic levels into the energy bands in the solid.

2.4   Kronig-Penney Model:

In the free electron theory, it is assumed that the potential to which the valence electrons are subjected is constant and therefore, it can be set equal to zero when solving the Schrödinger equation. Obviously, this is not true for the valence electrons in ionic and covalent solids, where the electrons are localized near the parent nuclei. Thus, a constant potential should be replaced by a periodically varying potential $V(r)$. In 1931, Kronig and Penney originally proposed a one dimensional model to describe the behaviour of electrons moving under a periodic potential (Kronig and Penney, 1931). The Kronig and Penney model is a simplified one-dimensional quantum mechanical model of a crystal. With the help of this model one obtains energy bands and energy band gaps in a crystal.

Kronig and Penney suggested a potential in the form of an array of square well potential as shown in figure 2.2.
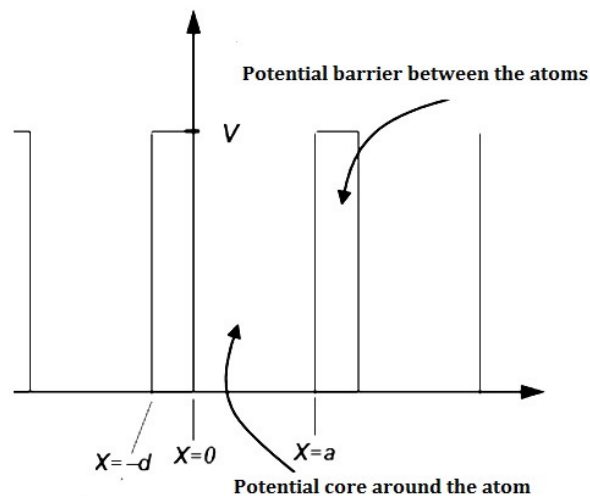

Figure 2.2: Ideal periodic square well potential suggested by Kronig & Penney

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Following the above form of the potential we can write the two Schrödinger equations as:

$$\frac{d^2\psi}{dx^2} + \alpha^2\psi = 0, \quad \text{for } 0 < x < a, \text{ where } \alpha^2 = \frac{2mE}{\hbar^2} \tag{2.23}$$

and

$$\frac{d^2\psi}{dx^2} - \gamma^2\psi = 0, \quad \text{for } -d < x < 0, \text{ where } \gamma^2 = \frac{2m(V-E)}{\hbar^2} \tag{2.24}$$

Since the expected solutions of the above Schrödinger equations have the form of Bloch function, this requires both ψ and $\frac{d\psi}{dx}$ to be continuous throughout the crystal. Therefore, if we suppose that the general solution of the equations (2.23) and (2.24) are of the form

$$\psi_1(x) = Ae^{i\alpha x} + Be^{-i\alpha x} \tag{2.25}$$

and

$$\psi_2(x) = Ce^{\gamma x} + De^{-\gamma x} \text{ for } E < V \tag{2.26}$$

where A, B and C, D are the constants in the region $0 < x < a$ and $-d < x < 0$ respectively, the values of $\psi_1(x)$ and $\psi_2(x)$ can be obtained by applying the following boundary conditions,

$$\left.\left|\psi_1(x)\right|\right|_{x=0} = \left.\left|\psi_2(x)\right|\right|_{x=0} \tag{2.27}$$

$$\left[\frac{d\psi_1}{dx}\right]_{x=0} = \left[\frac{d\psi_2}{dx}\right]_{x=0} \tag{2.28}$$

$$\left.\left|\psi_1(x)\right|\right|_{x=a} = \left.\left|\psi_2(x)\right|\right|_{x=-d} \tag{2.29}$$

and

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$$\left[\frac{d\psi_1}{dx}\right]_{x=a} = \left[\frac{d\psi_2}{dx}\right]_{x=-d} \tag{2.30}$$

Since, for a periodic lattice with $V(x+a)=V(x)$, the wave function will exhibit the same periodicity, therefore, we can write

$$\psi_k(x) = \psi_k(x+a+d)e^{-ik(a+d)}$$

Incorporating this requirement at $x=-d$ & $x=a$, the Eqs. (2.29) and (2.30) becomes

$$\psi_2(-d) = \psi_1(a)e^{-ik(a+d)} \tag{2.31}$$

and

$$\left[\frac{d\psi_2}{dx}\right]_{x=-d} = \left[\frac{d\psi_1}{dx}\right]_{x=a} e^{-ik(a+d)} \tag{2.32}$$

Now, applying the boundary conditions in Eq. (2.27), (2.28), (2.31) and (2.32), we obtain the following modified equations:

$$\left.\begin{array}{l} A+B = C+D \\ i\alpha(A-B) = \gamma(C-D) \\ Ce^{-\gamma d} + De^{\gamma d} = e^{-ik(a+d)}[Ae^{i\alpha a} + Be^{-i\alpha a}] \\ \gamma Ce^{-\gamma d} + \gamma De^{\gamma d} = i\alpha e^{-ik(a+d)}[Ae^{i\alpha a} - Be^{-i\alpha a}] \end{array}\right] \tag{2.33}$$

This Eq. (2.33) will have the non vanishing solutions if and only if the determinants of the coefficients A, B, C and D vanishes i.e.

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$$\begin{vmatrix} 1 & 1 & -1 & -1 \\ i\alpha & -i\alpha & -\gamma & \gamma \\ -e^{-ik(a+d)+i\alpha a} & -e^{-ik(a+d)-i\alpha a} & e^{-\gamma d} & e^{\gamma d} \\ -i\alpha e^{ik(a+d)+i\alpha a} & i\alpha e^{-ik(a+d)-i\alpha a} & \gamma e^{-\gamma d} & -\gamma e^{\gamma d} \end{vmatrix} = 0$$

On simplifying this determinant, we obtain

$$\frac{\gamma^2 - \alpha^2}{2\alpha\gamma}\sinh(\gamma d)\sin(\alpha a) + \cosh(\gamma d)\cos(\alpha a) = \cos[k(a+d)]$$

In order to simplify the above situation, Kronig and Penney assumed that the product of the height and the width of the potential barrier, Vd, remains finite; when $V \to \infty$ and $d \to 0$. Under this assumption the above equation becomes

$$\frac{\gamma^2 d}{2\alpha}\sin(\alpha a) + \cos(\alpha a) = \cos(ka) \tag{2.34}$$

From the above equation we see that the L. H. S of Eq. (2.34) is a function of energy E while the R. H. S. depends only upon the wave vector k.
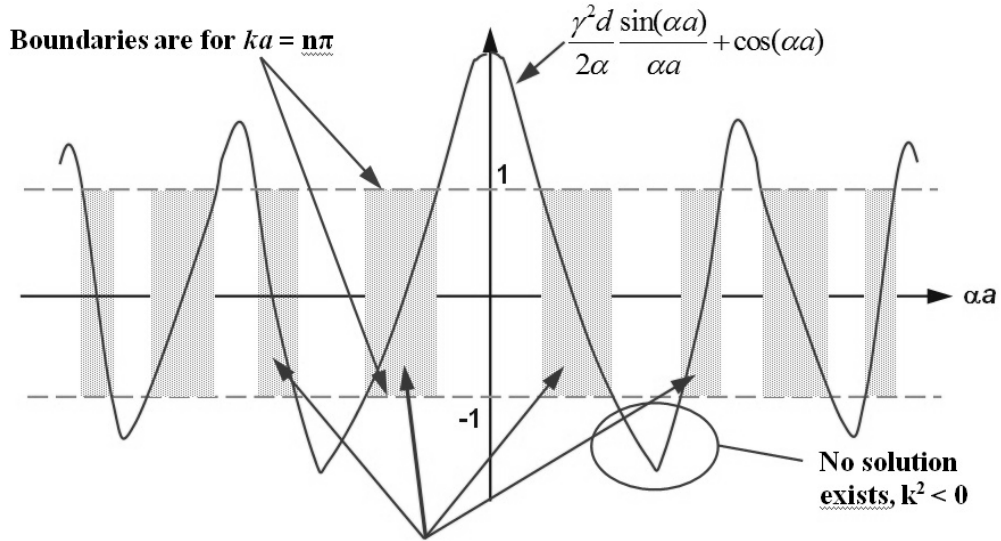

Figure 2.3: Plot of $\dfrac{\gamma^2 d}{2\alpha}\sin(\alpha a) + \cos(\alpha a)$ **Vs** $\cos(ka)$

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Analysis of Eq. (2.34) leads to following inferences:

1. Allowed range of αa permits a wave mechanical solution to exist as shown in figure 2.3. Thus the motion of electrons in a periodic potential is characterized by the bands of allowed energy separated by forbidden regions.

2. As the value of αa increases each successive band gets wider and other gets narrower. This is because of the fact that the first term on the left hand side of Eq. (2.34) on an average decreases with increasing αa.

Figure 2.4 shows a plot of energy k as a function of k. If k is to be real, the magnitude of $\cos ka$ should be less than 1 (i.e. $|\cos ka| < 1$) which corresponds to the allowed energy band. On the other hand, those value of energy E for which $|\cos ka| > 1$, only the imaginary values of k are possible which correspond to the forbidden bands.
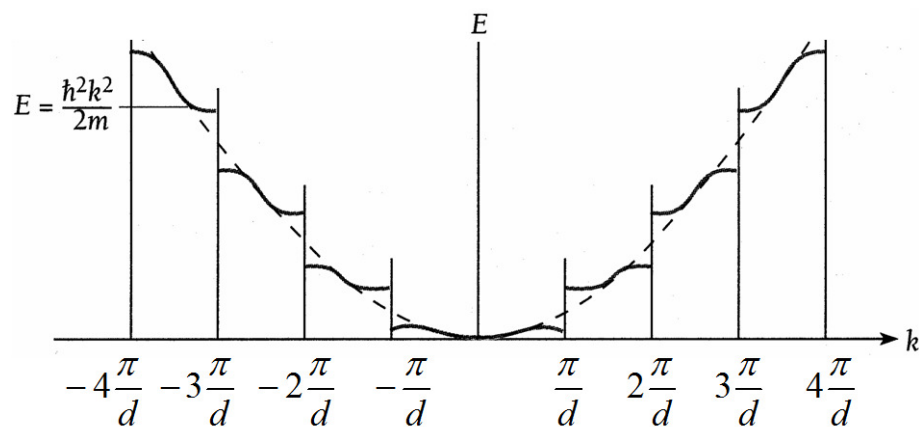

Figure 2.4: Energy Vs wave vector for a one dimensional lattice

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2.5   Green's Function Method:

To calculate the energy bands of solids one can apply Green's function methods. The poles of the Green's function corresponds to the energy bands of a solid.

The Green's function method for calculating energy bands in solids shares with other methods such as those of augmented (Slater, 1937) or orthogonalized plane waves (Herring, 1940) and various cellular methods (Slater, 1934; Lage and Bethe, 1947; Howarth and Jones, 1952; Kohn, 1952), the advantage of taking polyhedral shape of the atomic cell. With these other methods, it thus represents a major advance over the spherical approximation of Wigner and Seitz (Wigner and Seitz, 1933, 1934) which has been extensively used in band calculations on metals.

An especial advantage of the Green's function method is its rapid convergence. This is much better than that found in calculations with other methods as reported in the literature, though it is probably rivalled by recent work with forms of the Augmented Plane Waves (APW) method. In particular, the method permits accurate calculation at points of low symmetry within the Brillouin zone without requiring the use of unmanageably large determinants. This method has further advantage that the calculations are relatively simple and can be done by hand in general, once tables are prepared of "structure constants" which are characteristic of lattice type but independent of the particular crystal potential or lattice constant.

The mathematical basis of calculations of energy bands in periodic lattices using the Green's function method was formulated by Kohn and Rostoker (1954). In this method the problem of solving Schrödinger equation in a periodic potential is studied from the point of view of the variation-iteration method. This approach leads to a very compact scheme if the potential $V(r)$ is spherically symmetric

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within the inscribed spheres of the atomic polyhedra and constant in the space between them.

Introducing the method of Green's functions we have to solve an integral equation instead of the Schrödinger equation.

Let $V(r)$ be a periodic potential with periodicity property $V(r)=V(r+r_s)$. In order to get the energy bands one seek propagating solutions

$$\psi(r)=e^{ik.r_s}\psi(r) \tag{2.35}$$

of Schrödinger's equation,

$$\left(-\nabla^2+V(r)-E\right)\psi(r)=0 \tag{2.36}$$

Here k is the crystal momentum vector, r_s is any translation vector of the lattice

Now, we introduce the Green's function defined by

$$(-\nabla^2-E)G(r,r')=-\delta(r-r') \tag{2.37}$$

The Green's function has the following property

  i) $G(r,r')=G^*(r,r')$, hermitian property and

  ii) $G(r,r+r_s)=e^{ik.r_s}G(r,r')$

If K_n is the reciprocal lattice vector defined by

$$K_n.\tau_i=2\pi\times(\text{integer}),\ i=1,\ 2,\ 3,.....$$

Then G can be written as

$$G(r,r')=-\frac{1}{\tau}\sum_n\frac{\exp[i(K_n+k).(r-r')]}{(K_n+k)^2-E} \tag{2.38}$$

where τ is the volume of the atomic polyhedron

Alternatively, G can be expressed in the form

$$G(r,r')=-\frac{1}{4\pi}\sum_s\frac{\exp\left[ik|r-r'-r_s|\right]}{|r-r'-r_s|}e^{ik.r_s} \tag{2.39}$$

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$$\text{where} \qquad \left. \begin{array}{ll} k = +\sqrt{E}, & E > 0 \\ k = +i\sqrt{(-E)}, & E < 0 \end{array} \right] \qquad (2.40)$$

Eq. (2.38) is the standard expansion of a green function in terms of the eigen functions of the homogeneous boundary value problem. Kohn and Rostoker have shown that $\psi(r)$ satisfies the integral equation

$$\psi(r) = \int_{\tau} G(r,r') \, V(r') \, \psi(r') \, d\tau \qquad (2.41)$$

The integral Eq. (2.41) is equivalent to the variational principle

$$\delta\Lambda = 0 \qquad (2.42)$$

where

$$\Lambda = \int_{\tau} \psi^*(r) \, V(r) \, \psi(r) d\tau - \int_{\tau}\int_{\tau'} \psi^*(r) \, V(r) \, G(r,r') \, V(r') \, \psi(r') d\tau d\tau' \quad (2.43)$$

It should be noted that $\delta\Lambda$ vanishes for arbitrary variations of ψ.

Now let us use a trial function of the form $\psi = \sum_{n} C_i \varphi_i, \quad C_i = a_i + i b_i$ and

substitute it in Eq. (2.43), we get

$$\Lambda = \sum_{i,j=0}^{n} C_i^* \Lambda_{i;j} C_j \qquad (2.44)$$

where $\Lambda_{i;j}$ is hermitian and is takes the form

$$\Lambda_{i;j} = \int_{\tau} \varphi_i^*(r) \, V(r) \, \varphi_j(r) d\tau - \int_{\tau}\int_{\tau'} \varphi_i^*(r) \, V(r) \, G(r,r') \, V(r') \, \varphi_j(r') \, d\tau d\tau' \quad (2.45)$$

The conditions $\qquad \dfrac{\partial \Lambda}{\partial a_i} = \dfrac{\partial \Lambda}{\partial b_i} = 0, \quad i = 0,\ 1,............\ n, \qquad (2.46)$

which follow from Eq. (2.42) give the linear equations

$$\sum_{j=0}^{n} \Lambda_{i;j} \, C_j = 0, \quad i = 0,\ 1,............\ n, \qquad (2.47)$$

which are compatible only if

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$$\det \Lambda_{i;j} = 0 \qquad (2.48)$$

Since, for given functions φ_i, the $\Lambda_{i;j}$ are functions only of $\boldsymbol{k}$ and $\boldsymbol{E}$, Eq. (2.48) gives the required connection between $\boldsymbol{k}$ and $\boldsymbol{E}$ which in other words gives the required energy band. The coefficients $\boldsymbol{C_i}$ can be determined from Eq. (2.47) after Eq. (2.48) has been solved.

The detailed treatment is discussed by Kohn & Rostoker (1954), Ham & Segall (1961) and Kenan & Sievert (1974). H. Fock applied this technique for calculating the energy bands for a Perfect crystal and a Crystal with impurities (Fock, 1971).

The disadvantage of using the general Green's function is that it is a complicated function of the energy, which must be searched for the location of roots which yield the eigen energies of the problem. The Green's function must be evaluated many times in a computationally fast and efficient way for a tractable numerical scheme to be developed.

2.6   Density Functional Theory:

A large majority of the electronic structures and band plots are calculated using the density functional theory (DFT) which is not a model but rather an *ab initio* theory (Hohenberg and Kohn, 1964). In DFT, ground state of a system and the charge density of the relevant physical quantity are considered. DFT has proved to be highly successful in describing structural and electronic properties in a vast class of materials, ranging from atoms, molecules and simple crystals to complex extended systems (including glasses and liquids). For these reasons DFT has become a common tool in first-principle calculations aimed at describing or even predicting properties of molecular and condensed matter systems.

In contrast to the Hartree-Fock picture, which begins conceptually with a description of individual electrons interacting with the nuclei and all other

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electrons in the system, DFT starts with a consideration of the entire electron system. If there are N electrons in the system, the wave function of the electron system is a function of 3N variables. However, within DFT, all aspects of the electronic structure of the system of interacting electrons in an 'external' potential $V_{ext}(r)$ are completely determined by the electronic charge density $n(\boldsymbol{r})$.

In DFT, the total energy is decomposed into three contributions, a kinetic energy, a Coulomb energy due to classical electrostatic interactions among all charged particles in the system and a term called the exchange-correlation energy that captures all many-body interactions.

Density functional formalism is based on two theorems by Hohenberg and Kohn (1964), who considered the Hamiltonian

$$H = T + U + V$$

$$= \sum_i^M \left(-\nabla_i^2 \right) + \frac{1}{2} \sum_i^M \sum_j \frac{2}{r_i^2} + \sum_i^M V_{ext}(\boldsymbol{r}_i), \quad i \neq j \qquad (2.49)$$

of a system of M interacting electrons moving in some fixed external potential V_{ext}. Here T is the kinetic energy, U is the electron-electron Coulomb repulsion and V is the interaction with the external potential, which includes the electrostatic interaction with the fixed nuclei.

Firstly, Hohenberg and Kohn showed that the external potential is a unique functional of the electron density $n(\boldsymbol{r})$, and hence the ground state Φ and the energy functional

$$< \Phi | H | \Phi > \ = \ F[n] + \int V_{ext}(\boldsymbol{r}) \, n(\boldsymbol{r}) d\boldsymbol{r}$$

where $\qquad\qquad F[n] \ = \ < \Phi | T + U | \Phi > \qquad\qquad (2.50)$

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

In addition, they separated out the classical Hartree contribution

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$$F[n] \;=\; \frac{1}{2}\iint \frac{2n(r)n(r')}{|r-r'|}dr\,dr' + G[n] \tag{2.51}$$

by defining yet another functional $G[n]$, which represents the kinetic energy plus the difference between the true interaction energy and that given by the Hartree interaction term. It follows that $F[n]$ and $G[n]$ are universal functionals of the electron density, valid for any external potential and any number of electrons and that the freedom to specify the external potential may be used to generate different electron densities.

Hohenberg and Kohn showed secondly that the energy functional (2.50) assumes its minimum value, the ground-state energy, for the correct ground state density. Hence, if the universal functional $F[n] \;=\; <\Phi|T+U|\Phi>$ were known, it would be relatively simple to use this variational principle to determine the ground-state energy and density for any specified external potential. Unfortunately, the functional is not known and the full complexity of the many-electron problem is associated with its determination.

In this situation it is useful to note that the theorems described above apply equally well to the case of non-interacting electrons, i.e. to a system with the Hamiltonian

$$H_s = T + V$$

$$= \sum_i^M \left(-\nabla_i^2\right) + \sum_i^M V_s(r_i) \tag{2.52}$$

The ground state Φ_s of this single-particle problem is simply a Slater determinant obtained by populating the lowest lying one-electron orbitals defined by the Schrödinger equation

$$\left[-\nabla^2 + V_s(r)\right]\psi_j(r) = E_j\psi_j(r) \tag{2.53}$$

So, the density is given by

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$$n(\boldsymbol{r}) = \sum_{j} \left| \psi_j(\boldsymbol{r}) \right|^2 \qquad (2.54)$$

Hence, guided by the success of the one-electron picture, Kohn and Sham (1965) considered a system of non-interacting electrons together with the real system and proceeded to determine the external potential $V_s(\boldsymbol{r})$ such that Eq. (2.54) is also the ground-state density of the real system.

They wrote $G[n]$ in the form

$$G[n] = T_s[n] + E_{xc}[n] \qquad (2.55)$$

where $T_s[n]$ is the kinetic energy

$$< \Phi_s \left| T \right| \Phi_s > \; = \; \sum_{j} \int \psi_j^*(\boldsymbol{r})(-\nabla^2)\psi_j(k,\boldsymbol{r})d\boldsymbol{r} \qquad (2.56)$$

of the non-interacting electrons of density $n(r)$ and $E_{xc}[n]$ is the exchange correlation energy functional. In total we have now isolated two terms, the Hartree term in Eq. (2.51) and the kinetic energy in Eq. (2.55), which play a decisive role in the single-electron picture and which are presumably also the dominant terms in the interacting system. The remainder has been collected in $E[n]$, which therefore 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 the Hartree contribution. But the actual expressions for the many-body exchange and correlation interactions are unknown. The local density approximation (LDA) turned out to be computationally convenient and surprisingly accurate. In this approximation, the exchange correlation energy is taken from the known results of the many-electron interactions in an electron system of constant density. The LDA amounts to the following picture: at each point in a molecule or solid there exists a well defined electron density; it is assumed that an electron at such a point experiences the same many-body response by the surrounding electrons as if the density of these surrounding electrons had the same value throughout the entire space as at the point of the reference electron. The exchange-correlation energy of the total molecule or solid is then the integral

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over the contributions from each volume element. The contributions are different from each volume element depending on the local electron density. The LDA is exact for a perfect metal (which has a constant electron density) and becomes less accurate for systems with varying electron density. Remarkably, the LDA is also quite well suited for systems with a high electron density such as transition metals. In this LDA approximation

$$E_{xc}[n] = \int \varepsilon_{xc}(n(r))dr \tag{2.57}$$

The exchange-correlation energy density $\varepsilon_{xc}(n)$ is obtained from a homogeneous electron gas of density n.

Collecting together the above assumptions, the energy functional can be written in the form

$$<\Phi|H|\Phi> = <\Phi_s|T|\Phi_s> +$$

$$\int \left\{ \frac{1}{2} \int \frac{2n(r')}{|r-r'|} dr' + V_{ext}(r) + \varepsilon_{xc}(n(r)) \right\} n(r)dr \tag{2.58}$$

and a minimalisation with respect to the density $n(r)$ now leads to the effective single-particle Schrödinger equation

$$V_s(r) = \int \frac{2n(r')}{|r-r'|} dr' + V_{ext}(r) + V_{xc}(n(r)) \tag{2.59}$$

Here, the first term is the classical Hartree potential or electron-electron repulsion, the second term is the external potential which in most applications includes the Coulomb attraction from the nuclei and the final term is the exchange-correlation potential. The latter is given by

$$V_{xc}(r) = \frac{d\left[n\varepsilon_{xc}(n)\right]}{dn} \equiv \mu_{xc}[n(r)] \tag{2.60}$$

where μ_{xc} is the exchange-correlation part of the chemical potential in a homogeneous electron gas of density $n(r)$.

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Now specify the external potential included by the last term of (2.49) to be the Coulomb attraction $V_c(\mathbf{r}) = -\sum_R \dfrac{2Z}{|\mathbf{r} - R|}$ from the nuclei of charge Z and positioned at lattice vectors R and add to (2.49) the nuclear-nuclear repulsion

$$V_n = \frac{1}{2}\sum_R \sum_{R'} \frac{2Z^2}{|\mathbf{R} - \mathbf{R'}|} \quad , \quad \mathbf{R} \neq \mathbf{R'}$$

For the case of one atom per cell the number of electrons in the atomic sphere is Z. Hence, when V_c and V_n are included in the energy functional (2.58), one finds that the electrostatic interactions reduce to an interaction with the field $-\dfrac{2Z}{r}$ from the nucleus which is therefore the external potential $V_{ext}(r)$. Furthermore, since this interaction is restricted to the sphere, it led to minimise the energy functional (per atom)

$$< \Phi|H|\Phi > \;=\; <\Phi_S|T|\Phi_S> + \int_S \left\{ \frac{1}{2}V_H(r) - \frac{2Z}{r} + \varepsilon_{XC}(n(r)) \right\} n(r)dr \quad (2.61)$$

Here, the integrals extend over the atomic sphere of radius S and the Hartree potential $V_H(\mathbf{r})$ is given by $V_H(\mathbf{r}) = \int_S \dfrac{2n(\mathbf{r'})}{|\mathbf{r} - \mathbf{r'}|} d\mathbf{r'}$.

The minimalisation of Eq. (2.61) results in a one-electron Schrödinger equation of the form (2.53), valid inside each atomic sphere and with an effective one-electron potential given by

$$V_S(\mathbf{r}) = V_H(\mathbf{r}) - \frac{2Z}{r} + V_{xc}(n(\mathbf{r})) \quad (2.62)$$

Matching the solutions of Eq. (2.53) and Eq. (2.62) from sphere to sphere finally gives the electronic energy-band structure of the crystal in question.

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DFT calculated bands are found in many cases in agreement with experimental measured bands, for example by angle-resolved photoemission spectroscopy (ARPES). In particular, the band shape seems well reproduced by DFT. But also there are systematic errors of DFT bands with respect to the experiment. However DFT is not a theory to address excited state properties, such as the band plot of a solid that represents the excitation energies of electrons injected or removed from the system. What in literature, is quoted as a DFT band plot, is a representation of the DFT Kohn-Sham energies, which is the energy of a fictive non-interacting system, the Kohn-Sham system, which has no physical interpretation at all. The Kohn-Sham electronic structure must not be confused with the real, quasiparticle electronic structure of a system and there is no Koopman's theorem holding for Kohn-Sham energies, like on the other hand for Hartree-Fock energies that can be truly considered as an approximation for quasiparticle energies. Hence in principle DFT is not a band theory, not a theory suitable to calculate bands and band-plots.

2.7   Muffin-tin Approximation:

The muffin-tin approximation is a shape approximation of the potential field in an atomistic environment. It is most commonly employed in quantum mechanical simulations of electronic band structure in solids. The approximation was proposed by John C. Slater (Slater, 1937). Many modern electronic structure methods employ this approximation method, among them are the augmented plane wave (APW) method, the linear muffin-tin orbital method (LMTO) and various Green's function methods (Martin, 2004). In its simplest form, non-overlapping spheres are centred on the atomic positions. Within these regions, the screened potential experienced by an electron is approximated to be spherically symmetric about the given nucleus. In the remaining interstitial region, the potential is approximated as a constant. Continuity of the potential between the atom-centred spheres and interstitial region is enforced. In the interstitial region of constant potential, the single electron wave functions can be expanded in terms of plane

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waves. In the atom-centred regions, the wave functions can be expanded in terms of spherical harmonics and the eigen functions of a radial Schrödinger equation. Such use of functions other than plane waves as basis functions is termed as the augmented plane-wave approach. It allows for an efficient representation of single-particle wave functions in the vicinity of the atomic cores where they can vary rapidly (and where plane waves would be a poor choice on convergence grounds in the absence of a pseudo potential).