

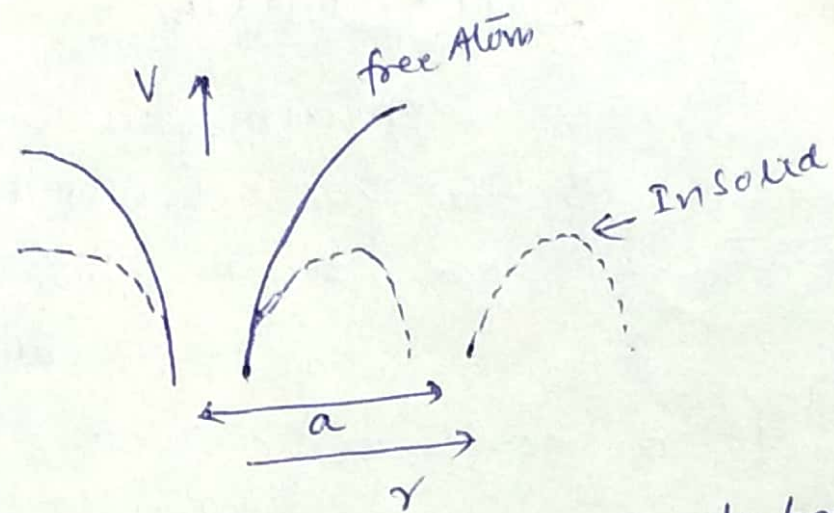
## Tight-Binding approximation

This is an approximation method of evaluating energy levels for an electron in a solid. In this approximation one starts from the wave function for an electron in a free atom and then constructs a crystal orbital i.e. Bloch function, which describe the electron in the periodic field of crystal as a whole. This method is also called LCAO since it is based on linear combinations of atomic orbitals. An individual energy level gets broken up to energy bands as atoms are brought together in a form of a crystal. This approximation is valid ~~only~~ for electrons corresponding to the inner electronic shells in the atoms.

Consider an electron in a free atom. Suppose the potential energy of the electron in the field of the nucleus plus that of the other electrons in the atom is given by  $V_a(r)$ , where 'r' represents the distance from the nucleus. The potential can be represented by fully drawn curve. The wave function of the electron in the free atom be  $\phi(r)$  and let its energy be  $E_0$ . The wave function satisfy the Schrodinger equation;

$$-\frac{\hbar^2}{2m} \nabla^2 \phi + V_a(r) \phi = E_0 \phi \quad \text{--- (1)}$$

Let us assume that the level is non degenerate. i.e. there is only one wave function corresponding to  $E_0$ , further we assume that the wave function is normalised. Suppose the similar atoms are brought together to form the crystal. Then the potential energy of the electron in the crystal then look like the dashed curve. The potential energy in this case be represented by  $V_c(r)$ , where



Representation of P.E. of an atom in an atom (Fully drawn) and in a solid (dashed curve).

$\psi(r)$  has the same periodicity as that of the lattice.

Taking one particular atom as a <sup>origin of our</sup> coordinate system, the position of any atom may then be represented by vector ' $R_j$ ' where  $R_j$  is a lattice vector.

In tight binding approximation it is assumed that the electron in the vicinity of a particular nucleus 'j' is only slightly influenced by the presence of other atoms i.e. when the end point of a vector ' $\vec{r}$ ' lies in the vicinity of ' $R_j$ ', the wave function for the electron is approximately given by  $\phi(\vec{r} - R_j)$  and the energy of the electron is still very close to the value  $E_0$  in the free atom. The energy of an electron with a wavevector  $\vec{k}$  in the crystal is calculated on the basis of  $\phi$  a linear combination of the form

$$\psi_k(r) = \sum_j c_j(k) \phi(\vec{r} - R_j) \quad \text{--- (2)}$$

Since we are dealing the electron in a periodic field, the wave function must be a Bloch function. This restricts the choice of the coefficient ' $c_j$ '. If we take  $c_j$  to be of the form  $e^{i\vec{k} \cdot R_j}$  we have

$$\psi_k(r) = \sum_j \phi(\vec{r} - R_j) e^{i\vec{k} \cdot R_j} \quad \text{--- (3)}$$

This has the property of Bloch function and can be verified by applying a transformation corresponding to a lattice vector, say  $R_m$ .

$$\begin{aligned} \psi_k(r + R_m) &= \sum_j e^{i\vec{k} \cdot R_j} \phi[\vec{r} - (R_j - R_m)] \\ &= \sum_j e^{i\vec{k} \cdot R_m} \sum_j e^{i\vec{k} \cdot (R_j - R_m)} \phi[\vec{r} - (R_j - R_m)] \end{aligned}$$

$$\psi_k(\vec{r} + \vec{R}_m) = e^{i\vec{k} \cdot \vec{R}_m} \psi_k(\vec{r}) \quad \text{--- (4)}$$

$\Rightarrow$  eq. (3) satisfy the property of a Bloch wave

The energy of the electrons having wavefunction given by (3) can be calculated using the expression.

$$E(k) = \frac{\int \psi_k^* H \psi_k d\tau}{\int \psi_k^* \psi_k d\tau} \quad \text{--- (5)}$$

where 'H' is Hamiltonian operator for an electron in the crystal. The denominator takes care of the proper normalization of the Bloch wave function. The denominator becomes

$$\int \psi_k^* \psi_k d\tau = \sum_j \sum_m e^{i\vec{k} \cdot (\vec{R}_j - \vec{R}_m)} \int \phi^*(\vec{r} - \vec{R}_m) \phi(\vec{r} - \vec{R}_j) d\tau \quad \text{--- (6)}$$

The  $\phi(\vec{r} - \vec{R}_m)$  has appreciable value only when the end point of the vector  $\vec{r}$  lies in the vicinity of the atom 'm'; similarly  $\phi(\vec{r} - \vec{R}_j)$  has appreciable value only in the vicinity of atom 'j'. In other words we can say there is only little overlapping between the wave function, even for nearest neighbors. Thus to a first approximation we shall neglect all ~~other~~ overlapping, so that the summation over 'j' only the term  $j=m$  will be retained. Since we have assumed the wave function to be normalised we can write

$$\int \psi_k^* \psi_k d\tau = \sum_m \int \phi^*(\vec{r} - \vec{R}_m) \phi(\vec{r} - \vec{R}_m) d\tau = N \quad \text{--- (7)}$$

'N' is total number of atoms in the crystal.

Let us now consider numerator of eq. (5). The Hamiltonian of an electron in the crystal may be written as.

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V_0 - V_0(\vec{r} - \vec{R}_j) + V_0(\vec{r} - \vec{R}_j)$$

$$\text{or } H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r} - \vec{R}_J) + V_a(\vec{r} - \vec{R}_J) \quad \text{--- (8)}$$

$$\text{where } V(\vec{r} - \vec{R}_J) = V(r) - V_a(\vec{r} - \vec{R}_J)$$

The physical meaning of  $V(\vec{r} - \vec{R}_J)$  is that it represents the potential energy of the electron in the crystal at the point 'r' minus the potential energy of the electron in the same point - if there were only a single atom viz located at  $R_J$ . In other words  $V(\vec{r} - \vec{R}_J)$  represents the potential energy of the electron in point 'r' resulting from the presence of all atoms except the one located at  $R_J$ . Thus it is a sort of perturbing potential. This potential is a negative quantity.

The equation (8) can be written as.

$$-\frac{\hbar^2}{2m} \nabla^2 \phi(\vec{r} - \vec{R}_J) + V_a(\vec{r} - \vec{R}_J) \phi(\vec{r} - \vec{R}_J) = E_0 \phi(\vec{r} - \vec{R}_J) \quad \text{--- (9)}$$

$$\text{and } E(k) = \frac{\int \psi_k^* H \psi_k d\tau}{\int \psi_k^* \psi_k d\tau} = \frac{1}{N} \int \psi_k^* H \psi_k d\tau$$

$$\text{or } = \frac{1}{N} \sum_J \sum_M e^{[i\vec{k} \cdot (\vec{R}_J - \vec{R}_M)]} \int \phi^*(\vec{r} - \vec{R}_M) \left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r} - \vec{R}_J) + V_a(\vec{r} - \vec{R}_J) \right] \phi(\vec{r} - \vec{R}_J) d\tau$$

$$= \frac{1}{N} \sum_J \sum_M e^{[i\vec{k} \cdot (\vec{R}_J - \vec{R}_M)]} \int \phi^*(\vec{r} - \vec{R}_M) [E_0 + V(\vec{r} - \vec{R}_J)] \phi(\vec{r} - \vec{R}_J) d\tau$$

using eq. (9)

$$= \frac{1}{N} \sum_J \sum_M e^{[i\vec{k} \cdot (\vec{R}_J - \vec{R}_M)]} \int \left\{ \phi^*(\vec{r} - \vec{R}_M) E_0 \phi(\vec{r} - \vec{R}_J) + \phi^*(\vec{r} - \vec{R}_M) V(\vec{r} - \vec{R}_J) \phi(\vec{r} - \vec{R}_J) \right\} d\tau$$

$$\text{The first term } [i\vec{k} \cdot (\vec{R}_J - \vec{R}_M)] \int \phi^*(\vec{r} - \vec{R}_M) E_0 \phi(\vec{r} - \vec{R}_J) d\tau \quad \text{--- (10)}$$

$$= \frac{1}{N} \sum_J \sum_M e^{[i\vec{k} \cdot (\vec{R}_J - \vec{R}_M)]} \int \phi^*(\vec{r} - \vec{R}_M) E_0 \phi(\vec{r} - \vec{R}_J) d\tau$$

As overlap is small, we can neglect the second term over all m except J=m then

$$= \frac{1}{N} \sum_J \int \phi^*(\vec{r} - \vec{R}_J) E_0 \phi(\vec{r} - \vec{R}_J) d\tau = \frac{E_0 N}{N} = E_0$$

$\frac{E_0 \int \phi^*(\vec{r} - \vec{R}_J) \phi(\vec{r} - \vec{R}_J) d\tau}{N} = \frac{E_0 N}{N}$

In second term, we neglect all overlap except- (5)  
 for wave function  $\phi$  corresponding to nearest neighbors.  
 further more we assume the wave function  $\phi$  are  
 spherically symmetric. we define two quantities

$$\alpha = - \int \phi^*(r-R_j) V'(r-R_j) \phi(r-R_j) dr$$

and  $\gamma = - \int \phi^*(r-R_m) V'(r-R_j) \phi(r-R_j) dr.$

where  $R_m$  is understood to correspond to the  
 location of one of the nearest neighbors  
 of atom 'J'. we finally write-

$$E_k = E_0 - \alpha - \gamma \sum_m e^{i\vec{k} \cdot (R_j - R_m)} \quad \text{--- (11)}$$

where summation extends over nearest neighbors  
 of atom 'J' only. Here  $\alpha$  and  $\gamma$  are positive  
 as  $V'(r-R_j)$  is negative. It is observed that  
 the energy of the electrons in the crystal differs  
 from the energy of the electrons in the free  
 atoms by a constant factor ' $\alpha$ ' plus a term  
 which depends on the wave vector ' $k$ '. It is  
 the last part which transforms the discrete  
 energy levels into a band in the solid.

————— 0 —————

Replace  $\beta$  by  $\beta$ :  
where  $\vec{r}_m$  connect origin to nearest-neighbor atoms.

Simple cubic crystal

$$\vec{r}_m = (\pm a, 0, 0), (0, \pm a, 0), (0, 0, \pm a) \quad \text{--- (15)}$$

Eqn (14) becomes

$$E_k = E_0 - \alpha - 2\beta [\cos k_x a + \cos k_y a + \cos k_z a] \quad \text{--- (16)}$$

this gives minimum value of energy at the point  
 $k_x = k_y = k_z = 0$  i.e. at the origin in a plot involving  
orthogonal coordinates  $(k_x, k_y, k_z)$  in  $k$ -space.

the ~~max~~ <sup>minimum</sup> energy is given by

$$E_{\min} = E_0 - \alpha - 6\beta$$

the max. energy occurs at corners of the cube in  
 $k$ -space whose coordinates are  $(\pm \pi/a, \pm \pi/a, \pm \pi/a)$

The max. energy is given by

$$E_{\max} = E_0 - \alpha + 6\beta$$

The diff. in between min. and max. points is equal to  $12\beta$  (centered about the energy  $(E_0 - \alpha)$  for simple cubic lattice, corresponding to the related s-state of isolated system. For B.C.C and F.C.C the diff. in min and max energy points can be shown to be equal to  $16\beta$  and  $24\beta$  respectively.

