Band Theory II:

Nearly Free Electrons

\[ \psi_k(x) = \sum \Gamma \cdot (k - \vec{G}) \cdot e^{i(k - \vec{G}) \cdot \vec{x}} \]

Since \( \psi_k(x) \) is a superposition of several different momentum states, separated by reciprocal lattice vectors, \( \vec{K} \) is only defined modulo a reciprocal lattice vector. Thus we may restrict \( \vec{K} \) to the first Brillouin Zone. \( E(\vec{K}) \) then becomes a multiple valued function.
1D Example

--- free electrons

--- nearly free electrons

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

We have seen that a periodic potential opens an energy gap in the dispersion relation at the boundary of the Brillouin zone.
Let us investigate this phenomenon using the central equation.

Assume the Fourier components of the potential $U_0$ are small compared to the kinetic energy of a free electron at the Brillouin zone boundary (nearly free electrons). Then $U_0$ can be treated as a perturbation.

At the zone boundary

\[ k = \frac{G}{2} = \frac{n\pi}{a}, \text{ one has} \]

\[ k^2 = \left(\frac{G}{2}\right)^2 = (k-G)^2. \]

$C\left(\frac{G}{2}\right)$ and $C\left(-\frac{G}{2}\right)$ are the most important coefficients in the central equation.
\[(\lambda - \varepsilon)C\left(\frac{G}{2}\right) + U_G C\left(-\frac{G}{2}\right) = 0 \]

\[(\lambda - \varepsilon)C\left(-\frac{G}{2}\right) + U_G C\left(\frac{G}{2}\right) = 0,\]

where \( \lambda = \frac{\hbar^2}{2m}(\frac{G}{2})^2 \) and \( U_G = U_{-G} \).

These equations have a solution if
\[
\begin{vmatrix}
\lambda - \varepsilon & U_G \\
U_G & \lambda - \varepsilon
\end{vmatrix} = 0
\]

\[\Rightarrow \varepsilon = \lambda \pm U_G = \frac{\hbar^2}{2m}(\frac{G}{2})^2 \pm U_G\]

The energy has two roots, one lower than the free electron energy by \( U_G \), one higher by \( U_G \). Thus the potential \( U(x) = 2U_G \cos Gx \) has created a gap \( 2U_G \) at the
Zone boundary, in agreement with the argument given in lecture 10. The ratios of the C's may be found from

\[(\lambda - \varepsilon) \, C(\frac{G}{2}) + U_0 \, C(-\frac{G}{2}) = 0\]

\[
\frac{C(\frac{G}{2})}{C(-\frac{G}{2})} = \frac{U_0}{\varepsilon - \lambda} = \frac{U_0}{\pm U_0} = \pm 1
\]

Thus \[\psi(x) \propto e^{i\frac{Gx}{2}} \pm e^{-i\frac{Gx}{2}}.\]

\[ \Rightarrow \text{standing waves, as we argued earlier on physical grounds.} \]

Now let's solve for orbitals with wavevector \( k \) near the zone boundary \( \frac{G}{2} \) using the same 2-component approximation.
\[ \Psi_k(x) = C(k) e^{ikx} + C(k-G) e^{i(k-G)x} \]

Central equation:

\[
(\lambda_k - \varepsilon) C(k) + U_G C(k-G) = 0
\]

\[
(\lambda_{k-G} - \varepsilon) C(k-G) + U_G C(k) = 0
\]

Solution exists provided

\[
\begin{vmatrix}
\lambda_k - \varepsilon & U_G \\
U_G & \lambda_{k-G} - \varepsilon
\end{vmatrix} = 0
\]

\[
\Rightarrow \varepsilon = \frac{\lambda_{k-G} + \lambda_k}{2} + \sqrt{\left(\frac{\lambda_{k-G} - \lambda_k}{2}\right)^2 + U_G^2}
\]

Let \( k = \frac{G}{2} + sk \)

\[\lambda_k = \frac{\hbar^2}{2m} \left( \frac{G}{2} + sk \right)^2 = \frac{\hbar^2 (G)^2}{2m} + \frac{\hbar^2 m}{2} sk + \frac{\hbar^2}{2m} sk^2 \]

\[\lambda_{k-G} = \frac{\hbar^2}{2m} \left( sk - \frac{G}{2} \right)^2 = \frac{\hbar^2 (G)^2}{2m} - \frac{\hbar^2 m}{2} sk + \frac{\hbar^2}{2m} sk^2 \]
\[ \lambda_{k-G} + \lambda_k = \frac{\hbar^2}{2m} \left[ \left( \frac{G}{\epsilon} \right)^2 + 8k^2 \right] \]

\[ \lambda_{k-G} - \lambda_k = -\frac{\hbar^2 G s k}{2m} \]

\[ \varepsilon_+(sk) = \frac{\hbar^2}{2m} \left( \frac{G}{\epsilon} \right)^2 + \frac{\hbar^2 s k^2}{2m} + \sqrt{\left( \frac{\hbar^2 G s k}{2m} \right)^2 + \varepsilon_{\text{c}}^2} \]

\[ \varepsilon_-(sk) \approx \frac{\hbar^2}{2m} \left( \frac{G}{\epsilon} \right)^2 + \varepsilon_{\text{c}} + \frac{\hbar^2 s k^2}{2m} \left( 1 \pm \frac{2\lambda}{\varepsilon_{\text{c}}} \right) \]

where \( \lambda = \frac{\hbar^2}{2m} \left( \frac{G}{\epsilon} \right)^2 \). Notice that by assumption, \( \frac{\lambda}{\varepsilon_{\text{c}}} \ll 1 \).

The graph shows the energy bands and the behavior of \( \varepsilon \) with respect to \( k \). The first derivative of the energy with respect to \( k \) is negative, indicating a decreasing rate of change.
Effective mass

Consider an electron in a one-dimensional crystal with an electric field \( \mathbf{E} \).

Newton's law states

\[
m \frac{dV_g}{dt} = -e \mathbf{E}
\]

\( V_g = \frac{1}{\hbar} \frac{dE}{dk} \) = group velocity

\[
\frac{dV_g}{dt} = \frac{1}{\hbar} \frac{d^2E}{dk^2} \frac{dk}{dt} = \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \frac{d\hbar k}{dt}
\]

Semiclassical equation of motion:

\[
\frac{d\hbar k}{dt} = -e \mathbf{E}
\]

But

\[
\frac{d\hbar k}{dt} = \left( \frac{1}{\hbar^2} \frac{d^2E}{dk^2} \right)^{-1} \frac{dV_g}{dt}
\]
\[
\Rightarrow \left( \frac{1}{\hbar^2} \frac{d^2 \mathcal{E}}{dk^2} \right)^{-1} \frac{dV_g}{dt} = -e E
\]

If \( \frac{d^2 \mathcal{E}}{dk^2} < 0 \), the wave packet behaves as if it has a positive charge! This is the explanation for the positive Hall coefficient in some metals. The effective mass \( m^* \) is defined as

\[
\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 \mathcal{E}}{dk^2}.
\]

In general, for three-dimensional systems, \( m^* \) is a tensor:

\[
\left( \frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{d^2 \mathcal{E}}{dk_i dk_j}.
\]
Number of orbitals in a band

Consider a linear crystal constructed of an even number $N$ of primitive cells of lattice constant $a$.
To count states, apply periodic boundary conditions over the length $L = Na$ of the crystal:

$k = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L}, \ldots, \frac{N\pi}{L}$.

We cut off the sequence at

$\frac{N\pi}{L} = \frac{\pi}{a}$, for this is the Brillouin zone boundary. The point $-\frac{N\pi}{L} = -\frac{\pi}{a}$ is not counted as an independent state since it is connected to $\frac{\pi}{a}$ by a reciprocal
lattice vector. The total # of points is exactly $N$, the # of primitive cells. Each primitive cell contributes exactly one independent value of $k$ to each energy band. This result carries over to 3 dimensions (counting the allowed wavevectors in the 1st Brillouin zone was done previously for phonons, verifying this result).

With account taken of the two independent orientations of the electron spin, there are $2N$ distinct orbitals in each energy band.
Metals and insulators

If the valence electrons fill one or more bands, leaving the others empty, the crystal will be an insulator. All available states are filled, with equal numbers of electrons moving to the right and to the left. No net current will flow if an electric field is applied, provided the field is not strong enough to excite electrons to a higher band. If one or more bands is partially filled, on the other hand, the crystal will be a metal.