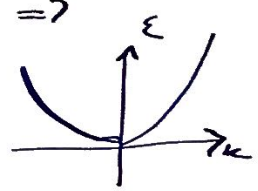


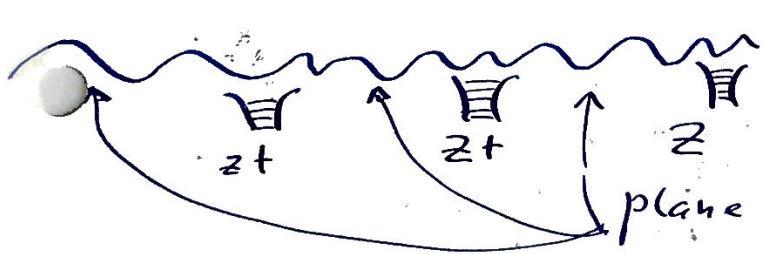
Nearly free electron model

Start with free electron model:

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} \Rightarrow \langle k | \hat{H}_0 | k \rangle = \epsilon(k) \Rightarrow \epsilon(k) = \frac{\hbar^2 k^2}{2m}$$

$$|k\rangle = \frac{1}{L^3} e^{i\vec{k}\cdot\vec{r}}$$


Let's include the periodic potential over the free electrons moving in the crystal



$$\hat{H} = \hat{H}_0 + V(\vec{r})$$

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

R is any lattice vector

plane wave in between

Let's transform it into k-space:

$$\langle k' | V | k \rangle = \frac{1}{L^3} \int d\vec{r} e^{i(\vec{k}' - \vec{k})\cdot\vec{r}} V(\vec{r}) \equiv V(\vec{k} - \vec{k}')$$

$$\begin{cases} = 0 & \text{if } \vec{k} - \vec{k}' \neq \vec{G} \\ \neq & \vec{k} - \vec{k}' = \vec{G} \end{cases}$$

To calculate the dispersion (eigenvalue) $\epsilon(k)$ we need to consider the perturbation theory (recall the potential is really weak)

$$\epsilon(k) = \epsilon_0(k) + \langle k | V | k \rangle = \epsilon_0(k) + V_0$$

1st order "BORING" just the shift

Move on to the 2nd term:

$$\epsilon(k) = \epsilon_0(k) + V_0 + \sum_{\substack{k' \neq k \\ \vec{k}' = \vec{k} + \vec{G}}} \frac{|\langle k' | V | k \rangle|^2}{\epsilon_0(k) - \epsilon_0(k')}$$

but for many states it can be that $\epsilon_0(k) = \epsilon_0(k') \Rightarrow$ the sum diverges!

This means that the ground state is degenerate and we need to apply the degenerate perturbation theory.

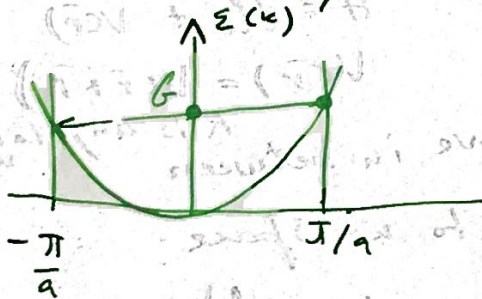
in the degenerate case

$$E_0(\bar{k}) = E_0(\bar{k}')$$

$$\text{and } \bar{k}' = \bar{k} + \bar{G}$$

It is easier to understand this in 1D.

Since $E(\bar{k}) \sim k^2$ we get $k' = -k = \frac{\pi}{a}$ which is precisely the zone boundary



which is also true for 3D. But this also means that at the zone boundary

the second pert. term diverges.

So let's ~~use~~ treat the case according to g.m. for the degenerate states, i.e.

If $|k\rangle$ and $|k+G\rangle$ are of the same energy then we must diagonalize their matrix elements 1st:

$$\begin{cases} \langle k | H | k \rangle = E_0(k) \\ \langle k' | H | k' \rangle = E_0(k') = E_0(\bar{k} + \bar{G}) \\ \langle k | H | k' \rangle = V_{k-k'} = V_G^* \\ \langle k' | H | k \rangle = V_{k-k'}^* = (V_G)^* \end{cases}$$

$$V_G^* = V_{-G} \text{ since } V \text{ is real}$$

Since $|k\rangle$ and $|k'\rangle$ are the basis states

(we write down any wave function as

$$|\Psi\rangle = \alpha |k\rangle + \beta |k'\rangle = \alpha |k\rangle + \beta |k+\bar{G}\rangle$$

or

$$\begin{pmatrix} \langle k | H | k \rangle & \langle k | H | k' \rangle \\ \langle k' | H | k \rangle & \langle k' | H | k' \rangle \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$\begin{pmatrix} \epsilon_0(k) & V_G^* \\ V_G & \epsilon_0(k+\bar{G}) \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

$$(\epsilon_0(k) - E)(\epsilon_0(k+\bar{G}) - E) - |V_G|^2 = 0$$

Note: once we diagonalize the degenerate state, the rest is OK in the normal non-degenerate theory.

A) k at the zone boundary

so $k' = k + \bar{G}$, in this case $\epsilon_0(k) = \epsilon_0(k + \bar{G})$

$$(\epsilon_0(k) - E)(\epsilon_0(k) - E) - |V_G|^2 = 0 \Rightarrow$$

$$(\epsilon_0(k) - E)^2 = |V_G|^2 \Rightarrow$$

$$E_{\pm} = \epsilon_0(k) \pm |V_G|$$

$E_+ - E_- = |V_G| \leftarrow$ the gap at the zone boundary!

Lets solve this in 1D:

Let me assume that $V(x) = V \cos(\frac{2\pi}{a}x)$

with $V > 0$

BZ $k = \frac{\pi}{a}$ $k' = -k = -\pi/a \Rightarrow k' - k = G = \frac{2\pi}{a}$

and $E(k) = E(k')$

From $\begin{pmatrix} E_0(k) \\ V_G \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$

$\begin{pmatrix} E_0(k) \\ V_G \end{pmatrix} = \begin{pmatrix} E_0(k) \\ E_0(k+G) \end{pmatrix} = \begin{pmatrix} E_0(k) \\ E_0(k) \end{pmatrix}$

$\alpha = \frac{+}{-} \beta$

we plug here
 $E_+ = E_0(k) + V_G$
 $E_- = E_0(k) - V_G$
 and solve for α and β

thus

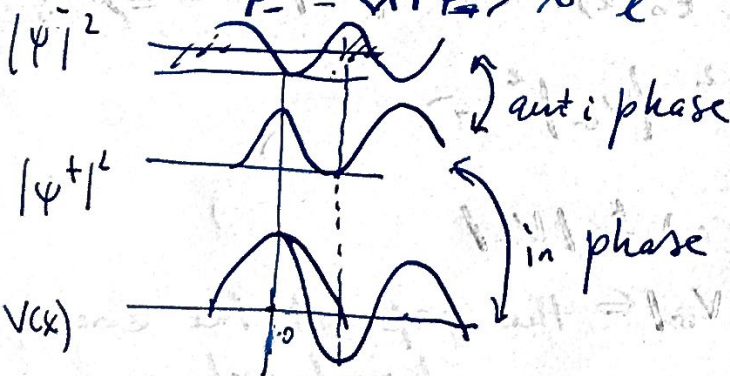
$|\Psi\rangle = \alpha |k\rangle + \beta |k'\rangle = \frac{1}{\sqrt{2}} (|k\rangle \pm |k'\rangle)$

$\Rightarrow |\Psi_{\pm}\rangle = \frac{1}{\sqrt{2}} (|k\rangle \pm |k'\rangle)$ or in the x-coordinated space

$\langle x | k \rangle = \frac{e^{ikx}}{\sqrt{L}}$ $|k\rangle \rightarrow e^{ikx} = e^{i\pi/a x}$
 $|k'\rangle \rightarrow e^{-ik'x} = e^{-i\pi/a x}$

so $\Psi_+ \equiv \langle x | \Psi_+ \rangle \sim e^{i\pi/a x} + e^{-i\pi/a x} \propto \cos(\frac{\pi}{a}x)$

$|\Psi_-|^2 \sim \Psi_- \equiv \langle x | \Psi_- \rangle \sim e^{i\pi/a x} - e^{-i\pi/a x} \sim \sin(\frac{\pi}{a}x)$



The periodic potential scatters off between Ψ_+ and Ψ_-

$|k\rangle$ States $|k+G\rangle$

Again $V(x)$ scatters between $|k\rangle$ and $|k+\pi/a\rangle$ states and if the energy is the same then mixing is very strong to form "entanglement" the state with $+V_0$ and $-V_0$ at the zone boundaries.

Another case

Away from the zone boundary.

Again lets consider a 1D case. This time we need to solve

$$(\epsilon_0(k) - E)(\epsilon_0(k+\pi/a) - E) - |V_G|^2 = 0$$

but not for the specific values of k . ~~at~~ away from the zone boundary.

The trick is to expand around the zone boundary k value. At the z.b. $k = \pm \frac{\pi}{a}n$ and the separation $G = \pm \frac{2\pi}{a}n$, $n=1,2,3,\dots$

Recall right at the z.b. gap opens up.

Lets move ^{away} from the z.b. $k = \frac{\pi}{a}n + \delta$

$$\text{and } k' = -\frac{\pi}{a}n + \delta \Rightarrow$$

$$\begin{aligned} \epsilon_0\left(\frac{\pi}{a}n + \delta\right) &= \frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a}n\right)^2 + \frac{2\pi n}{a}\delta + \delta^2 \right] \\ \epsilon_0\left(-\frac{\pi}{a}n + \delta\right) &= \frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a}n\right)^2 - \frac{2\pi n}{a}\delta + \delta^2 \right] \end{aligned}$$

The characteristic eqn. becomes:

$$\frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a} \cdot n \right)^2 + \delta^2 \right] - E + \frac{\hbar^2}{2m} 2n\pi\delta/a = 0$$

$$\left(\frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a} n \right)^2 + \delta^2 \right] - E - \frac{\hbar^2}{2m} 2\pi n \frac{\delta}{a} \right) - |V_0|^2 = 0 \Rightarrow$$

$$\left(\frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a} n \right)^2 + \delta^2 \right] - E \right)^2 = \left(\frac{\hbar^2}{2m} 2\pi n \frac{\delta}{a} \right)^2 + |V_0|^2$$

$$E_{\pm} = \frac{\hbar^2}{2m} \left[\left(\frac{\pi}{a} n \right)^2 + \delta^2 \right] \pm \sqrt{\left(\frac{\hbar^2}{2m} 2\pi n \frac{\delta}{a} \right)^2 + |V_0|^2}$$

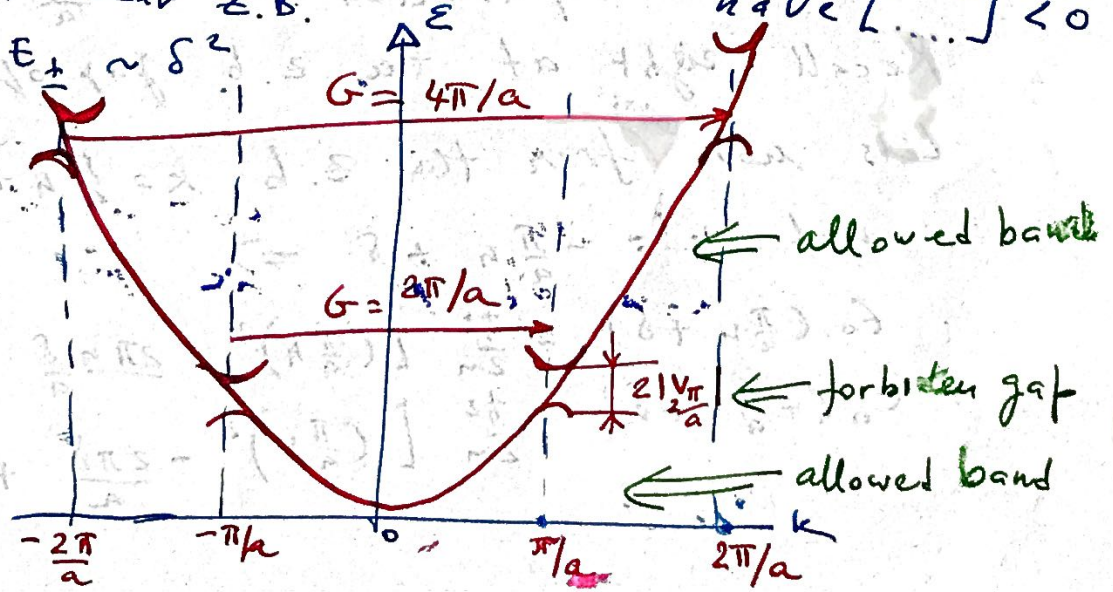
↑
since δ is very small
we can expand it $\sqrt{1+x}$

$$E_{\pm} = \frac{\hbar^2}{2m} \left(\frac{\pi}{a} n \right)^2 \pm |V_0| + \frac{\hbar^2 \delta^2}{2m} \left[1 \pm \frac{\hbar^2 \left(\frac{\pi}{a} n \right)^2}{m |V_0|} \right]$$

if $|V_0|$ is small

In short near Z.B.

So both solutions have $[...] < 0$



We can now introduce the mass as the amount of curvature at the bottom of the band.

So we can rewrite the eqn for E_{\pm} in terms of:

$$E_{\pm} (\epsilon_0 \epsilon + \delta) = \epsilon_{\pm} \pm \frac{\hbar^2 \delta^2}{2m_{\pm}^*}$$

Where

$$m_{\pm}^* = \frac{m}{\left| 1 \pm \frac{\hbar^2}{m} \left(\frac{\pi}{a} \right)^2 \cdot \frac{1}{|V_0|} \right|}$$

We use $| \dots |$ since this expression is < 0 .

Moving to 2D and 3D:

- at the z.b. potential opens the gap due to the scattering by the reciprocal lattice vector.



states just above z.b. go up in energy

and just below z.b. go down.

- The difference is that in 1D

if k is at the z.b. there is exactly one $k' = k - G$ at z.b.

$$\text{so } \epsilon(k) = \epsilon(k')$$

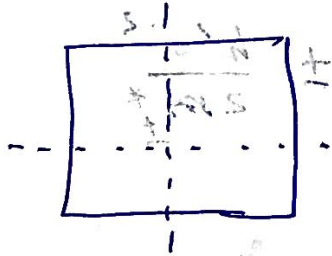
those 2 waves mix strongly and open the gap.

in 2D and ~~esp~~ especially in 3D

for a single k can be many k'
 so that $k - k' = G$

In this case one needs to mix all
 the waves with the same energy $E(k)$

e.g.



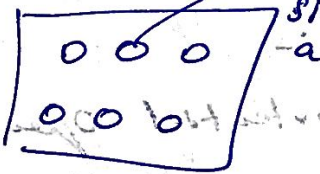
$$k = \left(\frac{\pi}{a}, \frac{\pi}{a} \right)$$

all degenerate!

and separated by G

B.T.W If you make a metamaterial

e.g. holes and shine light with $\lambda \approx a$



we ~~get~~ get exactly
 the same "band
 structure" with allowed
 a forbidden states

They called PHOTONIC CRYSTALS.

(natural example is opal)

made of a periodic array of
 sub-micron spheres of silica

and the wings of butterflies

made of periodic polymer.

But what if the scattering is strong?

Felix Bloch had to answer this Φ in 1928. His theory is known as the Bloch theorem:

Bl. th.: an electron in a periodic potential has eigenstates of the form $\Psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} U_{\mathbf{k}}^{\alpha}(\mathbf{r})$, where $U_{\mathbf{k}}^{\alpha}(\mathbf{r})$ is periodic inside the unit cell, and \mathbf{k} is chosen within the first Br. zone.

The periodic function $U_{\mathbf{k}}^{\alpha}$ is known as the Bloch function, and Ψ is known as the modified plane wave. Since $U_{\mathbf{k}}^{\alpha}$ is periodic we can write it as:

$$U_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{U}_{\mathbf{G},\mathbf{k}}^{\alpha} e^{i\mathbf{G}\cdot\mathbf{r}}$$

this form guarantees that $U_{\mathbf{k}}^{\alpha}(\mathbf{r}) = U_{\mathbf{k}}^{\alpha}(\mathbf{r} + \mathbf{R})$

$$U_{\mathbf{k}}^{\alpha}(\mathbf{r} + \mathbf{R}) = \sum_{\mathbf{G}} \tilde{U}_{\mathbf{G},\mathbf{k}}^{\alpha} e^{i\mathbf{G}\cdot\mathbf{R} + i\mathbf{G}\cdot\mathbf{r}} = \sum_{\mathbf{G}} \tilde{U}_{\mathbf{G},\mathbf{k}}^{\alpha} e^{i(\mathbf{G} + \mathbf{G}')\cdot\mathbf{r}} = U_{\mathbf{k}}^{\alpha}(\mathbf{r})$$

So the full wave function is:

$$\Psi_{\mathbf{k}}^{\alpha}(\mathbf{r}) = \sum_{\mathbf{G}} \tilde{U}_{\mathbf{G},\mathbf{k}}^{\alpha} e^{i(\mathbf{G} + \mathbf{k})\cdot\mathbf{r}}$$

this simply means that each state can be written as the sum of plane waves which differ by \mathbf{G} .

But recall that $\langle \mathbf{k}' | V | \mathbf{k} \rangle = 0$ unless $\mathbf{k} - \mathbf{k}' = \mathbf{G}$ so the Schrödinger eqn is block diagonal in \mathbf{k} space and for any given eigenfunction only waves with \mathbf{k} and $\mathbf{k} + \mathbf{G}$ can be mixed.

$$\text{i.e. } \left[\frac{p^2}{2m} + V(r) \right] \Psi(r) = E \Psi(r) \Rightarrow \text{FT}$$

$$\sum_{\bar{G}} V_{\bar{G}} \Psi_{\mathbf{k}-\bar{G}} = \left[E - \frac{\hbar^2 \mathbf{k}^2}{2m} \right] \Psi_{\mathbf{k}}$$

where we used the fact th $V_{\mathbf{k}-\mathbf{k}'}$ are non-zero if $\mathbf{k}-\mathbf{k}' = \bar{G}$

So the electrons are still labeled by \bar{G} . (in physical sense it means, doesn't matter how strong is the potential, the electrons behave: almost like free electrons and they see no ionic core at all!!! and they are distorted only at the ion core sites and \mathbf{k} is now crystal momentum.

This is the reason why the electron m.f.p. is NOT on the order of interatomic distance.

WHENEVER TRANS. INV. IS CORRUPTED SOLUTIONS WITH COMPLEX \bar{k} occur and represent localized wavefunction.