

ELECTRON I: Free electron model

Introduction

Free electron model, constructed by Drude and Lorentz near 1900 (well before quantum mechanics was developed), can qualitatively explain the DC electrical conductivity, AC electrical conductivity, Hall effect, and magnetoresistance. Later inclusion of Fermi-Dirac distribution (as opposed to Boltzmann distribution) helps to explain the thermal conductivity and specific heat of electrons. However, many properties still need a full quantum mechanical explanation. For example, the existence of a ‘bandgap’ for semiconductors.

We will then show that a periodic potential will introduce energy bands, and possibly a bandgap. And the solution (wave function of electrons) for a lattice will be always of a ‘Bloch function’ form. Once the wave functions are solved, basically all the properties of solid can be derived. A full band structure calculation by using tight-binding approach will be detailed, and calculation for band structure in various semiconductors will be used as projects.

REFERENCES:

1. Kittel: chapter 6, 7, 8
2. AM: chapter 1-3, 8-10, 12-14, 16, 17.

Free electron gas: good approximation for metals

The importance of Drude model is that it can be used to form quick, intuitive pictures for metals and heavily doped semiconductors. (We will talk about doping in great detail later in this course.) Its basic assumptions are discussed in the following.

- (i) Independent electron approximation: There is no electron-electron interaction, although the averaged spacing is small.
- (ii) Free electron approximation: Ignore electron-phonon interaction.
- (iii) Scattering: Somehow, electrons will bump into ion cores, and such scattering events are instantaneous and can abruptly alter the velocity of electrons.
- (iv) The probability of an electron undergoing scattering in an infinitesimal time interval of length dt is dt/τ . The time τ is called relaxation time, within this model, is independent of electron’s position, energy, momentum, temperature, etc.
- (v) A temperature is used to describe the energy distribution of electrons. The electron velocities before and after a collision have no relation.

Relaxation time

The relaxation time τ in free electron model is loosely connected to the elastic and inelastic scatterings (within the quantum picture). In average, an electron will travel at a speed for a time τ , scatter with an ion core, change its energy and momentum, and travel for a time τ before the next scattering occurs. The distribution of energy and momentum is according to the Fermi-Dirac distribution.

In the Drude model, the probability of an electron suffering a collision in any infinitesimal interval dt is dt/τ , therefore:

- (i) the probability of a randomly picked electron (we don’t know when this electron was last

scattered) that would not be scattered in the next T seconds is $e^{-T/\tau}$. Since

$$\lim_{n \rightarrow \infty} \left(1 - \frac{\lambda}{n}\right)^n = e^{-\lambda}, \quad (1)$$

$$Probability = \lim_{dt \rightarrow 0} \left(1 - \frac{dt}{\tau}\right)^{T/dt} = e^{-T/\tau}. \quad (2)$$

(ii) the probability that the time interval between two successive collisions of an electron falls in the range between t and $t + dt$ is $(dt/\tau)e^{-t/\tau}$ (one collision occurs at time zero, and the successive at interval $t + dt$).

(iii) based on (i), at any moment, the mean time back to the last collision (and up until the next collision) averaged over all electrons is τ .

$$\langle time \rangle = \frac{\int_0^{\infty} dt t e^{-t/\tau}}{\int_0^{\infty} dt e^{-t/\tau}} = \tau. \quad (3)$$

DC conductivity

The net current density (Coulomb/sec/cm²) can be expressed as a product of the carrier density and the speed: $j = nev$, where n is the local electron density, e the charge each electron carries, and v the velocity.

At thermal equilibrium, electrons will traverse in every direction. In the presence of an electric field E , there will be a mean electron velocity in the opposite direction. Now consider one electron at time = 0. If t is the time elapsed since its last collision, then its velocity at time = 0 will be its velocity v_o immediately after the last collision plus $-eEt/m$, where m is the electron mass. Since v_o is random in direction and amplitude, it cannot contribute to the net current, therefore:

$$v_{averaged} = -eE\tau/m, \quad j = nev = (ne^2\tau/m)E, \quad (4)$$

or,

$$j = \sigma E, \quad \sigma = ne^2\tau/m. \quad (5)$$

This explains the Ohm's law, i.e., a constant conductivity.

*Note that the τ and velocity together implies a mean free path, and it can be very long compared with lattice constant. How can electrons fly through (within Drude's picture, electrons are traveling freely in solids) many atoms without any scattering? This inconsistency prompted the development of quantum mechanical picture of electronic states (Bloch theorem, and the Bloch states are now in use for electronic states in a crystal).

Relaxation time approximation

The momentum of an electron at time t is $p(t)$. The probability that this electron will suffer a collision from t to $t + dt$ is dt/τ . Therefore, the probability that this electron will NOT suffer a collision from t to $t + dt$ is $(1 - dt/\tau)$. Under external forces (from electric field, magnetic field, etc.), the momentum will be changed by $f(t)dt$, at time $t + dt$. The equation of motion therefore can be expressed as:

$$p(t + dt) = (1 - \frac{dt}{\tau})[p(t) + f(t)dt + \text{terms of higher orders in } dt], \text{ i.e.,} \quad (6)$$

$$p(t + dt) - p(t) = dp(t) \sim dt[-\frac{p(t)}{\tau} + f(t)] . \quad (7)$$

Therefore, the time derivative of p is equal to the sum of the driving force and the time-relaxation term $-p/\tau$.

Hall effect

The sample is assumed to be a simple rectangle, with the length in the x direction, the width in the y direction, and the thickness in the z direction. Current is parallel to $+\hat{x}$, and thus electron current is parallel to $-\hat{x}$. The magnetic field is pointing to $+\hat{z}$ direction. In the following, we would like to derive that, as a result of Lorentz force, the electrons will accumulate along the surface and induce an electric field, $\hat{E} // +\hat{y}$.

Putting Lorentz force, $eB \times v$, in the relaxation equation:

$$\frac{dp}{dt} = [-eE + \frac{eB \times p}{m}] - \frac{p}{\tau} , \quad (8)$$

where the terms in the square bracket is the force applied, and the second term is from the relaxation of momentum. At steady state, the current is not a function of time, and take the direction of magnetic field parallel to z -axis, we pass a small current (so that the system is still very close to equilibrium) along the x direction, we want to calculate what is the voltage induced along the y direction:

$$0 = -eE_x - \omega_c p_y - \frac{p_x}{\tau}, \quad 0 = -eE_y - \omega_c p_x - \frac{p_y}{\tau}, \quad (9)$$

where ω_c is eB/m , the ‘‘cyclotron frequency.’’ (It’s not too early to read about Landau levels and cyclotron resonance in Kittel and AM.)

Multiplying both ends by $-ne\tau/m$ and move the terms, we get:

$$\sigma_o E_x = \omega_c \tau j_y + j_x; \quad \sigma_o E_y = \omega_c \tau j_x + j_y. \quad (10)$$

The Hall effect comes from the generated E_y term when j_y is zero, i.e.,

$$E_y = \left(\frac{\omega_c \tau}{\sigma_o}\right) j_x = -\left(\frac{B}{ne}\right) J_x. \quad (11)$$

The assumption that $j_y = 0$ is approximately correct by using an electrometer. That is, the transverse voltage V_y is measured by a voltmeter that is so ideal that there is no current ($j_y = 0$) needed. We really have voltmeters that sink about 1pA at 1V, corresponding to 1Tohm.

In real experiments, we plot E_y/J_x versus a scanning B , and the slope is $-1/nec$. By the way, the slope is called the Hall resistance, R_H . The condition that j_y being zero can be met by using a very good voltage meter with very large input impedance, so that it doesn't take much current (pico-Amps) to do a measurement of voltage.

*But, at high fields (more specifically, when $\omega_c \tau \gg 1$) the above linear relation does not work well. We need to use quantum picture to quantitatively explain the results.

Homework: Multi-carrier Hall measurement

Calculate the Hall resistivity (E_y/J_x) for the case where there are both electrons and holes in the solid. The result would be a function of the electron concentration, hole concentration, etc.

AC conductivity

When an AC electric field is applied to a metal, electrons will be driven, and the equation of motion is:

$$\frac{dp}{dt} = -\frac{p}{\tau} - eE, \quad E(t) = \text{Re}[E(\omega)e^{-i\omega t}]. \quad (12)$$

We are looking for solution of the form $p(t) = \text{Re}[p(\omega)e^{-\omega t}]$. Plugging this form into the equation of motion, and the imaginary part is:

$$-i\omega p(\omega) = -\frac{p}{\tau} - eE(\omega). \quad (13)$$

We therefore get:

$$p(\omega) = \frac{eE(\omega)}{(1/\tau) - i\omega}. \quad (14)$$

Taking that $j(t) = \text{Re}[j(\omega)e^{i\omega t}]$, and that $j(\omega) = -nep(\omega)/m = \sigma(\omega)E(\omega)$, we define the AC conductivity $\sigma(\omega)$ as:

$$\sigma(\omega) = \frac{\sigma_o}{1 - i\omega\tau}. \quad (15)$$

Note that the DC limit will be the DC conductivity.

3D Plasmon (chapter 1 of AM, chapter 10 of Kittel)

Using Maxwell's equations, we can derive the dielectric constant of free electron gas under the long wavelength limit, i.e., electric field is uniform in space:

$$\epsilon(\omega) = 1 + \frac{i4\pi\sigma(\omega)}{\omega}. \quad (16)$$

When $\omega\tau \gg 1$, ϵ will approach $1 - \omega_p^2/\omega^2$, where $\omega_p^2 = 4\pi ne^2/m$, the long wavelength limit of 3D plasma frequency.

Below this frequency, light will be reflected by electrons. Above this frequency, light can penetrate metal, with some loss due to scattering (τ).

Free electron 1D (one dimensional) density of states

Based on classical theory, the electronic density of states would be the same as the gas, i.e., the statistical properties follow the Boltzmann distribution. But, the fact is that electrons are 'Fermions,' and they follow the Pauli exclusion principle. (Particle with half-integral spin are called Fermions and they follow Fermi-Dirac statistics.)

Consider now a "strictly" 1D sample of length L , where the electron is free to move in one dimension, and in the other two dimensions there is absolutely no space to move about. The sample size L can be as large as you want. Later you will see that L is only a scaling parameter, and it would be cancelled for large samples. The Schrödinger equation is nothing but $\mathcal{H}\psi = \epsilon\psi$, and $\mathcal{H} = -\frac{\hbar^2 k^2}{2m}$, i.e., there is only the kinetic energy part. The potential energy is zero (or an arbitrary value), since we are considering free electrons. The boundary condition of Schrödinger equation is that $\psi(0) = \psi(L) = 0$. The solution of the Hamiltonian is that:

$\psi_n = A \sin(2\pi x/\lambda_n)$, $\epsilon_n = \hbar^2(n\pi/L)^2/(2m)$, where $\lambda_n = 2L/n$, $n=1,2,3\dots$. Note here that the spacing between neighboring states, Δk_n , is π/L .

The eigenenergies can be represented by the wavevector k_n : $\epsilon_n = \hbar^2(n\pi/L)^2/2m = \hbar^2 k_n^2/2m$, where k_n is $2\pi/\lambda_n$.

We can also choose to use the periodic boundary condition (as the one we used in the case of phonons). Then, we will arrive at solutions of the form $\psi = e^{ik_n x}$, where k_n can be either positive or negative. To satisfy the periodic boundary condition, we have $\psi(x+L) = \psi(x)$, which leads to that $k_n = 0, \pm 2\pi/L, \pm 4\pi/L$, etc. That is, Δk_n is $2\pi/L$. So, picking the periodic B.C. will lead to the same results as the fixed-end boundary condition, when the size L is large, because it takes two traveling waves (i.e., solutions using the periodic boundary condition) to construct a standing wave (which refers to those solutions obtained earlier by using the fixed-end boundary condition).

The eigenenergies can then be represented by the wavevector k_n : $\epsilon_n = \hbar^2 k_n^2/2m = \hbar^2(n2\pi/L)^2/2m$, where k_n is $2\pi/\lambda_n$, and $\lambda_n = L/n$.

According to the Pauli exclusion principle, only two electrons (spin up and spin down) can occupy one state with the same energy, a state labeled by quantum number n can accommodate two electrons.

The **Fermi energy**, defined as the energy of the topmost filled state (relative to the energy of the ground state), can be calculated by counting the number of electrons in the system at zero temperature. That is, all states below Fermi level are filled, and all states above Fermi level are empty, at $T=0$. Taking a convention that the state label n start from 1, and that the level degeneracy (the number of electrons at the same energy) is two, we simply plug the number of electrons in the system N into the equation: $\epsilon_F = \hbar^2((n_F)\pi/L)^2/2m = \hbar^2(N\pi/2L)^2/2m$.

Homework: Density of states

Derive the density of states $D(E)$ of free electrons in 1D. Assume that the sample size L is very large, and express $D(E)$ in the unit of # of states/energy.

Approach: Start from the definition, and make use of the result that $\epsilon = \hbar^2 k^2/2m$. $D(E)d\epsilon = L/(2\pi)d\epsilon/(d\epsilon/dk) = L/(2\pi)d\epsilon/(\hbar^2 k/m)$. Convert k back to energy, and we get: $D(E) = L/(2\pi)/(\hbar^2 k/m) = L\sqrt{m}/(2\sqrt{2}\pi\hbar\sqrt{\epsilon})$. Check the unit to see if this is right. Finally, take L away if the answer is to be per unit length. Plot the shape of $D(E)$ and understand the physical meaning of the state at $\epsilon = 0$.

Quantum statistics: Fermi-Dirac distribution

The distribution function (the probability that a state is filled at energy ϵ for Fermions at any temperature T is

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT} + 1}, \quad (17)$$

where ϵ is the energy of the particular electron of interest, and μ is the energy at Fermi level. At all temperatures greater than zero, $f(\mu) = 1/2$. Note that the Fermi-tail (at high energy side) approaches the expression of the Boltzmann distribution function.

Free electron gas in 2D and 3D

We can easily extend the 1D results to 2D and 3D.

Homework: Density of states in 2D and 3D

Calculate (and plot) the $D(E)$, ϵ_F , k_F , v_F (velocity of electrons at Fermi level) for the case of 2D and 3D, at $T=0$. Take N as the total number of electrons. At equilibrium, and at nonzero temperatures, the following relation holds by definition:

$$N = \int_{-\infty}^{\infty} d\epsilon f(\epsilon)D(\epsilon). \quad (18)$$

Specific heat of electrons: quantum picture

Now we can calculate the (kinetic) energy change as a function of temperature.

$$C_v = \frac{dE}{dT} = \frac{d[\int_0^{\infty} d\epsilon \epsilon D(\epsilon) f(\epsilon)]}{dT}. \quad (19)$$

The derivation of C_v is shown in the following. In addition, read chapter 2 of AM and chapter 6 of Kittel.

A useful relation: only electrons near Fermi level are active in transport

Given that f_0 is the Fermi-Dirac distribution function at equilibrium, the concentration of electrons will be $n = \int_0^\infty f_0 D(\epsilon) d\epsilon$, where $D(\epsilon)$ is the density of state. Here I would like to show that only those electrons near ϵ_F can contribute to transport properties. If we want to calculate a property that is related to function g , and the actual calculation involves the integration of the form:

$$F = \int_0^\infty d\epsilon g(\epsilon) f_0, \quad (20)$$

$$= G(\epsilon) f_0 \Big|_0^\infty - \int_0^\infty G(\epsilon) \frac{\partial f_0}{\partial \epsilon} d\epsilon, \quad (21)$$

where $G(\epsilon) = \int_0^\epsilon d\epsilon g(\epsilon)$. Note here that the first term is zero, since $G(0) = 0$ and $f_0(\infty) = 0$. The last integration is done through integration by parts: $d(uv) = u dv + v du \Rightarrow u dv = d(uv) - v du \Rightarrow \int u dv = uv - \int v du$. Now, we define dv as $d\epsilon g(\epsilon)$, i.e., v is $G(\epsilon)$, and define du as $\frac{\partial f_0}{\partial \epsilon} d\epsilon$, i.e., u is f_0 .

So, we get:

$$F = - \int_0^\infty G(\epsilon) \frac{\partial f_0}{\partial \epsilon} d\epsilon. \quad (22)$$

Now, use Taylor expansion on G around ϵ_F :

$$G(\epsilon) = G(\epsilon_F) + (\epsilon - \epsilon_F) G' \Big|_{\epsilon_F} + \frac{1}{2} (\epsilon - \epsilon_F)^2 G'' \Big|_{\epsilon_F} + \dots. \quad (23)$$

$$F = - \int_0^\infty G(\epsilon_F) \frac{\partial f_0}{\partial \epsilon} d\epsilon - \int_0^\infty (\epsilon - \epsilon_F) G' \Big|_{\epsilon_F} \left(\frac{\partial f_0}{\partial \epsilon} \right) d\epsilon + \dots \quad (24)$$

$$= G(\epsilon_F) \int_0^\infty \left(- \frac{\partial f_0}{\partial \epsilon} \right) d\epsilon + G' \Big|_{\epsilon_F} \int_0^\infty (\epsilon - \epsilon_F) \left(- \frac{\partial f_0}{\partial \epsilon} \right) d\epsilon + \frac{1}{2} G'' \Big|_{\epsilon_F} \int_0^\infty (\epsilon - \epsilon_F)^2 \left(- \frac{\partial f_0}{\partial \epsilon} \right) d\epsilon + \dots \quad (25)$$

Note that the integration in the first term is $f_0(0) - f_0(\infty) = 1 - 0 = 1$. The second integration (after G') is zero owing to symmetry. The third integration can be done by plugging in the functional form of the distribution function and change of variables. The results are shown in the following.

$$F = G(\epsilon_F) + \frac{\pi^2}{6} (kT)^2 G'' \Big|_{\epsilon_F} + \dots. \quad (26)$$

One example of using this relation

There is this important property that for a given concentration, the energy position of Fermi level will change as a function of temperature. We want to calculate such change. (When doing numerical analysis, we use a function to fit the known result to save computation time.) At any temperature, the concentration of electrons n is:

$$n = \int_0^{\epsilon_F(T=0)} D(\epsilon) d\epsilon = \int_0^{\infty} D(\epsilon) f_0 d\epsilon = \int_0^{\epsilon_F(T \neq 0)} D(\epsilon) d\epsilon + \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial D}{\partial \epsilon} \Big|_{\epsilon_F} \right) + \dots \quad (27)$$

That is, we have taken D as the g (therefore $G = \int_0^{\epsilon_F} d\epsilon D(\epsilon)$).

Homework: Based on the above equation, show that the solution of ϵ_F is:

$$\epsilon_F(T \neq 0) \sim \epsilon_F(T = 0) - \frac{\pi^2}{6} (kT)^2 \left(\frac{\partial \ln D}{\partial \epsilon} \Big|_{\epsilon_F} \right). \quad (28)$$

Therefore, if n is constant, then the change of ϵ_F as a function of T would be:

$$\frac{\partial \epsilon_F(T)}{\partial T} \sim 0 - \frac{\pi^2}{3} (k^2 T) \frac{1}{D} \left(\frac{\partial D}{\partial \epsilon} \Big|_{\epsilon_F} \right). \quad (29)$$

This property will be used later.

Calculation of electronic C_v

The total kinetic energy is:

$$U = \int_0^{\infty} d\epsilon \epsilon D f_0. \quad (30)$$

Now take function g as $\epsilon D(\epsilon)$, we get:

$$U = \int_0^{\infty} d\epsilon g f_0 = \int_0^{\epsilon_F} d\epsilon \epsilon D + \frac{\pi^2}{6} (kT)^2 \frac{\partial(\epsilon D)}{\partial \epsilon} \Big|_{\epsilon_F} = \text{term1} + \text{term2}. \quad (31)$$

$$\frac{\partial \text{term1}}{\partial T} = \frac{\partial \int_0^{\epsilon_F} d\epsilon \epsilon D}{\partial dT} = \epsilon_F D(\epsilon_F) \frac{\partial \epsilon_F}{\partial T}. \quad (32)$$

$$\frac{\partial \text{term2}}{\partial T} = \frac{\pi^2}{6} (k)^2 (2T) \frac{\partial(\epsilon D)}{\partial \epsilon} \Big|_{\epsilon_F} + O(T^2) \quad (33)$$

$$= \frac{\pi^2}{3} (k)^2 (T) [D(\epsilon_F) + \epsilon_F \frac{\partial D}{\partial \epsilon} \Big|_{\epsilon_F}] + O(T^2) \quad (34)$$

$$C_v = \frac{\partial term1}{\partial T} + \frac{\partial term2}{\partial T} = \frac{\pi^2}{3}(k)^2(T)D(\epsilon_F) + \epsilon_F D(\epsilon_F) \left[\frac{\partial \epsilon_F}{\partial T} + \frac{\pi^2}{3D}(k)^2(T) \frac{\partial D}{\partial \epsilon} \Big|_{\epsilon_F} \right]. \quad (35)$$

Plugging the results from the last section (temperature dependence of Fermi level), we can prove that the order of the second term is second order in T . So, as long as kT is much less than ϵ_F , we get:

$$C_v \sim \frac{\pi^2}{3}(k)^2(T)D(\epsilon_F). \quad (36)$$

The ratio between the quantum result and the classical result is:

$$\frac{C_v|_{quantum}}{C_v|_{classical}} = \frac{\frac{\pi^2}{3}(k)^2(T)D(\epsilon_F)}{3nk/2} = \frac{\pi^2 kT}{3\epsilon_F} \ll 1. \quad (37)$$

For most metals, the ϵ_F is in the order of a few eV, much larger than room temperature kT . The contribution to C_v from electrons is only going to dominate at very low temperatures (below 1K), since the phonon contribution is $\propto T^3$.

We understand the origin of the electronic C_v as coming from only those electrons near the Fermi level. Owing to the Pauli exclusion principle, that each quantum energy can only host two (spin up and spin down) electrons, the electrons at states several kT below ϵ_F cannot contribute to thermal conductivity, nor to the specific heat.