Wave equation of electron in Periodic Potential

Its solution at zone boundary and Near to zone boundary.

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Let $V(x)$ denote the potential energy of an electron in a linear lattice of lattice constant 'a', we know that the potential energy is invariant under a crystal lattice translation we can write

$$V_x = V_{(x+a)} \quad \text{——} (1)$$

As we know that any function which is invariant under a crystal lattice translation may be expanded as a Fourier series in the reciprocal lattice vectors 'G'. Hence the fourier series for the potential energy can be written as

$$V(x) = \sum_G V_G e^{iGx} \quad \text{——} (2)$$

where the values of the ~~Potential~~ coefficients V_G for actual crystal potentials tend to decrease rapidly with increasing Magnitude of 'G'. for a bare coulomb potential V_G decreases as $1/G^2$

for $V(x)$ to be a real function, it should be equal to its complex conjugate $V^*(x)$. from the fourier series we have

$$\sum_G V_G e^{iGx} = \sum_G V_G^* e^{-iGx} \quad \text{——} (3)$$

As $(e^{iGx})^* = e^{-iGx}$, we can satisfy (3) if

$$V_G^* = V_{-G} \quad \text{——} (4)$$

this is the restriction on the fourier series for $V(x)$.

We choose origin so that $V(x)$ is an even function of 'x', which means that

$$V(x) = + V(-x) \quad \text{——} (5)$$ this leads to a further restriction on V_G. Our eq (2) can be used to write

$$V(x) = \sum V_G e^{-iGx} \quad \text{——} (6)$$

On comparison ① and ⑥ we have the Series condition if $V_G = V_{-G}$ —⑦

When we combine the required ⑦ with ④ we have $V_G = V_G^*$, which shows that V_G themselves must be real if $V(x)$ is an even function of 'x'. Using ⑦ we may write

$$V(x) = \sum_{G>0} V_G \left[e^{iGx} + e^{-iGx} \right] = 2 \sum_{G>0} V_G \cos Gx \quad —⑧$$

We have set $V_0 = 0$ for convenience

The wave equation of an electron in the crystal is

$$H\psi = E\psi$$ where H → Hamiltonian or
E → Energy Eigen value
ψ → Eigen functions or orbitals

Now As $H = \left[\frac{p^2}{2m} + V(x) \right]$

we can write using the fourier series ②

$$\left[\frac{p^2}{2m} + V(x) \right] \psi(x) = \left[\frac{p^2}{2m} + \sum_G V_G e^{iGx} \right] \psi(x) = E\psi(x) \quad —⑨$$

This equation describes the motion of an electron in the potential of the ion cores and in the average Potential of the other conduction electron.

The wave function $\psi(x)$ may also be expressed as a fourier series summed over all values of the wavevector permitted by the boundary conditions to exist

$$\psi(x) = \sum_k C(k) e^{ikx} \quad —⑩$$

where 'k' is real. The set of values of 'k' is of the form $\frac{2\pi}{L} n$, which satisfy the periodic boundary condition over the length 'L'. Here 'n' is an integer may be either +ve or -ve.

To determine the values of coefficients 'C' in the fourier expansion in equation ⑩, we write the wave equation as a set of linear equations

in the (c's). We substitute the fourier expansion (10) into the wave equation (9). Our kinetic energy term is

$$\frac{1}{2m} p^2 \psi(x) = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 \psi(x) = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \frac{\hbar^2}{2m}\sum_k k^2 c(k) e^{ikx} \quad \text{—— (11)}$$

and the potential energy term is

$$\left(\sum_G V_G e^{iGx}\right)\psi(x) = \sum_G \sum_k V_G e^{iGx} c(k) e^{ikx} \quad \text{—— (12)}$$

Our the total wave equation can be obtained as the sum of (11) and (12)

$$\sum_k \frac{\hbar^2}{2m} k^2 c(k) e^{ikx} + \sum_G \sum_k V_G c(k) e^{i(k+G)x} = \epsilon \sum_k c(k) e^{ikx} \quad \text{—— (13)}$$

Multiply this eq both side by $e^{-ik'x}$ and integrate over dx, we have.

$$\int \sum_k \frac{\hbar^2}{2m} k^2 c(k) e^{i(k-k')x} dx + \int \sum_G \sum_k V_G c(k) e^{i(k+G-k')x} dx =$$

$$\int \sum_k \frac{\hbar^2}{2m} k^2 c_k e^{iGx} dx + \int \sum_G \sum_k V_G c_k e^{iGx} \cdot e^{-iGx} dx = \int \epsilon c(k) e^{i(k-k')x} dx$$

Taking $k+G = k'$ or $k = k'-G$

Also $\int_0^L e^{ikx} e^{-ik'x} dx = \begin{cases} \frac{1}{i(k-k')}\left[e^{i(k-k')L} - 1\right] = 0 & \text{when } k \neq k' \\ L & \text{when } k = k' \end{cases}$

Our $\frac{\hbar^2}{2m} k'^2 c(k') + \sum_G V_G c(k'-G) = \epsilon\, c(k')$ —— (14)

This equation is most important equation in band theory of solid. It can be written more compactly if we replace the arbitrary index symbol k' by k

Also $\lambda_k \equiv \frac{\hbar^2}{2m} k^2$ for kinetic energy of the fourier component 'k'. Our eq (14) becomes.

$$(\lambda_k - \epsilon) c(k) + \sum_G V_k c(k-G) = 0 \quad \text{—— (15)}$$

from which the values of ϵ's can be determined. Hence the wave function can be written as

$$\psi_k(x) = \sum c(k-G) e^{i(k-G)x} \quad \text{—— (16)}$$

central eqs. (15) can be written as

$$C(k) = \frac{\sum_G U_G C(k-G)}{\epsilon - \frac{\hbar^2}{2m} k^2} \quad \text{—— (17)}$$

which implies that the coefficient $C(k)$ may tend to be large if kinetic energy $\frac{\hbar^2 k^2}{2m}$ of the plane wave component $\exp(ikx)$ is nearly equal to the corresponding energy ϵ of the orbital $\psi_k(x)$ under consideration.

Approximate solution at the zone boundary.

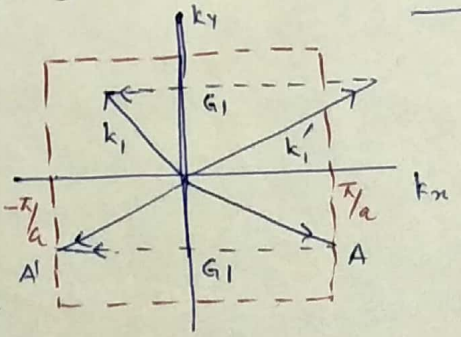
We suppose that the values of the fourier components U_G of the potential energy are small in comparision with the kinetic energy $\frac{\hbar^2 k_F^2}{2m}$ of a free electron on the fermi surface.

Consider the wavefunction with a wavevector exactly at the zone boundary i.e. at π/a or $\frac{G_1}{2}$

then $k^2 = \left(\frac{1}{2}G_1\right)^2$ $\quad (k-G_1)^2 = \left(\frac{1}{2}G_1 - G_1\right)^2 = \left[\frac{1}{2}G_1\right]^2$ —— (1)

$G_1 \rightarrow$ Reciprocal lattice vector and $k_1 = k_1' - G_1$

At the zone boundary the kinetic energy of the two component waves $\exp(ikx)$ and $\exp i(k-G_1)x$ are equal.



$$\frac{\hbar^2}{2m} k^2 = \frac{\hbar^2}{2m}(k-G_1)^2 = \frac{\hbar^2}{2m}\left(\tfrac{1}{2}G_1\right)^2 \quad \text{—— (2)}$$

Now if $C(\frac{1}{2}G_1)$ is an important coefficient in one orbital (16) of the zone boundary, then $C(-\frac{1}{2}G_1)$ is also an important coefficient in one orbital. Hence we retain only those equations in the central eq. that contain both coefficients $C(\frac{1}{2}G_1)$ and $C(-\frac{1}{2}G_1)$ and neglect all other coefficients. Then our central equation (15) becomes

with $k = \frac{1}{2}G_1$ and $\lambda_1 = \frac{\hbar^2(\frac{1}{2}G_1)^2}{2m}$

$$(\lambda_1 - \epsilon)\, c(\tfrac{1}{2}G_1) + V_1\, c(-\tfrac{1}{2}G_1) = 0 \quad \text{—(3)}$$

where $V_1 = V_{G_1} = V_{-G_1}$

Also with $k = -\frac{1}{2}G_1$, another eq. of (10) becomes

$$(\lambda_{-1} - \epsilon)\, c(-\tfrac{1}{2}G_1) + V_1\, c(\tfrac{1}{2}G_1) = 0 \quad \text{—(4)}$$

These two equations have nontrivial solution for the two coefficients $c(\frac{1}{2}G_1)$, $c(-\frac{1}{2}G_1)$ if ϵ satisfy

$$\begin{vmatrix} (\lambda_1 - \epsilon) & V_1 \\ V_1 & \lambda_{-1} - \epsilon \end{vmatrix} = 0.$$

which gives with $\lambda_1 = \lambda_{-1}$

$$(\lambda_1 - \epsilon)^2 = V_1^2 \quad \text{or} \quad \epsilon = \lambda_1 \pm V_1 = \frac{\hbar^2}{2m}(\tfrac{1}{2}G_1)^2 \pm V_1$$

Thus the energy has two roots, one lower than the free electron K.E by V_1 and one higher by V_1. Thus the potential energy has created an energy gap of extent $2V_1$ at the zone boundary.

The ratio of the c's may be found from either (3) or (4)

$$\frac{c(-\frac{1}{2}G_1)}{c(\frac{1}{2}G_1)} = \frac{\epsilon - \lambda_1}{V_1} = \frac{\lambda_1 \pm V_1 - \lambda_1}{V_1} = \pm 1$$

Thus the fourier expansion of $\psi(x)$ has the two solutions

$$\psi(x) = e^{i\frac{1}{2}G_1 x} \pm e^{-i\frac{1}{2}G_1 x} \quad \text{——(5)}$$

One solution gives the wavefunction at the bottom of the energy gap. while other gives the wavefunction at the top of the gap.

Near the zone boundary

We now solve for the orbitals with a wavevector 'k' near the zone boundary $\frac{1}{2}G_1$. We now use the same tight binding approximations, now with a wavefunction of the form:

$$\psi(x) = C_k e^{ikx} + C_{(k-G_1)} e^{i(k-G_1)x}$$

Now from the secular equation

$$(\lambda_k - E) C_k + U_1 C_{(k-G_1)} = 0 \quad \text{for wave vector 'k'}$$

$$(\lambda_{k-G_1} - E) C_{(k-G_1)} + U_1 C_k = 0 \quad \text{for wave vector } (k-G_1)$$

These have non-vanishing solution for C_k and $C_{(k-G_1)}$ provided we have

$$\begin{vmatrix} (\lambda_k - E) & U_1 \\ U_1 & \lambda_{k-G_1} - E \end{vmatrix} = 0.$$

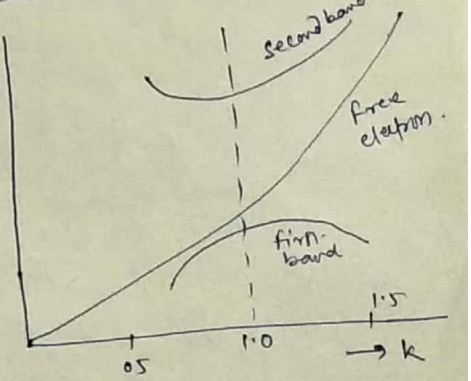
$$\text{or } (\lambda_k - E)(\lambda_{k-G_1} - E) - U_1^2 = 0.$$

$$\text{or } E^2 - E(\lambda_{k-G_1} + \lambda_k) + \lambda_{k-G_1}\lambda_k - U_1^2 = 0.$$

$$\Rightarrow E = \frac{[\lambda_{k-G_1} + \lambda_k] \pm \sqrt{(\lambda_{k-G_1} + \lambda_k)^2 - 4(\lambda_{k-G_1}\lambda_k - U_1^2)}}{2}$$

$$\text{or } E = \frac{1}{2}[\lambda_{k-G_1} + \lambda_k] \pm \left[\frac{1}{4}(\lambda_{k-G_1} - \lambda_k)^2 + U_1^2\right]^{1/2}$$

Thus 'E' has two roots and each root describes a band. These two roots are plotted in adjoining figure in periodic zone scheme.



Now if we define a parameter δ which measures the difference in wavevector between the zone boundary and 'k'

$$\Rightarrow \delta = \frac{1}{2}G_1 - k \quad \text{or} \quad k = \left(\frac{1}{2}G_1 - \delta\right)$$

Thus as $\lambda_{k-G_1} = \frac{\hbar^2}{2m}(k-G_1)^2$, $\lambda_k = \frac{\hbar^2 k^2}{2m}$

$$\lambda_{k-G_1} = \frac{\hbar^2}{2m}\left[\frac{1}{2}G_1 - \delta - G_1\right]^2 = \frac{\hbar^2}{2m}\left[-\frac{G_1}{2} - \delta\right]^2 = \frac{\hbar^2}{2m}\left[\delta^2 + \frac{G_1^2}{4} - G_1\delta\right]$$

and $\lambda_k = \frac{\hbar^2}{2m}\left[\frac{G_1}{2} - \delta\right]^2 = \frac{\hbar^2}{2m}\left[\frac{G_1^2}{4} + \delta^2 - G_1\delta\right]$.

Near Zone Boundary

We now take the wavefunction of the form

$$\psi(x) = C(k)\, e^{ikx} + C(k-G_1)\, e^{i(k-G_1)x} \quad \text{—— (A)}$$

from the central equation we have

$$(\lambda_k - \epsilon)\, C(k) + V_1\, C(k-G_1) = 0 \quad \text{—— (B)}$$

and $(\lambda_{(k-G_1)} - \epsilon)\, C(k-G_1) + V_1\, C(k) = 0$. —— (C)

where $\lambda_k = \frac{\hbar^2 k^2}{2m}$ and $\lambda_{(k-G_1)} = \frac{\hbar^2}{2m}(k-G_1)^2$

(B) and (C) have non-vanishing solution provided determinant of their coefficient is zero.

$$\begin{vmatrix} (\lambda_k - \epsilon) & V_1 \\ V_1 & \lambda_{(k-G_1)} - \epsilon \end{vmatrix} = 0.$$

or $(\lambda_k - \epsilon)(\lambda_{(k-G_1)} - \epsilon) - V_1^2 = 0$

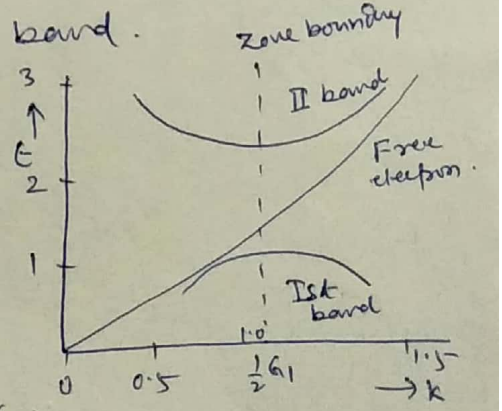
or $\lambda_k \lambda_{(k-G_1)} - \epsilon(\lambda_k + \lambda_{(k-G_1)}) + \epsilon^2 - V_1^2 = 0$.

or $\epsilon^2 - \epsilon(\lambda_k + \lambda_{(k-G_1)}) + \lambda_{(k-G_1)}\lambda_k - V_1^2 = 0$

which gives us.

$$\epsilon = \frac{1}{2}(\lambda_{(k-G_1)} + \lambda_k) \pm \left[\frac{1}{4}(\lambda_k - \lambda_{(k-G_1)})^2 + V_1^2\right]^{1/2} \quad \text{—— (d)}$$

Each root describes an energy band.



If we define a parameter δ such that it is equal to the difference in wavevector between the zone boundary and k'

$$\delta \equiv \tfrac{1}{2}G_1 - k \quad \text{or} \quad k = \tfrac{1}{2}G_1 - \delta \quad \text{—— (e)}$$

then

$$\epsilon = \frac{\hbar^2}{2m}\left(\tfrac{1}{4}G_1^2 + \delta^2\right) \pm \left[4\lambda_1\left(\frac{\hbar^2\delta^2}{2m}\right) + V_1^2\right]^{1/2}$$

or $\equiv \frac{\hbar^2}{2m}\left[\tfrac{1}{4}G_1^2 + \delta^2\right] \pm V_1\left[1 + 2\left(\frac{\lambda_1}{V_1^2}\right)\frac{\hbar^2\delta^2}{2m}\right]$ —— (f)

Comparing (f) with the energy values at zone boundary

i.e. $\epsilon = \frac{\hbar^2}{2m}\left(\frac{1}{2}G_1\right)^2 \pm V_1$

we can write

$$\epsilon_k(+) \equiv \epsilon_1(+) + \frac{\hbar^2\delta^2}{2m}\left(1 + \frac{2\Lambda_1}{V_1}\right) \quad \text{— (g)}$$

$$\epsilon_k(-1) \equiv \epsilon_1(-) + \frac{\hbar^2\delta^2}{2m}\left(1 - \frac{2\Lambda_1}{V_1}\right) \quad \text{— (h)}$$

eq. (h) and (g) gives the roots for the energy when the wave vector is very close to the zone boundary at $\left(\frac{1}{2}G_1\right)$. It is clear that the energy varies as δ^2. for V_1 negative, the solution $\epsilon_k(-)$ corresponds to the upper of the two band and $\epsilon_k(+)$ corresponds to the lower of the two bands.

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