

Lecture 13 – Properties of Energy Bands

Reading: Kittel: Chapter 7, pages 180-182, Chapter 9, pages 223-232;
Simon Chapter 16, pages 173-176, Chapter 17, pages 183-87

The consequence of electrons being in energy states with a weak periodic potential is that energy gaps appear in the $E(k)$ diagram at certain values of wavevector (the boundaries of the Brillouin zones 1st, 2nd 3rd etc.)

Electron states in periodic potentials are called Bloch states, and are described by the Bloch Theorem (see Lecture 12).

There are two alternative ways of describing the origin of the energy gap which appears in our calculation in the previous lecture.

These are

1. Bragg reflection
2. Interference between wavefunctions

1. Bragg reflection

Bragg reflection of X-rays is used to explain X-ray patterns. Bragg proposed that we can assume that a small fraction of an incident EM wave is reflected from parallel planes of atoms in a crystal. The path difference for rays reflected from adjacent planes is $2d \sin \theta$, where d is the separation between the planes and θ is the angle of the radiation to the normal to the plane. This leads to the well known Bragg condition $2d \sin \theta = n\lambda$. We know that $k = 2\pi / \lambda$ which means $k = n\pi / d \sin \theta$. If $\sin \theta = 1$ this gives us the corresponding k values at which energy gaps appear $k = n\pi / a$ where a is the lattice constant. Electron waves can be scattered in a similar fashion.

2. Interference

If we consider the electron states which propagate through the crystal as waves, there will be an interaction between the electron wavefunctions and the periodic potential. At certain special wavelengths, related to the crystal period, interference will occur which gives rise to energy gaps, or regions where there are no valid solutions to the Schrödinger equation.

Energy Bands

Energy bands describe the relationship between energy and wavevector. These are known as energy-wavevector dispersion diagrams as they indicate that electrons of different wavevectors can propagate differently through a crystal lattice as a result of the interaction between the electron wavefunction and the periodic potential. Knowing the $E(k)$ relationship allows us to determine a range of physical properties.

We know for ordinary travelling waves that the group velocity is given by:

$$v_{\text{group}} = \frac{d\omega}{dk}$$

In the case of electron waves the group velocity can be considered the velocity of the electron wavepacket.

As we know that $E = \hbar\omega$ we find that

$$v_{\text{group}} = \frac{1}{\hbar} \frac{dE(k)}{dk}$$

Velocity of Block electrons

For an electron at the bottom of an energy band in the nearly free electron model we know that

$$E = \frac{\hbar^2 k^2}{2m_e}$$

So that

$$v_{\text{group}} = \frac{1}{\hbar} \frac{d}{dk} \left[\frac{\hbar^2 k^2}{2m_e} \right] = \frac{\hbar k}{m_e} = \frac{p}{m_e} = v$$

In this case $p = \hbar k$ is called the *crystal momentum*. This is not the same as the electron momentum. It is considered the momentum an electron appears to have whilst moving through a crystal in a Bloch state or energy band, and is due to the interaction between the electron and the periodic potential of the crystal. When the electron in the energy band interacts (for example with an electric field) it appears to have a momentum given by the crystal momentum.

Knowing the $E(k)$ energy band structure for a solid allows us to predict the velocity of electrons in a state k .

This is important in understanding the nearly-free electron model. It tells us that despite the complex periodic structure of crystals, there are energy states occupied by electrons (Bloch states in a relatively weak periodic potential) which do not interact with the atoms – i.e. they are stationary time independent eigenstates.

This is in contrast to the classical Drude model. It also accounts for the limited successes of the free-electron model where electron atom interactions are ignored.

Current carried by Energy Bands

Once we know the velocity of an electron in an energy band, we can determine the current carried by a collection of electrons in an energy band. The current density is given by

$$j = ne \langle v \rangle$$

where n is the electron density and $\langle v \rangle$ is the average velocity of electrons in a band.

Suppose we have M energy states in an energy band occupied by $2M$ electrons. We have:

$$\begin{aligned}\langle v \rangle &= \frac{1}{\hbar} \int_{k=-\pi/a}^{k=\pi/a} \frac{dE}{dk} \frac{a}{2\pi} dk \\ &= \frac{a}{2\pi \hbar} \left[E\left(\frac{\pi}{a}\right) - E\left(\frac{-\pi}{a}\right) \right]\end{aligned}$$

We know from our earlier discussion that $k = \pm \frac{\pi}{a}$ are physically equivalent values of the Bloch wavevector (think of Bragg scattering for example).

From this we know that $E\left(\frac{\pi}{a}\right) = E\left(\frac{-\pi}{a}\right)$ and thus $\langle v \rangle = 0$. In this case $j = 0$ and the total current carried is zero.

We can understand this from the fact that for each state in an energy band with a vector k with corresponding crystal momentum and velocity, there is a state with an equal and opposite wavevector $-k$.

This is an important result:

A completely filled energy band makes no contribution to the current carried by a crystal.

Some **mysteries** revisited:

We now know the solution to some of the problems in describing electrons in solids.

1. The Bloch electron states in an arbitrary complicated lattice have a non-zero group velocity. This explains why electrons in metals are apparently not scattered by the crystal lattice.
2. The only electrons we have to consider when it comes to the transport of electric current and thermal conductivity are those in partially filled bands. Completely filled bands average to zero current flow.
3. Any crystal which has only completely filled energy bands will be an insulator. (Note that a small level of conductivity is possible where electrons can jump across forbidden energy bandgaps – which can be induced by thermal energy.)

Equation of motion for Bloch Electrons

For a Bloch electron in an energy band we can describe it with a wavevector coordinate k . This gives a corresponding group velocity and crystal momentum from the $E(k)$ relation.

We can now develop an equation of motion for Bloch electrons.

Consider a force F applied to an electron in a crystal. (Assume that it does not change energy bands). It reacts by changing its wavevector k . We know that the rate

at which energy changes must be the rate at which the force does work. So then we have:

$$F v_{\text{group}} = \frac{dE}{dt} = \frac{dE}{dk} \times \frac{dk}{dt}$$

We know that:

$$v_{\text{group}} = \frac{1}{\hbar} \frac{dE}{dk}$$

rearranging gives

$$\hbar \frac{dk}{dt} = F$$

The rate of change of *crystal momentum* $\hbar k$ is equal to the applied force.

This equation allows us to predict how an electron in a given k state will respond to an external force such as an electric field. This leads to the concept of the effective mass.

The Effective Mass

One of the consequences of energy bands in solids is that Bloch electrons which occupy these energy bands may respond to an external force as though they had a mass which is different to the free electron mass. As seen above this will be related to the rate at which the electron can change its energy (or crystal momentum). This is called the *effective mass*.

Consider the $E(k)$ relationship near a band extremum at $k = k_0$ where $\frac{dE}{dk} = 0$ (i.e. zero group velocity).

It will be of a general form

$$E = E(k_0) + \frac{1}{2} A (k - k_0)^2$$

The group velocity as a function of k is then

$$v_{\text{group}}(k) = \frac{A(k - k_0)}{\hbar}$$

If we compare this with free particles we have

$$v_{\text{free}} = \frac{p}{m} = \frac{\hbar k}{m}$$

The electrons behave as though they had an effective mass $m_{\text{eff}} = \frac{\hbar^2}{A}$

From Taylor's theorem it can be shown that:

$$A = \left. \frac{d^2 E}{dk^2} \right|_{k=k_0}$$

From this the effective mass is given by:

$$m_{\text{eff}} = \hbar^2 \left[\frac{d^2 E(k)}{dk^2} \right]^{-1}$$

The second derivative is the curvature of the energy band $E(k)$ relationship.

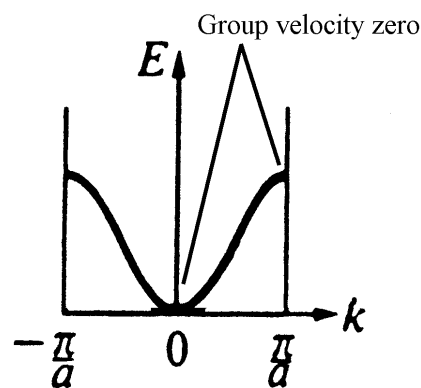
The effective mass is therefore proportional to the inverse curvature of the $E(k)$ band.

At the centre of the Brillouin zone we can write:

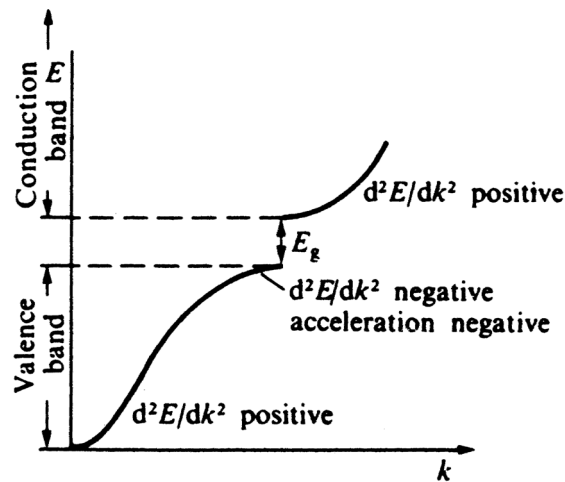
$$E = \frac{\hbar^2 k^2}{2m_{\text{eff}}}$$

We have a constant curvature and therefore a constant effective mass. (This is often called the parabolic approximation).

By now we realise that the effective mass and the group velocity vary as the wavevector changes across the Brillouin zone.



The group velocity is zero at the centre of the Brillouin zone and the Brillouin zone boundaries (where the slope of the $E(k)$ relation is zero).



This allows us to understand electrons and holes. Considering the equation of motion where the force on a particle is produced by an electric field \underline{E} we can see that electrons and holes will experience a force in different directions because of their different positive and negative charges. This is described by positive effective mass (electrons) and negative effective mass (holes).

Electrons and Holes

When an energy band is almost filled and has a very small number of unoccupied states close to the top, it is easier to describe the properties of the band using holes rather than electrons. A hole is simply an empty or unoccupied electron state.

The properties of the holes are:

1. The charge on the hole is $+e$
2. The hole wavevector is $k_h = -k_e$ where k_e is the wavevector of the missing electron.
3. The hole energy is $E_h(k_h) = -E(k_e)$
4. The hole velocity is $v_h = v_e$
5. The hole effective mass is $m_{eff}(hole) = -m_{eff}(e)$ and is positive at the top of a band.

This explains the positive Hall coefficients experimentally observed in some metals.

Metals Insulators and Semiconductors

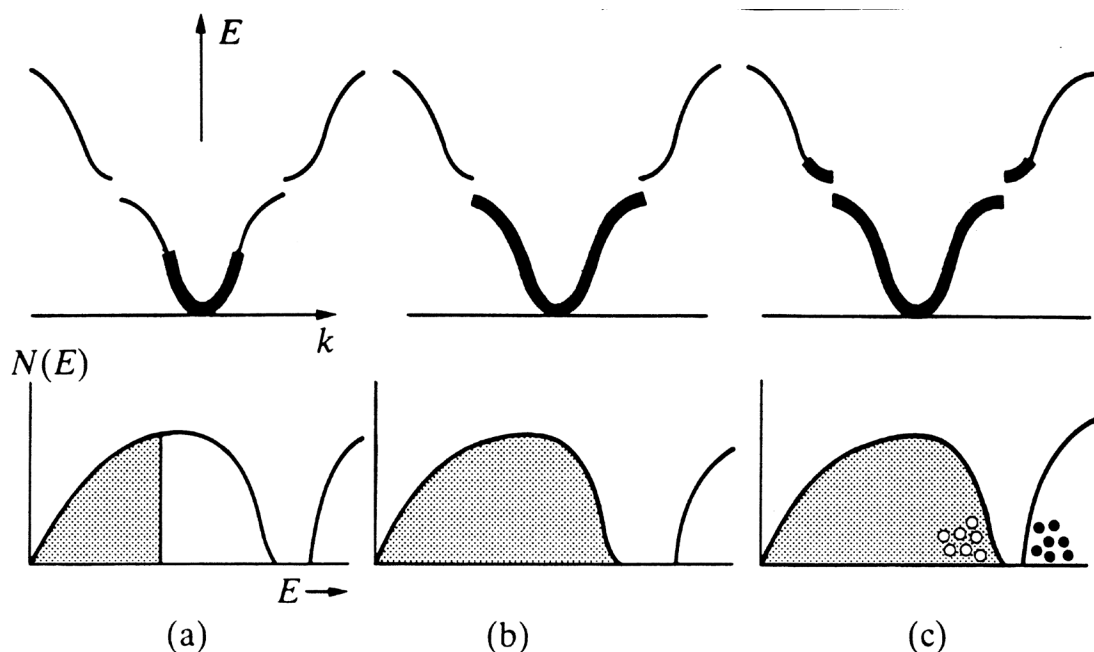
The nearly free electron model with energy gaps allows us to explain the electrical behaviour of a wide range of elements.

We know that the number of k -states in each band is equal to N the number of atoms in the crystal. Each k -state is populated by 2 electrons giving $2N$ electron energy states.

If a metal has only one conduction electron per atom the bottom half of the band will be occupied. This leaves large numbers of empty states for electrons to move into. The energy distribution in this system is that predicted by the free and nearly-free electron model. In this situation the energy gaps are not important. (In an energy band that is half full there is effectively no energy bandgap between the occupied and unoccupied electron energy states.)

The situation when there is an even number of electrons per atom is different. In this case the electrons would occupy all the energy states in the energy band. As there are no empty k -states to occupy when an electric field is applied this material will be an insulator. If the bandgap is sufficiently small a proportion of electrons may be excited across the bandgap. In this case we have a semiconductor.

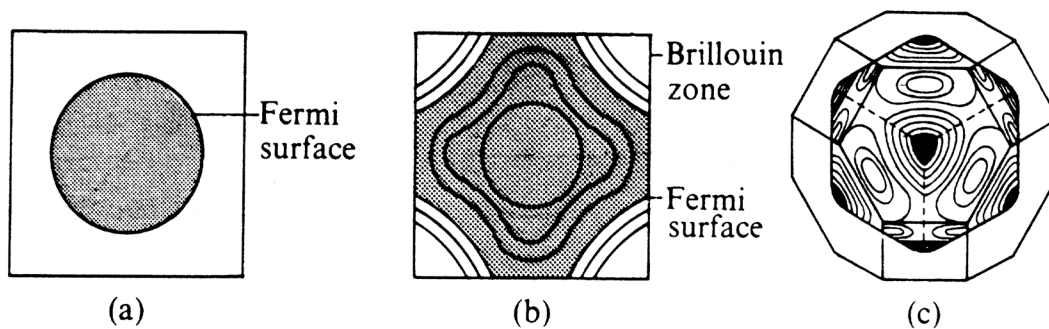
In a metal the conductivity decreases with increasing temperature
In a semiconductor the conductivity increases with increasing temperature.



There are also a number of divalent metals (Mg, Ca, Zn, Cd, Hg etc). These should be insulators. In this case there is no energy gap between the valence and conduction bands, they overlap in energy.

In metals the Fermi surface encloses all the occupied electron states up to k_F . In the simple free electron model this is a sphere.

If the Fermi surface touches the edges of the first Brillouin zone a more complex structure results.



{BACKGROUND INFORMATION ONLY BELOW – NOT COVERED IN LECTURE}

Tight Binding Approximation

This is an alternative description for the formation of energy bands. It considers the effect of bringing atoms close together from large distances. When the atoms are isolated each will have the same series of discrete energy levels – the Bohr model of the atom.

As the atoms come closer together the energy levels must change to follow the Pauli Exclusion Principle. This change will become larger as the atoms get closer together and will be more significant for the electrons in outer orbits at higher energies.

If there are N atoms, each electron state in a single atom will spread into an energy band containing $2N$ discrete levels.

