

Last time: Discussed the free electron (Drude) model applied to electronic specific heat and electrical conductivity.

Today: Finish with Free electron model.

Thermal conductivity.

Motion in magnetic field: cyclotron resonance and Hall effect

Start new chapter: energy bands in solids

Summary Last Lecture

- Free electron model – simplest way to describe electronic properties of metals: the valence electrons of free atoms become conduction electrons in crystal and move freely throughout the crystal.

1D case.

$$\psi_n(x) = A \sin\left(\frac{\pi n}{L}x\right) \quad E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2$$

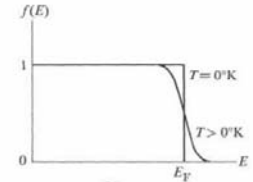
Fermi energy for the 1D system of N electrons:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2$$

Finite temperature:

the Fermi - Dirac distribution:

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1}$$



High energy tail of $f(E)$, when $E = \mu \gg k_B T$

$$f(E) = e^{-(\mu-E)/k_B T} \quad \text{Maxwell - Boltzmann distribution}$$

Summary Last Lecture

(continued)

- Fermi energy - energy of the highest occupied electronic level at $T = 0$ K; 3D case:

$$E_F = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad v_F = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3}$$

- Density of states of 3D free electron gas:

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2} = \frac{3N}{2E}$$

- Electrical conductivity:

$$\sigma = -\frac{ne^2\tau}{m^*}$$

$$\rho = \rho_i + \rho_{ph}(T)$$

- Heat capacity of free electron gas at low temperatures $k_B T \ll E_F$:

$$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

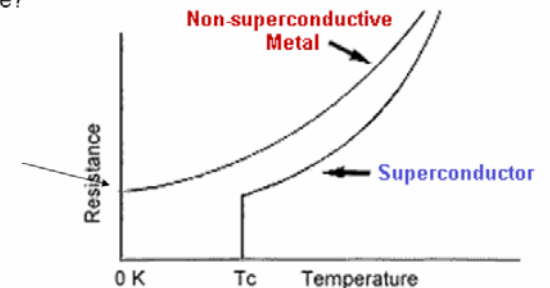
- Thermal conductivity: Wiedemann-Franz law

$$K = L\sigma T \quad L = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2$$

Breakdown of Fermi Electron Gas Theory

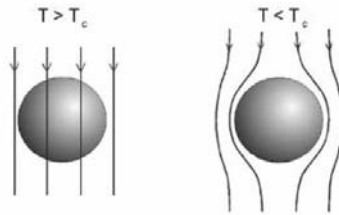
- At extremely low temperatures for some metals, the resistivity undergoes a remarkable change
- Metals such as Zn, Ti, and V superconduct! (at $T_c = 0.875$ K, 0.39 K, and 5.38 K respectively)
- This means that the resistivity drops to zero – the electron free paths become infinite!
- Kammerlingh Onnes was the first one to notice this for Hg at ~ 4.153 K
- What is happening here?

Some residual resistivity at $T = 0$ K



Superconductivity

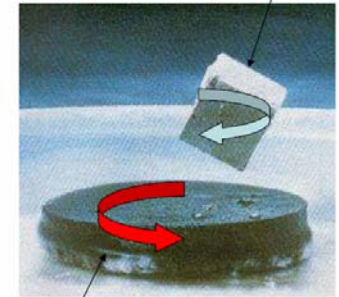
- In a superconductor, the currents effectively run forever – there are no collisions to slow them down (measurements by File and Mills suggest that the decay time of a supercurrent through a solenoid is no less than 100 000 years)
- Another odd property of superconductors:
 - The Meissner Effect
- If a superconducting sample is cooled in a small magnetic field, the magnetic field lines will be expelled from the sample (due to the supercurrents forming in a direction to oppose the field, and therefore the field inside the superconductor is zero)



Magnetic Levitation

- This is what causes the levitation of magnets above superconducting samples (the supercurrents form to counterbalance the magnetic force, and when the forces are equal and opposite, the magnet floats)
- Potential application: levitation of magnetic trains (no friction)

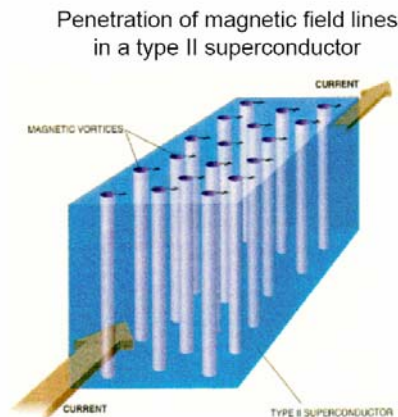
Electrons in magnet, which create a fixed magnetic field



Superconducting electrons in sample (in a direction which counters the magnet to expel the magnetic field)

Type I and Type II Superconductors

- Type I superconductor: A field can be applied to some maximum value before it becomes "normal". The field does not penetrate the superconductor (Meissner effect). Most metals belong to this class (eg. Zn, V, Ti)
- Type II superconductor: A field can be applied up to a critical value, H_{C1} , where the field lines penetrate the sample. This is known as the vortex state. After the field is increased to H_{C2} , the material is no longer superconducting. These are the "high- T_c " superconductors, like $YBa_2Cu_3O_7$.

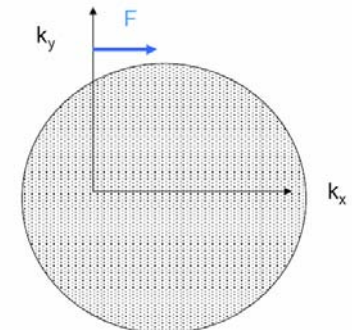


Motion in Magnetic Field

- Last time, we looked at what happens when you apply an electric field to a Fermi gas
- Now, we are going to look at what happens when you apply a magnetic field
- For the application of an electric field, we found that the Fermi sphere is displaced by Δk

$$\vec{F} = m\vec{a} = \hbar \frac{d}{dt} \Delta \vec{k} = -e\vec{E}$$

(for a field in the x-direction)



Effect of Collisions

- We also showed that the electrons undergo collisions in a material after a collision time τ . This means that the equation we wrote above has to be modified:

$$\vec{F} = \hbar \left(\frac{d}{dt} + \frac{1}{\tau} \right) (\Delta \vec{k})$$

- This second term, which takes collisions into account, acts like a frictional force. Since there is no derivative in this form, it says that the force is proportional to $\Delta k/\tau$, which is like saying it is proportional to the velocity of the particles ($k \sim$ momentum).
- Other frictional forces act this way, like friction due to air resistance (this is proportional to the velocity, and explains why a terminal velocity exists. Similarly, it explains why the electrons' velocity doesn't grow without limit when you apply an electric field)

Electric and Magnetic Fields

- Using this expression for the force, let's go back to our original equation (which included both electric and magnetic fields):

$$\vec{F} = \hbar \left(\frac{d}{dt} + \frac{1}{\tau} \right) (\Delta \vec{k}) = -e \left(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \quad (\text{CGS units})$$

$$= -e \left(\vec{E} + \vec{v} \times \vec{B} \right) \quad (\text{SI units})$$

- Now, assuming that $m\vec{v} = \hbar \Delta \vec{k}$ (ie. the electrons velocities are shifted by this amount due to the electric/magnetic field) we have:

$$\vec{F} = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \vec{v} = -e \left(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right)$$

Motion in a magnetic field: cyclotron resonance

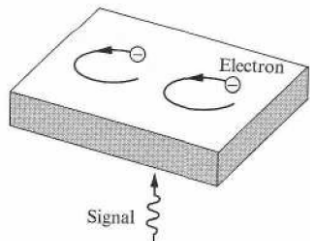
Applied magnetic field \rightarrow the Lorentz force: $\mathbf{F} = -e[\mathbf{E} + (\mathbf{v} \times \mathbf{B})]$

Perfect metal, no electric field - the equation of motion is:

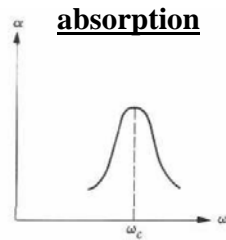
$$m \frac{d\mathbf{v}}{dt} = -e\mathbf{v} \times \mathbf{B}$$

Let the magnetic field to be along the z-direction. Then

$$\frac{dv_x}{dt} = -\omega_c v_y, \quad \frac{dv_y}{dt} = \omega_c v_x \quad \text{where } \omega_c = \frac{eB}{m} \text{ - cyclotron frequency}$$



For moderate magnetic fields (\sim few kG), $\omega_c \sim$ few GHz.
e.g. for $B = 0.1$ T,
 $f_c = \omega_c / 2\pi = 2.8$ GHz



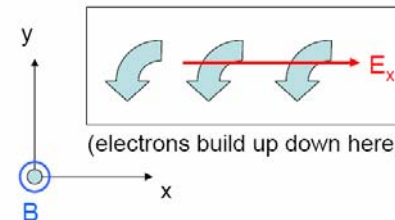
Cyclotron resonance – peak in absorption of electromagnetic waves at ω_c
Used to measure the effective mass in metals and semiconductors

The Hall Effect

- Consider the motion of the electrons in the x, y, and z direction
- Initially: $\mathbf{v} = (v_x, v_y, v_z)$, $\mathbf{E} = (E_x, 0, 0)$, $\mathbf{B} = (0, 0, B)$
- Apply the fields, and observe what happens

$$\vec{F} = m \left(\frac{d}{dt} + \frac{1}{\tau} \right) \vec{v} = -e \left(\vec{E} + \frac{1}{c} \vec{v} \times \vec{B} \right) \rightarrow m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_x = -e \left(E_x + \frac{1}{c} v_y B \right)$$

(net force in $-x$ direction)



Initial state: electrons start to flow in the $-y$ direction. This **creates** a field E_y

$$m \left(\frac{d}{dt} + \frac{1}{\tau} \right) v_y = e \left(\frac{1}{c} v_x B \right)$$

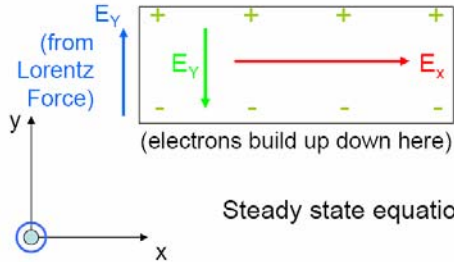
(net force in the $-y$ direction)

We need to consider what happens after this initial electron drift to the bottom part of the metal slab

The Hall Effect

- The electrons will build up in the lower part of the metal, generating an electric field E_y
- This will occur until the motion reaches a steady state – that is, when the forces are balanced in the y-direction (the Lorentz force from the magnetic field, and the Electric force from the build-up of the electrons will be equal and cancel each other out)

Steady-state conditions: d/dt part = 0 \rightarrow $m\left(\frac{d}{dt} + \frac{1}{\tau}\right)v_x = -e\left(E_x + \frac{1}{c}v_y B\right)$
(forces are balanced)



$$m\left(\frac{d}{dt} + \frac{1}{\tau}\right)v_y = -e\left(E_y - \frac{1}{c}v_x B\right)$$

$$\rightarrow \frac{mv_x}{\tau} = -e\left(E_x + \frac{1}{c}v_y B\right)$$

$$\rightarrow \frac{mv_y}{\tau} = -e\left(E_y - \frac{1}{c}v_x B\right)$$

Steady state equations:

The Hall Effect

- So, what happens is that we get a net flow of electrons in the x-direction, but we also get an electric field set up in the y-direction.
- Hall Effect measurements compare the ratio of the field created in the y-direction, to the current in the x-direction, and the magnetic field in the z-direction
- The Hall coefficient is defined by:

(from steady state solution)

$$R_H = \frac{E_y}{j_x B} = -\frac{eB\tau E_x / mc}{ne^2\tau E_x B / m} = -\frac{1}{nec} \quad (\text{CGS units})$$

(from last lecture)

$$R_H = -\frac{1}{ne} \quad (\text{SI units})$$

(electric charge)

(density of conduction electrons)

The Hall Effect

- Why is this an important measurement?
- It relates 3 simple, easily measured quantities (the current density, the electric field in y-direction, and the magnetic field in the z-direction) to the density of conduction electrons (which we can calculate)
- Also, it gives some strange results!
- In particular, R_H changes signs for some materials!
- Why?

Metal	R_H (exp)	No of carriers /atom	R_H (theory)
Li	-1.89	1 el.	-1.48
Na	-2.619	1 el.	-2.603
K	-4.946	1 el.	-4.944
Rb	-5.6	1 el.	-6.04
Cu	-0.6	1 el.	-0.82
Ag	-1.0	1 el.	-1.19
Au	-0.8	1 el.	-1.18
Al	1.136	1 hole	1.135
In	1.774	1 hole	1.780

Electrons and holes

- The Hall Effect was an important experiment historically because it suggested that a carrier could have a positive charge
- These carriers are “holes” in the electron sea (and thus, being the absence of an electron, they have a net positive charge). These were first explained by Heisenburg.
- We can't explain why this would happen with our free electron theory (but it arises naturally in band theory)
- Note: the conditions we derived for the steady state can be invalid for several conditions (ie. when there is a distribution of collision times). But in general, it is a very powerful tool for looking at properties of materials

Summary of free electron model

❖ Free electron model – simplest way to describe electronic properties of metals: the valence electrons of free atoms become conduction electrons in crystal and move freely throughout the crystal.

❖ Fermi energy - the energy of the highest occupied electronic level at T = 0 K;

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3\pi^2 N}{V} \right)^{2/3} \quad k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3} \quad v_F = \frac{\hbar}{m} \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

❖ Density of states of 3D free electron gas:

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2} = \frac{3N}{2E}$$

❖ Electrical conductivity:

$$\sigma = -\frac{ne^2\tau}{m^*}$$

$$\rho = \rho_i + \rho_{ph}(T)$$

❖ Heat capacity of free electron gas at low temperatures $k_B T \ll E_F$:

$$C_{el} = \frac{\pi^2}{2} N k_B \frac{T}{T_F}$$

❖ Thermal conductivity: Wiedemann-Franz law

$$K = L\sigma T \quad L = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2$$

Limitations of free electron model

The free electron model gives a good insight into many properties of metals, such as the heat capacity, thermal conductivity and electrical conductivity. However, it fails to explain a number of important properties and experimental facts, for example:

- the difference between metals, semiconductors and insulators
- It does not explain the occurrence of positive values of the Hall coefficient.
- Also the relation between conduction electrons in the metal and the number of valence electrons in free atoms is not always correct. Bivalent and trivalent metals are consistently less conductive than the monovalent metals (Cu, Ag, Au)

⇒ need a more accurate theory, which would be able to answer these questions – **the band theory**

The problem of electrons in a solid – a many-electron problem

The full Hamiltonian contains not only the one-electron potentials describing the interactions of the electrons with atomic nuclei, but also pair potentials describing the electron-electron interactions

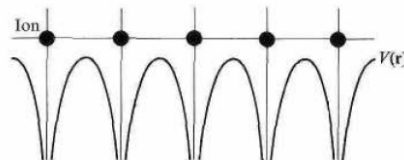
The many-electron problem is impossible to solve exactly ⇒ simplified assumptions needed

The simplest approach we have already considered - a free electron model

The next step is an independent electron approximation: assume that all the interactions are described by an effective potential.

One of the most important properties of this potential - its periodicity:

$$U(\mathbf{r}) = U(\mathbf{r} + \mathbf{T})$$



Bloch theorem

Write the Schrödinger equation the approximation of non-interacting electrons:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r})$$

$\psi(\mathbf{r})$ – wave function for one electron.

Independent electrons, which obey a one-electron Schrödinger equation a periodic potential $U(\mathbf{r}) = U(\mathbf{r} + \mathbf{T})$ - Bloch electrons

Bloch theorem: the solution has the form $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$ - a periodic function with the same period as the lattice

Bloch theorem introduces a wave vector \mathbf{k} , which plays the same fundamental role in the motion in a periodic potential that the free electron wave vector \mathbf{k} plays in the free-electron theory.

$\hbar\mathbf{k}$ is known as the *crystal momentum* or *quasi-momentum*

Another conclusions following from the Bloch theorem:
the wave vector \mathbf{k} can always be confined to the first Brillouin zone

This is because any \mathbf{k}' not in the first Brillouin zone can be written as $\mathbf{k}' = \mathbf{k} + \mathbf{G}$. Then, if the Bloch form holds for \mathbf{k}' , it will also hold for \mathbf{k}

Energy bands

Substitute the solutions in the Bloch form $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ into the Schrodinger equation, obtain:

$$\left[-\frac{\hbar^2}{2m} (i\mathbf{k} + \nabla)^2 + U(\mathbf{r}) \right] u_{\mathbf{k}}(\mathbf{r}) = E(\mathbf{k}) u_{\mathbf{k}}(\mathbf{r})$$

with periodic condition: $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{T})$

For any \mathbf{k} , find an infinite number of solutions with discrete energies $E_n(\mathbf{k})$, labeled with the band index n

For each n , the set of electronic levels specified by $E_n(\mathbf{k})$ is called an *energy band*. The information contained in these functions for different n and \mathbf{k} is referred to as the *band structure* of the solid.

Number of states in a band

The number of states in a band within the first Brillouin zone is equal to the number of primitive unit cells N in the crystal.

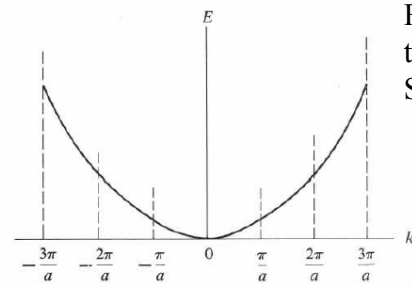
Consider the one-dimensional case, periodic boundary conditions. Allowed values of k form a uniform mesh whose unit spacing is $2\pi/L$

\Rightarrow The number of states inside the first zone, whose length is $2\pi/a$, is $(2\pi/a)/(2\pi/L) = L/a = N$, where N is the number of unit cells

A similar argument may be applied in 2- and 3-dimensional cases.

Taking into account two spin orientations, conclude that there are $2N$ independent states (orbitals) in each energy band.

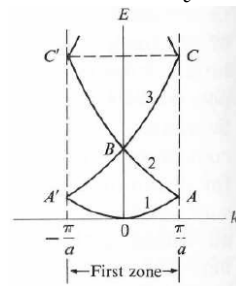
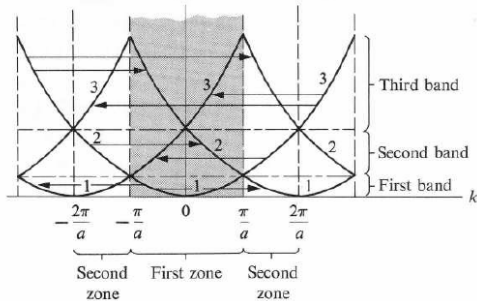
Nearly free electron (weak binding) model



First step: empty-lattice model. When the potential is zero the solutions of the Schrödinger equation are plane waves:

$$E^0(k) = \frac{\hbar^2 k^2}{2m_0} \quad \psi_k^0(\mathbf{r}) = \frac{1}{\sqrt{V_c}} e^{i\mathbf{k}\cdot\mathbf{r}}$$

where the wave function is normalized to the volume of unit cell V_c



Now, turn on a weak potential. Consider it as a weak periodic perturbation in Hamiltonian.

From perturbation theory have:

$$E_i(k) = E_i^0(k) + \langle \psi_{i,k}^0 | U | \psi_{i,k}^0 \rangle + \sum_{k',j} \frac{|\langle j,k' | U | i,k \rangle|^2}{E_i^0(k) - E_j^0(k)}$$

where index i refers to i^{th} band; 0 refers to empty-lattice model.

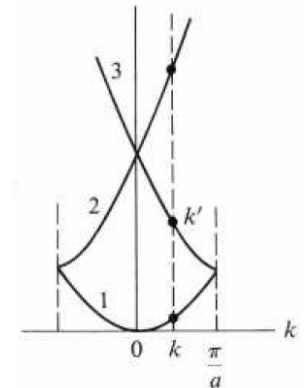
The first term is the undisturbed free-electron value for the energy.

The second term is the mean value of the potential in the state i, k

– constant independent of k – can set to zero

The third term – the 2nd order correction

– vanishes except $\mathbf{k}' = \mathbf{k} + \mathbf{G}$



The third term can be rewritten as

$$\langle \psi_{\mathbf{k}}^0 | U | \psi_{\mathbf{k}-\mathbf{G}}^0 \rangle = \frac{1}{V_c} \int_{cell} e^{-i\mathbf{k}\mathbf{r}} U(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{G})\mathbf{r}} d\mathbf{r} = \frac{1}{V_c} \int_{cell} U(\mathbf{r}) e^{-i\mathbf{G}\mathbf{r}} d\mathbf{r} = U_{\mathbf{G}}$$

$U_{\mathbf{G}}$ - Fourier transform of the crystal potential U

Finally we obtain for the energy:

$$E(\mathbf{k}) = E^0(\mathbf{k}) + \sum_{\mathbf{G} \neq 0} \frac{|U_{\mathbf{G}}|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})}$$

However, the perturbation theory cannot be applied when the potential cannot be considered as a small perturbation

This happens when the magnitude of the potential becomes comparable with the energy separation between the bands, i.e.

$$|E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})| \leq U$$

In this case we have to solve the Schrödinger equation explicitly

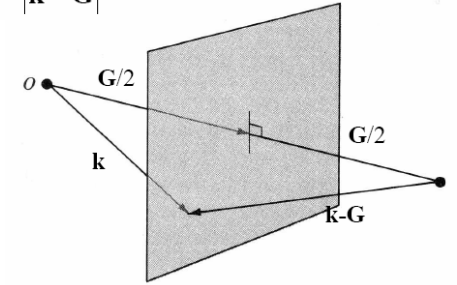
There are special \mathbf{k} points for which the energy levels become

$$\text{degenerate and the relationship } |E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G})| \leq U$$

holds for any non-zero value of the potential:

$$E^0(\mathbf{k}) = E^0(\mathbf{k}-\mathbf{G}) \quad |\mathbf{k}| = |\mathbf{k}-\mathbf{G}|$$

This condition implies that \mathbf{k} must lie on a Bragg plane bisecting the line joining the origin of \mathbf{k} space and the reciprocal lattice point \mathbf{G}

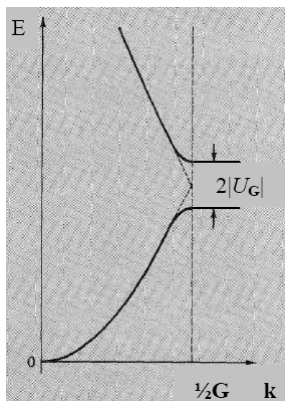


⇒ a weak periodic potential has its major effect on those free electron levels whose wave vectors are close to ones at which the Bragg reflection can occur.

In order to find the energy levels and the wave functions near these points we need to invoke the degenerate perturbation theory.

The result:

$$E = \frac{1}{2} (E^0(\mathbf{k}) + E^0(\mathbf{k}-\mathbf{G})) \pm \left[\frac{1}{4} (E^0(\mathbf{k}) - E^0(\mathbf{k}-\mathbf{G}))^2 + |U_{\mathbf{G}}|^2 \right]^{1/2}$$



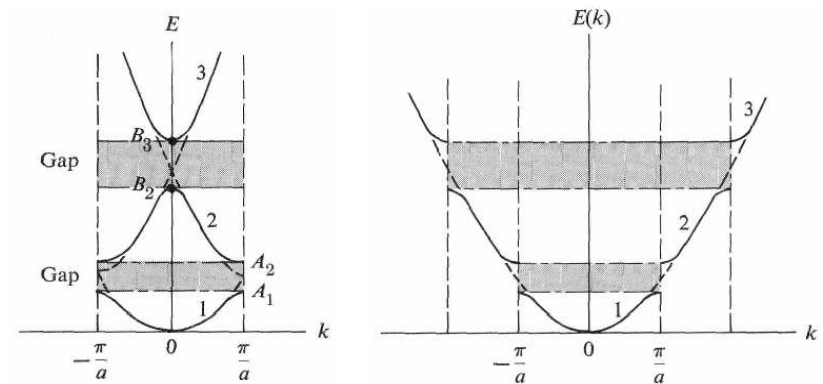
This result is particularly simple for point lying on the Bragg plane: $E^0(\mathbf{k}) = E^0(\mathbf{k}-\mathbf{G})$

Obtain
$$E = E^0(\mathbf{k}) \pm |U_{\mathbf{G}}|$$

The magnitude of the band gap is equal to twice the Fourier component of the crystal potential.

Illustrate this behavior using a one-dimensional lattice

The splitting of the bands at each Bragg plane in the extended-zone scheme results in the splitting of the bands both at the boundaries and at the centre of the first Brillouin zone.



Intermediate Summary

- ❖ The Bloch theorem: the wave function for an electron in periodic potential can be written in the form: $\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}}(\mathbf{r})$ where $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{T})$ - a periodic function with the period of the lattice
- ❖ The energy spectrum of electrons consists of a set of continuous *energy bands*, separated by regions with no allowed states - *gaps*
- ❖ Function $E(\mathbf{k})$ satisfies the symmetry properties of a crystal, in particular, the translational invariance: $E(\mathbf{k}) = E(\mathbf{k} + \mathbf{G})$

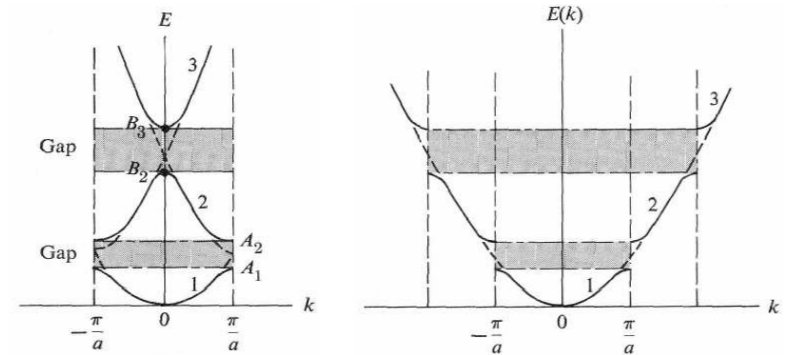
This allows considering the first Brillouin zone only.

Also, inversion symmetry: $E(\mathbf{k}) = E(-\mathbf{k})$

- ❖ Nearly free electron model – weak crystal potential. Electron behaves essentially as a free particle, except the wave vectors close to the boundaries of the zone.

In these regions, energy gaps appear: $E_g = 2|U_G|$

Origin of the energy gaps



We focused on the energy values

$$\text{got } E(\mathbf{k}) = E^0(\mathbf{k}) + \sum_{\mathbf{G} \neq 0} \frac{|U_{\mathbf{G}}|^2}{E^0(\mathbf{k}) - E^0(\mathbf{k} - \mathbf{G})} \quad \text{away from the zone edges}$$

$$\text{and } E = \frac{1}{2} (E^0(\mathbf{k}) + E^0(\mathbf{k} - \mathbf{G})) \pm \left[\frac{1}{4} (E^0(\mathbf{k}) - E^0(\mathbf{k} - \mathbf{G}))^2 + |U_{\mathbf{G}}|^2 \right]^{1/2}$$

near the zone edges.

Now, let's see how the wave functions are modified by (weak) crystal potential. From the perturbation theory, have for the first band (away from the zone edge):

$$\psi_1(k) = \psi_1^0(k) + \frac{U_G}{E_1^0(k) - E_2^0(k)} \psi_2^0(k)$$

Here, again, we leave only the nearest-band (2nd) term, as we did for the energy levels – because of the large denominator for higher bands.

Functions $\psi^0(k)$ are those of free electrons: $\psi_2^0(k) \sim e^{ikx}$

If k is not close to the zone edge, the coefficient of $\psi_2^0(k)$ is very small

So,

$$\psi_1(k) \approx \psi_1^0(k) = \frac{1}{L^{1/2}} e^{ikx} \quad \text{- behaves like free-electron}$$

However, near the edge, the denominator becomes very small – must use the degenerate perturbation theory – the functions $\psi_1^0(k)$ and $\psi_2^0(k)$ are treated equally

For simplicity we consider a one-dimensional lattice, for which the zone edges are $\mathbf{k} = \pm \frac{1}{2}\mathbf{G} = \pm \pi/a$ (**Bragg reflection** occurs)

The result:

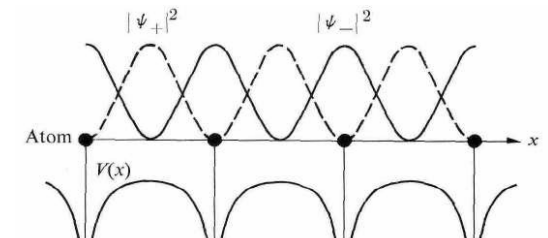
$$\psi_{\pm} = \frac{1}{L^{1/2}} [\psi_1^0(\pi/a) \pm \psi_2^0(\pi/a)] = \frac{1}{L^{1/2}} (e^{i(\pi/a)x} \pm e^{-i(\pi/a)x})$$

at the zone edge, the scattering is so strong that the reflected wave has the same amplitude as the incident wave \Rightarrow the electron is represented there by a standing wave, unlike a free particle

The distribution of the charge density is proportional to $|\psi|^2$, so that

$$\psi_+ \sim \cos^2 \frac{\pi}{a} x \quad \text{- higher energy}$$

$$\psi_- \sim \sin^2 \frac{\pi}{a} x \quad \text{- lower energy}$$



Periodic Lattice

- The simplest solution is a combination of wavefunctions of the electrons

$$\Psi_1 = \exp(ikx) = \exp(i\frac{\pi x}{a})$$

$$\Psi_2 = \exp(-ikx) = \exp(-i\frac{\pi x}{a})$$

$$\rightarrow \Psi^+ = \Psi_1 + \Psi_2 = \exp(ikx) + \exp(-ikx) = 2 \cos\left(\frac{\pi x}{a}\right)$$

$$\rightarrow \Psi^- = \Psi_1 - \Psi_2 = \exp(ikx) - \exp(-ikx) = 2i \sin\left(\frac{\pi x}{a}\right)$$

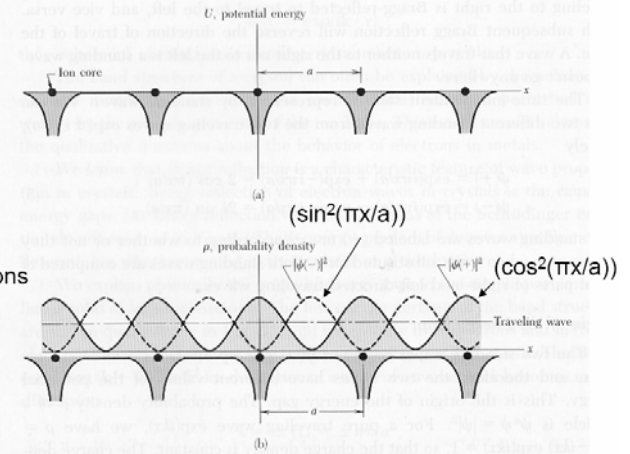
- Note: the combinations of these 2 travelling waves ($\exp(ikx)$) give standing wave solutions (sin and cos)

Periodic Lattice

- What does the electron density (ψ^2) look like?

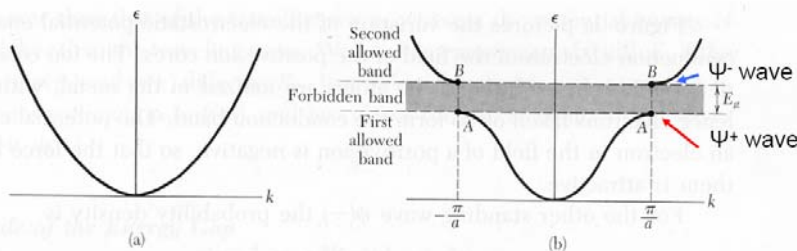
Note: only electrons which have a wavelength commensurate with the lattice ($k = \pi/a$) feel the periodic potential, and they form standing wave patterns

One of these (+) has electrons near the positive cores, the other has the electrons in between the cores (so they have different energies)



The Energy Gap

- So, there are 2 solutions for the energies at this K-value
- This is what gives rise to the energy gap



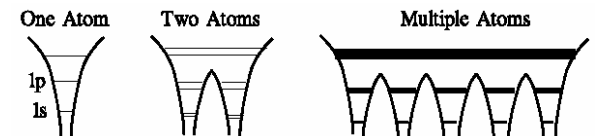
$$E_g = \int U(x) [|\psi^+|^2 - |\psi^-|^2] dx$$

(difference between the expectation values of these 2 energy levels)

Tight binding model

Assumptions:

- atomic potential is strong, electrons are tightly bound to the ions
- the problem for isolated atoms is solved: know wave functions ϕ_n and energies E_n of atomic orbitals
- weak overlapping of atomic orbitals



Start with 1D case

$$\text{Bloch function in the form: } \psi(k, x) = \frac{1}{N^{1/2}} \sum_{j=1}^N e^{ikX_j} \phi_n(x - X_j)$$

where $X_j = ja$ – position of the j^{th} atom, a – lattice constant;
 $\psi_n(x - X_j)$ – atomic orbital centered around the j^{th} atom – large near X_j , but decays rapidly away from it.

Small overlap exists only between the neighboring atoms

The function chosen satisfies the Bloch theorem:

$$\psi(k, x) = \frac{1}{N^{1/2}} \sum_{j=1}^N e^{ikX_j} \phi_n(x - X_j) = \frac{1}{N^{1/2}} e^{ikx} \underbrace{\sum_{j=1}^N e^{-ik(x-X_j)} \phi_n(x - X_j)}_{\text{periodic function}}$$

near X_j , $\psi(k, x) \approx e^{ikX_j} \phi_n(x - X_j) \sim \phi_n(x - X_j)$ - behaves like atomic orbital

The energy of the electron described by $\psi(k)$ is $E(k) = \langle \psi(k) | H | \psi(k) \rangle$

Obtain
$$E(k) = \frac{1}{N} \sum_{j, j'} e^{ik(X_j - X_{j'})} \langle \phi_n(x - X_{j'}) | H | \phi_n(x - X_j) \rangle$$

Summation over j, j' covers all the atoms in the lattice.

For each j' , the sum over j gives the same result \Rightarrow get N equal terms

$$E(k) = \sum_{j=-N/2}^{(N-1)/2} e^{ikX_j} \langle \phi_n(x) | H | \phi_n(x - X_j) \rangle \quad (\text{put } j' = 0)$$

got
$$E(k) = \sum_{j=-N/2}^{(N-1)/2} e^{ikX_j} \langle \phi_n(x) | H | \phi_n(x - X_j) \rangle$$

separate the term $j = 0$ from the others:

$$E(k) = \underbrace{\langle \phi_n(x) | H | \phi_n(x) \rangle}_{\substack{\text{energy of electron} \\ \text{in an isolated atom}}} + \sum_j' e^{ikX_j} \underbrace{\langle \phi_n(x) | H | \phi_n(x - X_j) \rangle}_{\substack{\text{includes tunneling effects} \\ \text{significant only for } j = \pm 1}}$$

Write the Hamiltonian
$$H = -\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + V(x)$$

with crystal potential as a sum of atomic potentials:

$$V(x) = \sum_j v(x - X_j) = v(x) + V'(x) \quad \begin{array}{l} v(x) - \text{potential due to the} \\ \text{atom in the origin;} \\ V'(x) - \text{due to all the others} \end{array}$$

$V'(x)$ is small compared to $v(x)$ near the origin. Return to $E(k)$:

$$E(k) = \langle \phi_n(x) | H | \phi_n(x) \rangle + \sum_j' e^{ikX_j} \langle \phi_n(x) | H | \phi_n(x - X_j) \rangle$$

The first term:

$$\langle \phi_n(x) | H | \phi_n(x) \rangle = \underbrace{\langle \phi_n(x) | -\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + v(x) | \phi_n(x) \rangle}_{E_n - \text{energy of atomic level}} + \underbrace{\langle \phi_n(x) | V'(x) | \phi_n(x) \rangle}_{-\beta}$$

$$\beta = -\int \phi_n^*(x) V'(x) \phi_n(x) dx \quad \begin{array}{l} \text{sign is chosen so that } \beta \text{ is positive,} \\ \text{since } V' \text{ is negative} \end{array}$$

β is small: ϕ_n are large only near the origin, where V' is small

Have
$$E(k) = E_n - \beta + \sum_j' e^{ikX_j} \langle \phi_n(x) | H | \phi_n(x - X_j) \rangle$$

Let's consider the interaction term - has two terms in the sum: $X = \pm a$

For $X = a$ have
$$\langle \phi_n(x) | H | \phi_n(x - a) \rangle = \underbrace{\langle \phi_n(x) | -\frac{\hbar^2}{2m_0} \frac{d^2}{dx^2} + v(x - a) | \phi_n(x - a) \rangle}_{E_n \langle \phi_n(x) | \phi_n(x - a) \rangle - \text{negligible}} + \underbrace{\langle \phi_n(x) | V'(x - a) | \phi_n(x - a) \rangle}_{-\gamma}$$

 because of small overlap *overlap integral*

$$\gamma = -\int \phi_n^*(x) V'(x - a) \phi_n(x - a) dx$$

the atomic functions are symmetric \Rightarrow get the same result for $X = -a$

Return to
$$E(k) = E_n - \beta + \sum_j' e^{ikX_j} \langle \phi_n(x) | H | \phi_n(x - X_j) \rangle$$

Now have
$$E(k) = E_n - \beta - \gamma(e^{ika} + e^{-ika}) = E_n - \beta - 2\gamma \cos ka$$

Let $E_0 = E_n - \beta - 2\gamma$ then
$$E(k) = E_0 + 4\gamma \sin^2\left(\frac{ka}{2}\right)$$

$$E(k) = E_0 + 4\gamma \sin^2\left(\frac{ka}{2}\right)$$

Original energy level E_n has broadened into an *energy band*.

The bottom of the band is E_0
- located at $k = 0$

The band width = 4γ – proportional to the overlap integral

For small k , $ka/2 \ll 1$ (near the zone center)

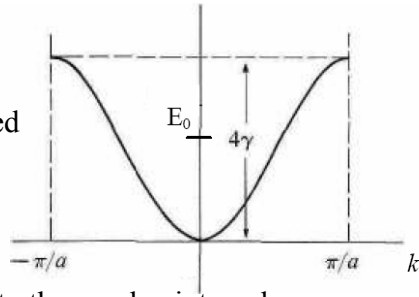
$E(k) - E_0 = \gamma a^2 k^2$ - quadratic dispersion, same as for free electron

$$E(k) - E_0 = \frac{\hbar^2 k^2}{2m^*} \quad \text{where} \quad m^* = \frac{\hbar^2}{2a^2 \gamma} \quad \text{- effective mass}$$

For $k = \pi/2$, you will find that

$$m^* = -\frac{\hbar^2}{2a^2 \gamma}$$

Generally,
$$m^* = \hbar^2 \left(\frac{d^2 E}{dk^2} \right)^{-1}$$

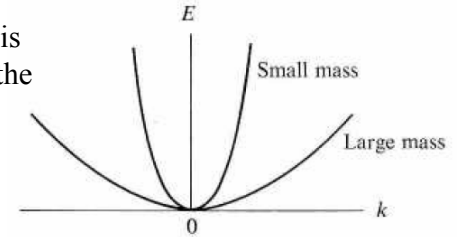


The results obtained can be extended to 3D case.

For simple cubic lattice, get

$$E(k) = E_0 + 4\gamma \left[\sin^2\left(\frac{k_x a}{2}\right) + \sin^2\left(\frac{k_y a}{2}\right) + \sin^2\left(\frac{k_z a}{2}\right) \right]$$

$m^* = \hbar^2 \left(\frac{d^2 E}{dk^2} \right)^{-1}$ Effective mass is determined by the curvature of dispersion

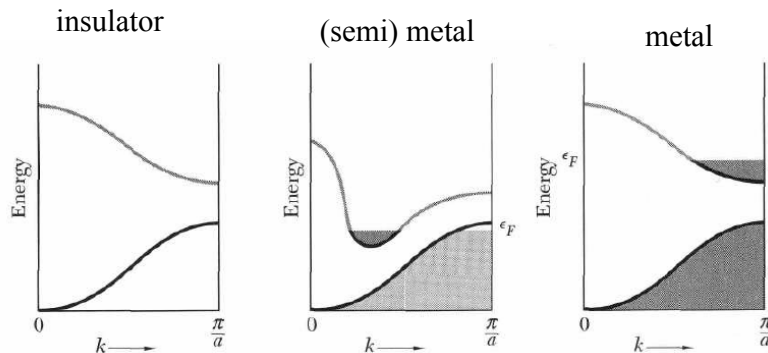


Generally, anisotropic:

$$\left(\frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \quad i, j = x, y, z \quad \text{- inverse effective mass tensor}$$

Velocity of the Bloch electron: $v = \frac{1}{\hbar} \frac{\partial E}{\partial k}$ 3D: $v = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k})$

Metals, Insulators, semimetals, semiconductors



Density of states

Number of electronic states per unit energy range ($E, E+dE$): $D(E)dE$

$D(E)$ – density of states.

In the effective mass approximation, $E(k) = \frac{\hbar^2 k^2}{2m^*}$

Number of states dN_{states} in the shell ($E, E+dE$):

$$dN_{states} = \frac{1}{(2\pi)^3} 4\pi k^2 dk = \frac{1}{4\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2} dE$$

Taking into account spin, multiply by 2.

Get

$$D(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2} \right)^{3/2} E^{1/2}$$

Summary

- ❖ Tight binding model – strong crystal potential, weak overlap. The band width increases and electrons become more mobile (smaller effective mass) as the overlap between atomic wave functions increases
- ❖ Concept of effective mass: in a periodic potential electron moves as in free space, but with different mass:

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \quad i, j = x, y, z$$

- ❖ Metals: partially filled bands; insulators – at 0 K the valence band is full, conduction band is empty. Semiconductors and semimetals.
- ❖ Velocity of the Bloch electron: $v = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k})$
remains constant in perfectly periodic lattice
- ❖ Density of states. Simple case: $D(E) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}$

Summary

- ❖ Velocity of the Bloch electron: $\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} E(\mathbf{k})$
- ❖ In the presence of an electric field the electron moves in k-space according to the relation: $\hbar \frac{d\mathbf{k}}{dt} = \mathbf{F}(\mathbf{r}, t) = -e\mathbf{E}(\mathbf{r}, t)$
This is equivalent to the Newton's second law if we assume that the electron momentum is equal to $\hbar\mathbf{k}$

- ❖ Dynamical effective mass: $m^* = \hbar^2 \left(\frac{d^2 E}{dk^2}\right)^{-1}$
 m^* is inversely proportional to the curvature of the dispersion.
In a general case the effective mass is a tensor: $\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j} \quad i, j = x, y, z$
- ❖ $\mathbf{p}_c = \hbar\mathbf{k}$ is called the *crystal momentum* or *quasi-momentum*.

The actual momentum is given by $\langle \psi_{\mathbf{k}} | -i\hbar\nabla | \psi_{\mathbf{k}} \rangle$

Can show that $\mathbf{p} = m_0\mathbf{v}$, where m_0 is the free electron mass, \mathbf{v} is given by the above expression

Physical origin of the effective mass

Since $\mathbf{p} = m_0\mathbf{v}$ - true momentum, one can write: $m_0 \frac{d\mathbf{v}}{dt} = \mathbf{F}_{tot} = \mathbf{F}_{ext} + \mathbf{F}_L$

The total force is the sum of the external and lattice forces.

But
$$m_0 \frac{d\mathbf{v}}{dt} = m_0 \frac{\mathbf{F}_{ext}}{m^*}$$

So, we can write

$$m^* = m_0 \frac{\mathbf{F}_{ext}}{\mathbf{F}_{ext} + \mathbf{F}_L}$$

The difference between m^* and m_0 lies in the presence of the lattice force \mathbf{F}_L

Current density

Free electron model: $\mathbf{j} = -en\mathbf{v}$; n - the number of valence electrons per unit volume, and \mathbf{v} - the velocity of electrons.

Generalize this expression to the case of Bloch electrons.

In this case the velocity depends of the wave vector \Rightarrow need to sum up over \mathbf{k} vectors

for which there are occupied states available: $\mathbf{j} = \frac{-e}{V} \sum_{\mathbf{k}, occupied} \mathbf{v}(\mathbf{k})$

Convenient to replace the summation by the integration.

The volume of \mathbf{k} -space per allowed \mathbf{k} value is $\Delta\mathbf{k} = 8\pi^3/V \Rightarrow$ we can write the sum over \mathbf{k} as

$$\sum_{\mathbf{k}} = \frac{V}{8\pi^3} \int d\mathbf{k}$$

obtain for the current density: $\mathbf{j} = -e \int_{occupied} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k})$

Holes

Already know that *completely filled bands do not contribute to the current*

Therefore, can write:
$$0 = \int_{\text{zone}} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}) = \int_{\text{occupied}} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k}) + \int_{\text{unoccupied}} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k})$$

we had for the current density:
$$\mathbf{j} = -e \int_{\text{occupied}} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k})$$

can equally well write this in the form:
$$\mathbf{j} = +e \int_{\text{unoccupied}} \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}(\mathbf{k})$$

\Rightarrow *the current produced by electrons occupying a specified set of levels in a band is precisely the same as the current that would be produced if the specified levels were unoccupied and all other levels in the band were occupied but with particles of charge $+e$ - holes.*

Convenient to consider transport of the holes for the bands which are almost occupied, so that only a few electrons are missing.

Can introduce the effective mass for the holes. It has a *negative* sign.

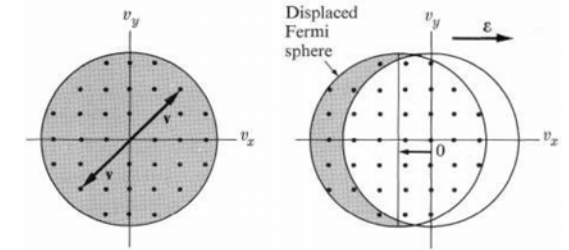
Electrical conductivity

Free electron model:
$$\sigma = -\frac{ne^2\tau_F}{m^*}$$

Let's obtain the corresponding expression within the band theory.

Same idea:

No electric field - the Fermi sphere is centered at the origin. The total current of the system is zero.



Applied field \rightarrow the whole Fermi sphere is displaced

The average displacement is
$$\delta k_x = -\frac{eE}{\hbar} \tau \quad \hbar \frac{d\mathbf{k}}{dt} = \mathbf{F}(\mathbf{r}, t) = -e\mathbf{E}(\mathbf{r}, t)$$

The current density:
$$j_x = -ev_{F,x} n_{\text{uncomp.}} = -ev_{F,x} g(\epsilon_F) \left(\frac{\partial E}{\partial k_x} \right)_{\epsilon_F} \delta k_x$$

$$\left(\frac{\partial E}{\partial k_x} \right)_{\epsilon_F} = \hbar v_{F,x} \Rightarrow j_x = e^2 \bar{v}_{F,x} \tau_F g(\epsilon_F) E \Rightarrow \sigma = \frac{1}{3} e^2 v_F^2 \tau_F g(\epsilon_F)$$

Cyclotron resonance

Lorentz force:
$$\mathbf{F} = -e(\mathbf{v} \times \mathbf{B})$$

Equation of motion:
$$\hbar \frac{d\mathbf{k}}{dt} = -e(\mathbf{v}(\mathbf{k}) \times \mathbf{B})$$

Change in \mathbf{k} in a time interval δt :
$$\delta \mathbf{k} = -\frac{e}{\hbar} (\mathbf{v}(\mathbf{k}) \times \mathbf{B}) \delta t$$

Period of cyclic motion:
$$T = \oint \delta t = -\frac{\hbar}{eB} \oint \frac{\delta \mathbf{k}}{v(\mathbf{k})}$$

Generalized cyclotron frequency for Bloch electron:
$$\omega_c = \frac{2\pi eB}{\hbar} \left(\oint \frac{\delta \mathbf{k}}{v(\mathbf{k})} \right)^{-1}$$

When effective mass approximation is applicable, $v(\mathbf{k}) = \hbar k / m^* \Rightarrow \omega_c = \frac{eB}{m^*}$

Hall effect

We had
$$R_e = -\frac{1}{n_e e}$$

analogously, if only holes are present, have
$$R_h = \frac{1}{n_h e}$$

if both electrons and holes are present

$$R = \frac{R_e \sigma_e^2 + R_h \sigma_h^2}{(\sigma_e + \sigma_h)^2}$$

You will show this in your next homework

Summary

- ❖ Physical origin of effective mass: crystal field
- ❖ Concept of the hole: consider transport of the holes for the bands, which are nearly occupied.

❖ Electrical conductivity: $\sigma = \frac{1}{3} e^2 v_F^2 \tau_F g(\epsilon_F)$

❖ Generalized cyclotron frequency: $\omega_c = \frac{2\pi eB}{\hbar} \left(\oint \frac{\delta \mathbf{k}}{v(\mathbf{k})} \right)^{-1}$

- ❖ Hall coefficient for metals with both electrons and holes:

$$R = \frac{R_e \sigma_e^2 + R_h \sigma_h^2}{(\sigma_e + \sigma_h)^2}$$