Nearly free electron model

Start with free electron model:

\[ \hat{H}_0 = \frac{\hat{p}^2}{2m} = \Rightarrow \hat{H} |k\rangle = E(k) |k\rangle = \frac{\hbar^2 k^2}{2m} \]

\[ E(k) = \frac{\hbar^2 k^2}{2m} \]

\[ k^2 = \frac{2m}{\hbar^2} \]

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

\[ H = \hat{H}_0 + V(r) \]

\[ V(r) = V(r + R) \]

\[ R \text{ is any lattice vector} \]

Plane wave in between.

Let's transform it into k-space:

\[ \langle k' | V(r) | k \rangle = \frac{1}{L^3} \int d^3r \ e^{i(k-r).r} V(r) \delta(k-k') \]

\[ = \begin{cases} 0 & \text{if } \bar{k} - \bar{k}' \neq \bar{G} \\ \neq \bar{k}, \bar{k}' = \bar{G} \end{cases} \]

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

\[ E(k) = E_0(k) + \langle k | V | k \rangle \]

1st order (not really boring).

Move on to the 2nd term:

\[ E(k) = E_0(k) + V_0 + \sum \frac{\langle k' | V | k \rangle^2}{E_0(k) - E_0(k')} \]

but for many states it can be that \( E_0(k) = E_0(k') = \) the sum diverges!
This means that the ground state is degenerate and we need to apply the degenerate perturbation theory.

In the degenerate case

\( E_0(k) = E_0(k') \)

and \( k' = k + \bar{\varepsilon} \)

It is easier to understand this in 1D.

Since \( E(k) \sim k^2 \) we get \( k' = -k = \frac{\pi n}{a} \)

which is precisely the zone boundary \( E(k) = E(\pi/a) \)

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

the second pert. term diverges.

So let's treat the case according to

Q.M. for the degenerate states, i.e.

If \( |k\rangle \) and \( |k + \bar{\varepsilon}\rangle \) are of the same energy then we must diagonalize their matrix elements 1st:

\[
\begin{align*}
\langle k | H | k \rangle &= E_0(k) \\
\langle k' | H | k' \rangle &= E_0(k') = E_0(k + \bar{\varepsilon}) \\
\langle k' | H | k \rangle &= V_{k - k'} = V^* \\
\langle k | H | k' \rangle &= V_{k - k' - (V \bar{\varepsilon})} \\
\end{align*}
\]

\[ V^* = V \bar{\varepsilon} \text{ since } V \text{ is real} \]
Since \( |k\rangle \) and \( |k'\rangle \) are the basis states, we write down any wave function as

\[
|\psi\rangle = \alpha |k\rangle + \beta |k'\rangle = \alpha |k\rangle + \beta |k+6\rangle
\]

or

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

\[
\begin{pmatrix}
\varepsilon_0(k) & V_0 \\
V_0 & \varepsilon_0(k+6)
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} = E
\]

\[
(\varepsilon_0(k) - E)(\varepsilon_0(k+6) - E) - |V_0|^2 = 0
\]

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

A) \( k \) at the zone boundary

\[
\begin{pmatrix}
\varepsilon_0(k) & V_0 \\
V_0 & \varepsilon_0(k+6)
\end{pmatrix}
\begin{pmatrix}
\alpha \\
\beta
\end{pmatrix} = E
\]

\[
(\varepsilon_0(k) - E)^2 - |V_0|^2 = 0
\]

\[
(\varepsilon_0(k) - E)^2 = |V_0|^2
\]

\[
E_+ = \varepsilon_0(k) + |V_0|
\]

\[
E_+ - E_- = 1|V_0| \leq \text{the gap at the zone boundary!}
\]
Let's solve this in 1D:

Let us assume that \( V(x) = V \cos \left( \frac{2\pi}{a} x \right) \)

With \( V > 0 \)

\[
\begin{align*}
BZ \quad k = \frac{\pi}{a} \quad &k' = -k = -\frac{\pi}{a} \Rightarrow k' - k = \frac{2\pi}{a} \\
\text{and} \quad \epsilon(k) = \epsilon(k')
\end{align*}
\]

From

\[
\begin{pmatrix}
\epsilon_0(k) \\
V_0
\end{pmatrix}
\begin{pmatrix}
V_0^* \\
\epsilon_0(k+\omega)
\end{pmatrix}
= E(k)
\]

\[
\begin{pmatrix}
\epsilon_0(k) \\
V_0
\end{pmatrix}
\begin{pmatrix}
V_0^* \\
\epsilon_0(k+\omega)
\end{pmatrix}
= E(k)
\]

\[
\begin{pmatrix}
E_+ = \epsilon_0(k) + V_0 \\
E_- = \epsilon_0(k) - V_0
\end{pmatrix}
\]

and solve for \( \alpha \) and \( \beta \)

\[
\begin{align*}
|\psi\rangle &= \alpha |k\rangle + \beta |k\rangle \\
&= \frac{1}{\sqrt{2}} \left( |k\rangle \pm |k\rangle \right)
\end{align*}
\]

\[
\begin{align*}
\langle x | k \rangle &= \frac{e^{ikx}}{\sqrt{2}} \\
|k\rangle &\rightarrow e^{ikx} = e^{i\pi/a} x \\
|k\rangle &\rightarrow e^{-i\pi/a} x = e^{-i\pi/a} x
\end{align*}
\]

So \( \psi_+ = \langle x | \psi_+ \rangle = e^{i\pi/a} x + e^{-i\pi/a} x \propto \cos \left( \frac{\pi}{a} x \right) \)

\( \psi_- = \langle x | \psi_- \rangle \propto e^{i\pi/a} x - e^{-i\pi/a} x \propto \sin \left( \frac{\pi}{a} x \right) \)

\[
\begin{align*}
|\psi\rangle^2 &= \text{in phase} \\
|\psi+\rangle^2 &= \text{anti-phase} \\
V(x)
\end{align*}
\]

The periodic potential scatters off between \( |k\rangle \) and \( |k+\omega\rangle \)
Again $V(x)$ scatters between $1k>$ and $1k+6>$ states and if the energy is the same then mixing is very strong to form "entanglement" the state with $\frac{+V_0}{2} \alpha_n - \frac{V_0}{2} \beta_n$ at the zone boundaries.

Another case Away from the zone boundary.

Again let's consider a 1D case. This time we need to solve

$$(E_0(n) - E)(E_0(n+6) - E) - 1V_0/\hbar^2 = 0$$

but not for the specific values of $k$. Away from the zone boundary.

The trick is to expand around the zone boundary $k$ value. At the Z.B. $k = \pm \frac{\pi}{a} \hbar$ and the separation $6 = \pm \frac{2\pi}{a} \hbar$, $n = 1, 2, \ldots$.

Recall right at the Z.B. jail opens up.

Let's move away from the Z.B. $k = \frac{\pi}{a} \hbar + \delta$ and $k' = -\frac{\pi}{a} \hbar + \delta = \Rightarrow$

$$E_0 \left( \frac{\pi}{a} \hbar + \delta \right) = \frac{h^2}{2m} \left( \left( \frac{\pi}{a} \hbar \right)^2 + \frac{2\pi \hbar \delta}{a} + \delta^2 \right)$$

$$E_0 \left( -\frac{\pi}{a} \hbar + \delta \right) = \frac{h^2}{2m} \left[ \left( \frac{\pi}{a} \hbar \right)^2 - \frac{2\pi \delta}{a} + \delta^2 \right]$$
The characteristic equation becomes:

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

or

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

since \( \delta \) is very small, we can expand it \( \sqrt{1+x} \)

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

In short, near \( \pm \frac{\pi}{a} \)

\[ E_+ \sim \delta^2 \]

So both solutions have \( \left[ \cdots \right] < 0 \)

\[ G = 4\pi/a \]

\[ \text{allowed band} \]

\[ \text{forbidden gap} \]

\[ \text{allowed band} \]
We can now introduce the mass $m$ as in the amount of curvature at the bottom of the band.

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

$$E_\pm (\delta C + \delta) = C_\pm \pm \frac{\hbar^2 \delta_{\pm}^2}{2 m^*}$$

Where

$$m^* = \frac{m}{1 \pm \frac{\hbar^2}{m} \left( \frac{n}{a} \right)^2 \cdot \frac{1}{1 + \frac{1}{4}} \cdot \frac{1}{4}}$$

We use $\frac{1}{4}$ since this expression is $< 0$.

Moving to 2D and 3D:

At the 2D potential opens the gap due to the scattering by the reciprocal lattice vector.

I state just above 2.B. go up in energy and just below 2.B. go down.

The difference is that in 1D

If $k$ is at the 2.B. there is exactly one $k' = k - \delta$ at 2.B.

So $E(k) = E(k')$.

Those 2 waves mix strongly and open the gap.
In 2D and especially in 3D, a single wave can be any \( \mathbf{k} \) so that \( \mathbf{k} - \mathbf{k}' = \mathbf{G} \). In this case, one needs to mix all the waves with the same energy \( E(k) \).

\[ E = \pm \frac{1}{2} \omega + \frac{1}{2} \left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right) \]

all degenerate.

and separated by \( \mathbf{G} \).

B.T.W. If you make a metamaterial,

holes and shine light with it/a,

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

They called **photonic crystals**.

(natural example is gemstone 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 question in 1928. His theory is known as the Bloch theorem:

\[
\Psi_k^\alpha(r) = e^{i k \cdot r} V_k^\alpha(r), \quad \text{where } V_k^\alpha(r) \text{ is periodic inside the unit cell, and } k \text{ is chosen within the first Brillouin zone.}
\]

The periodic function \( V_k^\alpha \) is known as the Bloch function, and \( \Psi_k^\alpha \) is known as the modified plane wave. Since \( V_k^\alpha \) is periodic we can write it as:

\[
V_k^\alpha(r) = \sum_{\mathbf{G}} V_{\mathbf{G}+\mathbf{k}}^\alpha e^{i \mathbf{G} \cdot r}
\]

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

\[
V_k^\alpha(r+\mathbf{R}) = \sum_{\mathbf{G}} V_{\mathbf{G}+\mathbf{k}}^\alpha e^{i \mathbf{G} \cdot (r+\mathbf{R})} = e^{i \mathbf{G} \cdot \mathbf{R}} = 1
\]

So the full wave function is:

\[
\Psi_k^\alpha(r) = \sum_{\mathbf{G}} V_{\mathbf{G}+\mathbf{k}}^\alpha e^{i (\mathbf{G}+\mathbf{k}) \cdot r}
\]

This simply means that each state can be written as the sum of plane waves which are different by \( \mathbf{G} \).

But recall that \( \langle k | V | k \rangle = 0 \) unless \( |k-k'| = 1 \) so the Schrödinger equation is block diagonal in \( k \) space and for any given eigenfunction, only waves with \( k \) and \( k+\mathbf{G} \) can be mixed.
\[ \left( \frac{p^2}{2m} + V(r) \right) \psi(r) = E \psi(r) \Rightarrow FT \]

\[ \sum V_g \psi_{k-g} = \left[ E - \frac{\hbar^2 k^2}{2m} \right] \psi_k \]

When we used the fact that \( V_{k-k'} \) are non-zero if \( k-k' = g \).

So the electrons are still labeled by \( g \).

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 \( k \) is now crystal momentum.

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

\[ \text{WHENEVER TRANS. INV. IS CORRUPTED WITH COMPLEX } \bar{E} \text{ OCCUR AND REPRESENT LOCALIZED \ WAVEFUNCTIONS} \]