Physics 460/560 Lecture 11

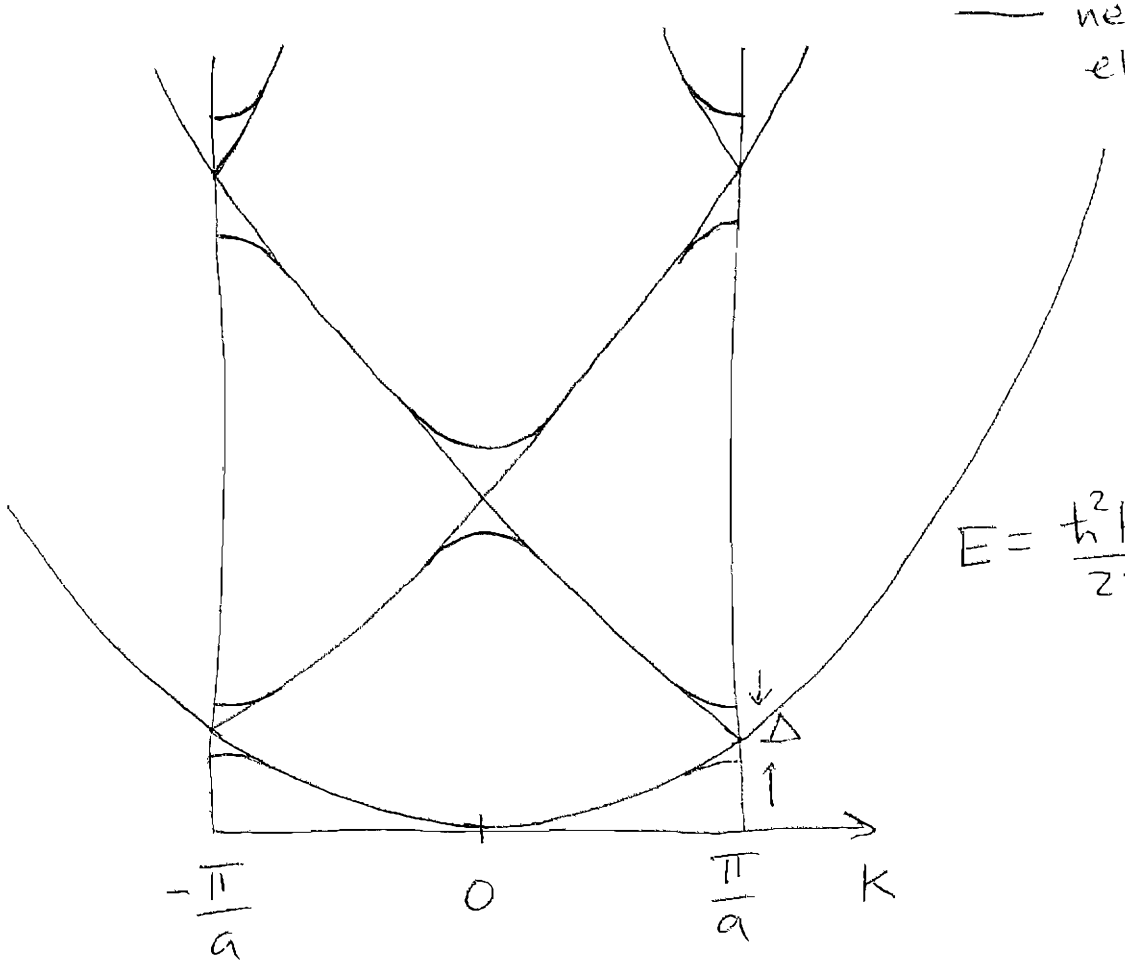
Band Theory II:

Nearly Free Electrons

$$\psi_{\vec{k}}(\vec{x}) = \sum_{\vec{G}} C(\vec{k}-\vec{G})\, e^{i(\vec{k}-\vec{G})\cdot\vec{x}}$$

Since $\psi_{\vec{k}}(\vec{x})$ 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. $\mathcal{E}(\vec{k})$ then becomes a multiple valued function.

1D Example



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_G are small compared to the kinetic energy of a free electron at the Brillouin zone boundary (nearly free electrons). Then U_G can be treated as a perturbation.

At the zone boundary $k = \frac{G}{2} = n\frac{\pi}{a}$, 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:

$$(\lambda - \varepsilon)\, C\left(\tfrac{G}{2}\right) + U_G\, C\left(-\tfrac{G}{2}\right) = 0$$

$$(\lambda - \varepsilon)\, C\left(-\tfrac{G}{2}\right) + U_{-G}\, C\left(\tfrac{G}{2}\right) = 0 \,,$$

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

These equations have a solution if

$$\begin{vmatrix} \lambda - \varepsilon & U_G \\ U_G & \lambda - \varepsilon \end{vmatrix} = 0$$

$$\Rightarrow \quad \varepsilon = \lambda \pm U_G = \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 \pm U_G$$

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

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

$$\frac{C\left(\frac{G}{2}\right)}{C\left(-\frac{G}{2}\right)} = \frac{U_G}{\varepsilon - \lambda} = \frac{U_G}{\pm U_G} = \pm 1$$

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

$\Rightarrow$ 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

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

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

Let $k = \frac{G}{2} + \delta k$

$$\lambda_k = \frac{\hbar^2}{2m}\left(\frac{G}{2} + \delta k\right)^2 = \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 + \frac{\hbar^2 G}{2m}\delta k + \frac{\hbar^2}{2m}\delta k^2$$

$$\lambda_{k-G} = \frac{\hbar^2}{2m}\left(\delta k - \frac{G}{2}\right)^2 = \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 - \frac{\hbar^2 G}{2m}\delta k + \frac{\hbar^2}{2m}\delta k^2$$

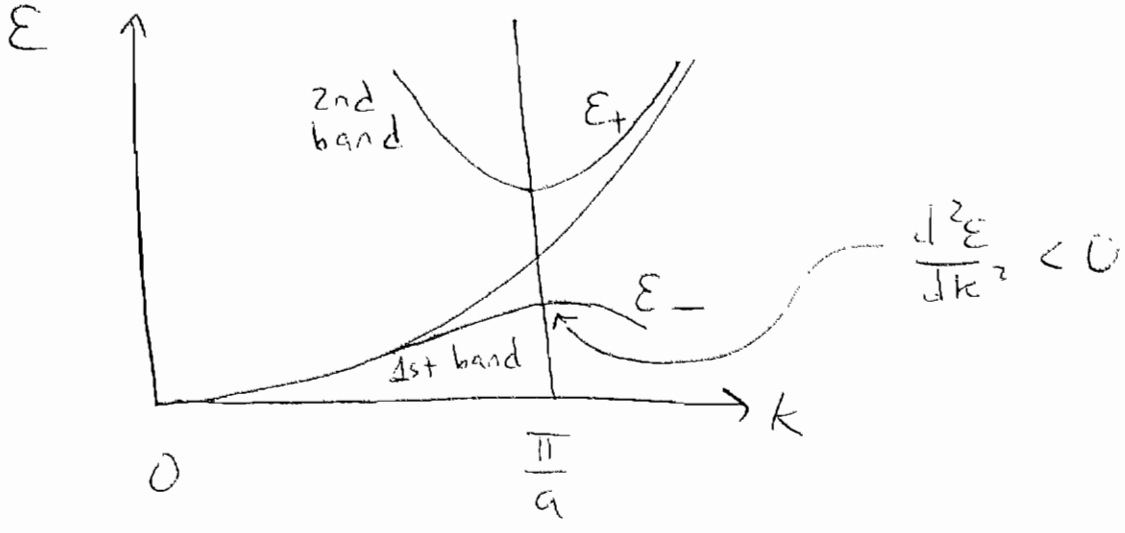
$$\frac{\lambda_{k-G} + \lambda_k}{2} = \frac{\hbar^2}{2m}\left[\left(\frac{G}{2}\right)^2 + \delta k^2\right]$$

$$\frac{\lambda_{k-G} - \lambda_k}{2} = -\frac{\hbar^2 G\, \delta k}{2m}$$

$$\mathcal{E}_{\pm}(\delta k) = \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 + \frac{\hbar^2 \delta k^2}{2m} \pm \sqrt{\left(\frac{\hbar^2 G\, \delta k}{2m}\right)^2 + U_G^2}$$

$$\mathcal{E}_{\pm}(\delta k) \simeq \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2 \pm U_G + \frac{\hbar^2 \delta k^2}{2m}\left(1 \pm \frac{2\lambda}{U_G}\right),$$

where $\lambda = \frac{\hbar^2}{2m}\left(\frac{G}{2}\right)^2$. Notice that by assumption, $\frac{\lambda}{U_G} \gg 1$.



Effective mass

Consider an electron in a one-dimensional crystal with an electric field $\mathcal{E}$:

Newton's law states

$$m \frac{dv_g}{dt} = -e\mathcal{E}$$

$$v_g = \frac{1}{\hbar}\frac{d\varepsilon}{dk} = \text{group velocity}$$

$$\frac{dv_g}{dt} = \frac{1}{\hbar}\frac{d^2\varepsilon}{dk^2}\frac{dk}{dt} = \frac{1}{\hbar^2}\frac{d^2\varepsilon}{dk^2}\frac{d\hbar k}{dt}$$

Semiclassical equation of motion:

$$\frac{d\hbar k}{dt} = -e\mathcal{E}$$

But $$\frac{d\hbar k}{dt} = \left(\frac{1}{\hbar^2}\frac{d^2\varepsilon}{dk^2}\right)^{-1}\frac{dv_g}{dt}$$

$$\Rightarrow \left(\frac{1}{\hbar^2}\frac{d^2\varepsilon}{dk^2}\right)^{-1}\frac{dv_g}{dt} = -e\,E$$

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

$$\frac{1}{m^*} = \frac{1}{\hbar^2}\frac{d^2\varepsilon}{dk^2}.$$

In general, for three dimensional systems, m^* is a tensor:

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\frac{\partial^2\varepsilon}{\partial k_i\,\partial k_j}.$$

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:

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

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 #'s 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.