

Notes of Solid State Physics

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Chapter 1

The Drude Theory of Metal

1.1 Basic Assumptions of the Model

Drude constructed his model after J.J.Thompson's discovery of electrons by applying the simplest kinetic theory to describe the motion of negative charged gas of electrons in the metal, which achieved great success. Drude applied kinetic theory to the gas of conduction electrons by the mass m , which move against in the background of immobile ions. The number of electrons in per unit volume is introduced by the following expression

$$n = N_A \frac{Z\rho_m}{A} \quad (1.1)$$

where N_A is the Avogadro constant; Z is the charge carried by the nucleus; ρ_m is the density of the metal; A is the mass of this element. If each electron can be seen as occupying a spherical space, then the radius of such a sphere is

$$r_s = \left(\frac{3}{4\pi n}\right)^{1/3} \quad (1.2)$$

To specify the kinetic motion of the gas, Drude raised four assumptions:

1. Between collisions the interaction of a given electrons, both with others and with the ions, is neglected.
2. Collisions are instantaneously happened that brusquely change the velocity of the electrons.
3. An electron experiences a collision with a probability per unit time $1/\tau$.
4. Electrons are considered to be at equilibrium with the surroundings only through the collisions.

Remarks

1. The third assumption illustrates that an electron will experience a collision by a probability of dt/τ in the infinitesimal time interval dt , and without collision by $1 - dt/\tau$.
2. We assume that the electrons are subjected in an external field that provides external force $\mathbf{F}(t)$ on the electrons. The momentum of a single electron is a function of time $\mathbf{p}(t)$. Since the probability to survive a collision in a infinitesimal time is $1 - dt/\tau$, then this portion of electrons will contribute to the momentum by

$$\mathbf{p}(t + dt) = (1 - \frac{dt}{\tau})(\mathbf{p}(t) + \mathbf{F}(t)dt) \quad (1.3)$$

Or in another expression

$$\frac{d\mathbf{p}(t)}{dt} = \mathbf{F}(t) - \frac{\mathbf{p}(t)}{\tau} \quad (1.4)$$

Equation (1.4) display the equation of a free electron in an external field.

1.2 DC Electrical Conductivity of a Metal

In the absence of electric field, the electrons are likely to moving at any directions, with velocity averages to zero. If the electric field is added, the average velocity yields to $-e\mathbf{E}t/m$. Since the average of time is τ , therefore

$$\langle \mathbf{v} \rangle = \frac{-e\mathbf{E}\tau}{m} \quad (1.5)$$

So the electric current density is

$$\mathbf{j} = -ne \langle \mathbf{v} \rangle = \frac{ne^2\tau}{m} \mathbf{E} \quad (1.6)$$

Hence we get the expression of the conductivity with respect to the relaxation time τ

$$\sigma = \frac{ne^2\tau}{m} \quad (1.7)$$

1.3 Hall Effect and Magnetoresistance

The Hall effect was discovered by E.Hall in 1879, which indicates that a voltage difference is generated in a electric conductor, transverse to both the current through it and the external magnetic field, as figure 1.1 shows.

An electric field E_x is applied on the conductor producing a current density j_x inside. A magnetic field \mathbf{H} is along z-direction. The Lorentz force on an electron can be given by

$$\mathbf{F} = -e\mathbf{E} - \frac{e}{c} \mathbf{v} \times \mathbf{H} \quad (1.8)$$

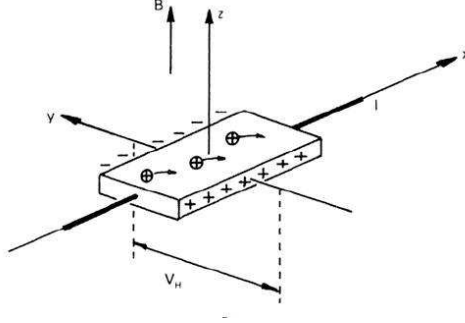


Figure 1.1: Hall effect.

Then the motion of equation of the electron is

$$\frac{d\mathbf{p}(t)}{dt} = -e\mathbf{E} - \frac{e}{c}\mathbf{v} \times \mathbf{H} - \frac{\mathbf{p}(t)}{\tau} \quad (1.9)$$

Rearrange equation (1.9) and we obtain the x- and y-components of the electric field by

$$\begin{aligned} \sigma_0 E_x &= j_x + \omega_c \tau j_y \\ \sigma_0 E_y &= j_y - \omega_c \tau j_x \end{aligned} \quad (1.10)$$

where σ_0 is the DC conductivity in the absence of magnetic field and $\omega_c = eH/mc$ is the cyclotron frequency. When $j_y = 0$, then the y-direction electric field exists.

$$E_y = -\frac{\omega_c \tau}{\sigma_0} j_x = -\frac{H}{nec} j_x \quad (1.11)$$

Therefore the Hall coefficient is defined by

$$R_H = -\frac{1}{nec} \quad (1.12)$$

which only depends on the number density of the free electrons.

The ratio of the transverse electric field and the current density

$$\rho(H) = \frac{E_y}{j_x} \quad (1.13)$$

is called magnetoresistance, which is found to be strong dependent with magnetic field experimentally.

1.4 AC Electrical Conductivity of a Metal

We first express the time-dependent electric field in the form of

$$\mathbf{E}(\omega, t) = \text{Re}\{\mathbf{E}(\omega)e^{-i\omega t}\} \quad (1.14)$$

We seek for a time-dependent solution for momentum

$$\mathbf{p}(\omega, t) = \text{Re}\{\mathbf{p}(\omega)e^{-i\omega t}\} \quad (1.15)$$

According to equation (1.4), we have

$$-i\omega\mathbf{p}(\omega) = -e\mathbf{E}(\omega) - \frac{\mathbf{p}(\omega)}{\tau} \quad (1.16)$$

So

$$\mathbf{p}(\omega) = \frac{-\tau e\mathbf{E}(\omega)}{1 - i\omega\tau} \quad (1.17)$$

Since the current density is $\mathbf{j} = -nev = -ne\mathbf{p}/m$, so

$$\mathbf{j} = -\frac{ne\mathbf{p}(\omega)}{m} = \frac{(ne^2/m)\mathbf{E}(\omega)}{(1/\tau) - i\omega} \quad (1.18)$$

So the AC conductivity is

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \quad (1.19)$$

Hence the complex dielectric constant can be derived by applying Maxwell's equations and equation (1.19)

$$\epsilon(\omega) = 1 + \frac{4\pi i\sigma(\omega)}{\omega} = 1 + \frac{4\pi i\sigma_0}{\omega(1 - i\omega\tau)} \quad (1.20)$$

If the frequency is high enough so that

$$\omega\tau \gg 1 \quad (1.21)$$

then

$$\epsilon(\omega) \approx 1 - \frac{4\pi}{\omega^2} \frac{ne^2}{m} = 1 - \frac{\omega_p^2}{\omega^2} \quad (1.22)$$

where $\omega_p = (4\pi ne^2/m)^{1/2}$ is the plasma frequency.

Remarks We consider the frequency of the light and the consequential propagating behaviour in the metal. The refractive index, if magnetic reaction is neglected, is $n(\omega) = \sqrt{\epsilon(\omega)}$

1. If $\omega > \omega_p$, then $\epsilon > 0$ and n has only real part. In this case light can transmit the metal.
2. If $\omega < \omega_p$, then $\epsilon < 0$ and n has both real and imaginary parts. In this case light will be absorbed.

1.5 Thermal Conductivity of a Metal

Drude theory successfully explained the empirical law of Wiedemann and Frantz, which states that the ratio of thermal conductivity and the electrical conductivity is proportional to the temperature. In this model, the electrons are regarded to conduct heat in the metal. Fourier's law displays that the heat flow, which described by thermal current density, is proportional to the gradient of temperature

$$\mathbf{j}^q = -\kappa \nabla T \quad (1.23)$$

The proportionality constant is called the thermal conductivity.

To simplify our case, we consider a 1-D bar whose two ends are at different temperature. The temperature at each point on the bar is position-dependent, thus the kinetic energy of electrons is also with respect to the position. Electrons from both the hotter side and the colder side will move towards the middle after experiencing collisions, with half the number per unit volume. If we consider a point x on the bar, then the thermal current density at x should be

$$\mathbf{j}^q = \mathbf{j}_{\text{left}}^q + \mathbf{j}_{\text{right}}^q = \frac{1}{2}nv[\epsilon(T(x-v\tau)) - \epsilon(T(x+v\tau))] \quad (1.24)$$

Expand the right hand side since $v\tau$ is very small, then

$$\mathbf{j}^q = -nv^2\tau \frac{d\epsilon}{dT} \frac{dT}{dx} \quad (1.25)$$

Since $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = 1/3v^2$ and $nd\epsilon/dT = dE/dT/V = c_v$, so

$$\mathbf{j}^q = \frac{1}{3}v^2\tau c_v(-\nabla T) \quad (1.26)$$

or

$$\kappa = \frac{1}{3}v^2\tau c_v \quad (1.27)$$

Divide both sides by σ , then we obtain

$$\frac{\kappa}{\sigma} = \frac{c_v m v^2}{3n e^2} = \frac{3}{2} \left(\frac{k_B}{e} \right)^2 T \quad (1.28)$$

Equation (1.28) verifies the law of Wiedemann and Frantz.

We next discuss the thermopower, which illustrate that a gradient of temperature should accompanied by an electric field in the opposite direction.

$$\mathbf{E} = Q \nabla T \quad (1.29)$$

Similarly we consider a 1-D bar. The velocity of electrons at point x is

$$v_Q = \frac{1}{2}[v(x-v\tau) - v(x+v\tau)] = -\tau v \frac{dv}{dx} = -\tau \frac{d}{dx} \left(\frac{v^2}{2} \right) \quad (1.30)$$

Since, as mentioned before, $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = 1/3 v^2$, so we have

$$\mathbf{v}_Q = -\frac{\tau}{6} \frac{d}{dT} \langle v^2 \rangle \nabla T \quad (1.31)$$

The mean velocity due to the electric field is

$$\mathbf{v}_E = -\frac{\mathbf{j}}{ne} = -\frac{e\mathbf{E}\tau}{m} \quad (1.32)$$

To have $\mathbf{v}_Q + \mathbf{v}_E = 0$ we must require

$$Q = -\frac{1}{3e} \frac{d}{dT} \left(\frac{mv^2}{2} \right) = -\frac{c_v}{ne} \quad (1.33)$$

The observed thermopower, however, is smaller by a factor of 100. The same error also occurs in the derivation of Wiedemann-Frantz law. This consequence also shows the insufficiency of Drude Theory.

Chapter 2

The Sommerfeld Theory of Metals

2.1 Fermi-Dirac Distribution

After Drude's discovery, people found that the velocity of electrons distribution obeys the Maxwell-Boltzmann distribution:

$$f_B(\mathbf{v}) = n \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_B T} \quad (2.1)$$

After the recognition of quantum mechanics and Pauli's exclusion principle, the distribution was noticed to be replaced by Fermi-Dirac distribution

$$f(\mathbf{v}) = \left(\frac{m/\hbar}{4\pi} \right)^3 \frac{1}{\exp\{(1/2mv^2 - k_B T_0)/k_B T\} + 1} \quad (2.2)$$

2.2 Ground State of the Electron Gas

We first introduce the ground state of the electron gas at $T = 0$. N electrons are confined in a volume V . For simplicity, we describe the volume by a cube with side L , hence $V = L^3$. The interaction between a single electron and other particles is ignored, so the only concerned energy is the kinetic energy ϵ . If we specify the state of an electron by a wavefunction $\psi(\mathbf{r})$, then the Schrodinger equation writes

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r}) \quad (2.3)$$

In such case the normalized solution can be written in the form of

$$\psi(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{-i\mathbf{k} \cdot \mathbf{r}} \quad (2.4)$$

and the corresponding energy eigenvalues are

$$\epsilon(\mathbf{k}) = \frac{\hbar^2 k^2}{2m} \quad (2.5)$$

The wavefunction must append the periodic boundary conditions. So the wave vectors along each directions can only be valued by discrete numbers.

$$k_i = \frac{2\pi n_i}{L}, \quad n_i \in \mathbb{Z}, \quad i = x, y, z \quad (2.6)$$

So the volume occupied by a single \mathbf{k} point in k-space is $(2\pi/L)^3$ and the density of states, which indicates the number of \mathbf{k} points per unit volume of k-space is thus

$$V/(8\pi^3) \quad (2.7)$$

According to these results we can calculate the ground-state energy. Firstly, the total number of electrons is

$$N = 2 \frac{V}{8\pi^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^{k_F} k^2 dk = \frac{V k_F^3}{3\pi^2} \quad (2.8)$$

The total ground-state energy (for all the electrons) is

$$E = 2 \frac{V}{8\pi^3} \int_0^{2\pi} d\phi \int_0^\pi \sin\theta d\theta \int_0^{k_F} \frac{\hbar^2 k^2}{2m} k^2 dk = \frac{V \hbar^2 k_F^5}{10\pi^2 m} \quad (2.9)$$

So the energy per electron reads

$$\epsilon = \frac{E}{N} = \frac{3}{5} \frac{\hbar^2 k_F^2}{2m} = \frac{3}{5} \epsilon_F \quad (2.10)$$

We can rewrite the density of state in terms of energy. Since the energy per electron is $\epsilon = \hbar^2 k^2/2m$, then $k = \sqrt{2m\epsilon/\hbar^2}$. Hence $dk = d\epsilon \sqrt{m/(2\hbar^2\epsilon)}$. So

$$N = \frac{V}{\pi^2} \int_0^\infty k^2 f(k) dk = V \int_0^\infty f(\epsilon) \frac{(2m^3\epsilon)^{1/2}}{\pi^2 \hbar^2} d\epsilon = V \int_0^\infty f(\epsilon) g(\epsilon) d\epsilon \quad (2.11)$$

where $g(\epsilon) = \frac{(2m^3\epsilon)^{1/2}}{\pi^2 \hbar^2}$ is the density of levels per unit volume. It can also be written in another form

$$g(\epsilon) = \frac{3}{2} \frac{n}{\epsilon_F} \sqrt{\frac{\epsilon}{\epsilon_F}} \quad (2.12)$$

Hence the energy density per unit volume is

$$u = \frac{U}{V} = \int_0^\infty d\epsilon f(\epsilon) g(\epsilon) \epsilon \quad (2.13)$$

and the electron number density

$$n = \int_0^\infty d\epsilon f(\epsilon) g(\epsilon) \quad (2.14)$$

where

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1} \quad (2.15)$$

2.3 The Sommerfeld Expansion

The integrals in (2.13) and (2.14) is complicated. The method applied to approximate such integrals is called the Sommerfeld expansion, which was established by A. Sommerfeld, generally of the form of

$$\int_{-\infty}^{\infty} f(\epsilon) H(\epsilon) d\epsilon \quad (2.16)$$

where $H(\epsilon)$ vanishes to zero for $\epsilon \rightarrow 0\infty$ and diverges on more than the power of ϵ for $\epsilon \rightarrow \infty$. We first define

$$K(\epsilon) = \int_0^{\epsilon} H(\epsilon') d\epsilon' \quad (2.17)$$

so that

$$H(\epsilon) = \frac{dK(\epsilon)}{d\epsilon} \quad (2.18)$$

so the aiming integral becomes

$$\int_{-\infty}^{\infty} f(\epsilon) H(\epsilon) d\epsilon = \int_{-\infty}^{\infty} \left(-\frac{df(\epsilon)}{d\epsilon}\right) K(\epsilon) d\epsilon \quad (2.19)$$

We expand $K(\epsilon)$ around $\epsilon = \mu$, then

$$K(\epsilon) = K(\mu) + \sum_{n=1}^{\infty} \frac{(\epsilon - \mu)^n}{n!} K^{(n)}(\mu) \quad (2.20)$$

Thus the integral on the right hand side in equation (2.19) becomes

$$\begin{aligned} & \int_{-\infty}^{\infty} \left(-\frac{df(\epsilon)}{d\epsilon}\right) K(\epsilon) d\epsilon \\ &= \int_{-\infty}^{\infty} \left(-\frac{df(\epsilon)}{d\epsilon}\right) K(\mu) d\epsilon + \sum_{n=1}^{\infty} \frac{K^{(n)}(\mu)}{n!} \int_{-\infty}^{\infty} (\epsilon - \mu)^n \left(-\frac{df(\epsilon)}{d\epsilon}\right) d\epsilon \end{aligned} \quad (2.21)$$

Since $-\frac{df(\epsilon)}{d\epsilon}$ is a even function of $\epsilon - \mu$, so the terms with odd n vanish in last term in equation (2.21) and only even n survive. We also have

$$\int_{-\infty}^{\infty} \left(-\frac{df(\epsilon)}{d\epsilon}\right) d\epsilon = 1 \quad (2.22)$$

So

$$\begin{aligned} & \int_{-\infty}^{\infty} \left(-\frac{df(\epsilon)}{d\epsilon}\right) K(\epsilon) d\epsilon \\ &= \int_{-\infty}^{\infty} \left(-\frac{df(\epsilon)}{d\epsilon}\right) K(\mu) d\epsilon + \sum_{n=1}^{\infty} \frac{K^{(2n)}(\mu)}{(2n)!} \int_{-\infty}^{\infty} (\epsilon - \mu)^{2n} \left(-\frac{df(\epsilon)}{d\epsilon}\right) d\epsilon \\ &= K(\mu) + \sum_{n=1}^{\infty} \frac{K^{(2n)}(\mu)}{(2n)!} \int_{-\infty}^{\infty} (\epsilon - \mu)^{2n} \left(-\frac{df(\epsilon)}{d\epsilon}\right) d\epsilon \end{aligned} \quad (2.23)$$

Make a substitution $x = (\epsilon - \mu)/k_B T$, then we have

$$\int_{-\infty}^{\infty} \frac{(\epsilon - \mu)^{2n}}{(2n)!} \left(-\frac{df(\epsilon)}{d\epsilon}\right) d\epsilon = (k_B T)^{2n} \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1}\right) dx = a_n (k_B T)^{2n} \quad (2.24)$$

In order to acquire a_n we should first calculate the following integral

$$a_n = \int_{-\infty}^{\infty} \frac{x^{2n}}{(2n)!} \left(-\frac{d}{dx} \frac{1}{e^x + 1}\right) dx \quad (2.25)$$

which can be calculated by separating the it into two parts

$$\begin{aligned} a_n &= - \int_0^{\infty} \frac{x^{2n}}{(2n)!} d\left(\frac{1}{e^x + 1}\right) + \int_0^{-\infty} \frac{x^{2n}}{(2n)!} d\left(\frac{1}{e^x + 1}\right) \\ &= - \left[\frac{x^{2n}}{(2n)!(e^x + 1)}\right]_0^{\infty} + \int_0^{\infty} \frac{x^{2n-1}}{(2n-1)!(e^x + 1)} dx \\ &\quad + \left[\frac{x^{2n}}{(2n)!(e^x + 1)}\right]_0^{-\infty} - \int_0^{\infty} \frac{x'^{2n-1}}{(2n-1)!(e^{-x'} + 1)} dx' \\ &= 2 \int_0^{\infty} \frac{x^{2n-1}}{(2n-1)!(e^x + 1)} dx \\ &= 2 \left(1 - \frac{1}{2^{2n}} + \frac{1}{3^{2n}} - \frac{1}{4^{2n}} + \dots\right) \\ &= \frac{1}{2} \left(1 - \frac{1}{2^{2n}}\right) \zeta(2n) \\ &= (-1)^{n+1} \frac{1}{2} \left(1 - \frac{1}{2^{2n}}\right) \frac{B_{2n} (2\pi)^{2n}}{2(2n)!} \end{aligned} \quad (2.26)$$

where B_{2n} is the Bernoulli number with order $2n$. So equation (2.16) can finally be written in the form of

$$\begin{aligned} \int_{-\infty}^{\infty} f(\epsilon) H(\epsilon) d\epsilon &= K(\mu) + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} K^{(2n)}(\mu) \\ &= K(\mu) + \frac{\pi^2}{6} (k_B T)^2 K^{(2)}(\mu) + \frac{7\pi^4}{360} (k_B T)^4 K^{(4)}(\mu) + \dots \\ &= \int_{-\infty}^{\mu} H(\epsilon) d\epsilon + \frac{\pi^2}{6} (k_B T)^2 K'(\mu) + O(T^4) \end{aligned} \quad (2.27)$$

The higher terms beyond T^2 are neglected because the temperature is relatively low comparing to the Fermi temperature. Hence, only the first two terms are reserved. To obtain the number density by (2.14) and (2.27)

$$\begin{aligned} n &= \int_0^{\infty} g(\epsilon) f(\epsilon) d\epsilon \\ &\approx \int_0^{\infty} g(\epsilon) d\epsilon + \frac{\pi^2}{6} g'(\mu) (k_B T)^2 \\ &\approx n \left(\frac{\mu}{\epsilon_F}\right)^{3/2} + \frac{\pi^2}{8} n \left(\frac{k_B T}{\epsilon_F}\right)^2 \left(\frac{\mu}{\epsilon_F}\right)^{-1/2} \end{aligned} \quad (2.28)$$

Hence, the chemical potential can be written in the form of a function of T

$$\mu(T) \approx \epsilon_F \left(1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F}\right)^2\right) \quad (2.29)$$

Obviously, as the temperature rises, the chemical potential decrease by a small rate. For example, if the Fermi energy $\epsilon_F = 5\text{eV}$, then as the temperature ascends from 0K to 300K, the chemical potential descends about $5 \times 10^{-3}\text{K}$.

Similarly, from equation (2.13) and (2.27) we can obtain the energy density

$$u \approx \frac{3}{5} n \epsilon_F + \frac{\pi^2}{4} \frac{n}{\epsilon_F} (k_B T)^2 \quad (2.30)$$

So the specific heat is given by

$$c_v = \frac{\partial u}{\partial T} = \frac{\pi^2}{2} \frac{n}{\epsilon_F} (k_B)^2 T = \frac{\pi^2}{3} \left(\frac{k_B T}{\epsilon_F}\right) \frac{3}{2} n k_B \quad (2.31)$$

This specific heat in equation (2.31) is significantly smaller than the result given by the ideal gas law, $3/2 n k_B$, by a factor to the order to about 10^{-2} , which compensates the error in Drude model. It also displays that the specific heat is proportional to the temperature. Experimentally, however, besides the proportional term, another term is given with proportionality to T^3 , which is effected by phonons.

Chapter 3

Crystal Structure

3.1 Bravais Lattice, Primitive Cells

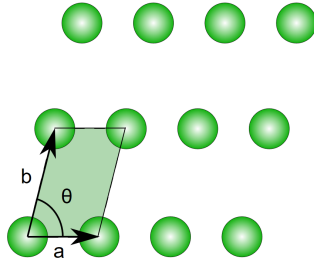


Figure 3.1: A 2-D Bravais lattice. The green area is a typical primitive cell. Source: <https://upload.wikimedia.org/wikipedia/commons/e/ee/2d-bravais.svg>

To describe the periodic structure of crystal, shown in figure 3.1, we first introduce the concepts of the Bravais lattice and the primitive cells. Two equivalent definitions of Bravais lattice are given

Definition 3.1 (Bravais lattice). *A Bravais lattice is:*

1. *An infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.*
2. *A 3-D Bravais lattice consists all the points with position vector of the form of*

$$\mathbf{R}_n = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \quad n_i \in \mathbb{Z} \quad (3.1)$$

where \mathbf{a}_i are three vectors not all in the same plane.

Remarks The vectors \mathbf{a}_i in the second definition are called the primitive vectors and are said to generate or span the lattice.

Definition 3.2 (Primitive cell). *A primitive cell is a volume of space that, when translated through all the vectors in a Bravais lattice, just fills all of space without either overlapping itself or leaving voids.*

Remarks

1. The primitive should be the cell with the smallest volume in a 3-D Bravais lattice. Sometimes we choose a unit cell, which is bigger than a primitive cell and have the same symmetry.
2. The volume of the primitive cell is given by

$$\Omega = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \quad (3.2)$$

3. The Bravais lattice can be partitioned into primitive cells in different ways. One typical partition is called Wigner-Seitz primitive cell, named after Eugene Wigner and Frederick Seitz, which is constructed by applying Voronoi decomposition to a crystal lattice. The Wigner-Seitz primitive of a BCC is shown in figure 3.2.

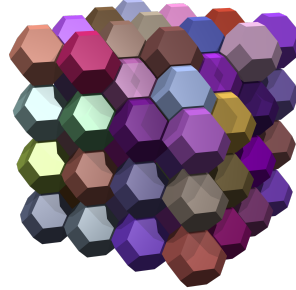


Figure 3.2: The Wigner-Seitz primitive of a Body-centered cubic. Source: https://en.m.wikipedia.org/wiki/Wigner-Seitz_primitive_cell

3.2 Common Bravais Lattices

3.2.1 Cubics

The primitive vectors:

1. Simple Cubic:

$$\mathbf{a}_1 = a\hat{\mathbf{e}}_x, \mathbf{a}_2 = a\hat{\mathbf{e}}_y, \mathbf{a}_3 = a\hat{\mathbf{e}}_z \quad (3.3)$$

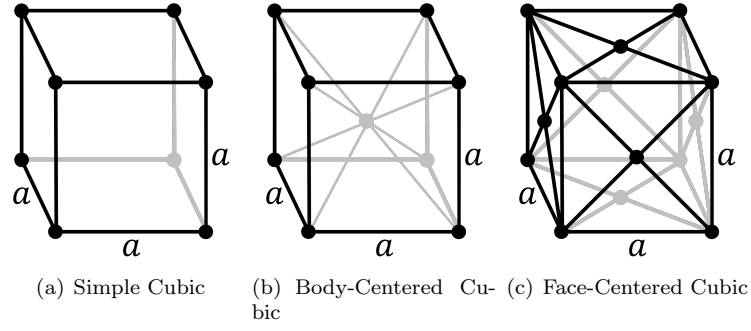


Figure 3.3: Cubic lattices.

2. Body-Centered Cubic:

$$\mathbf{a}_1 = \frac{a}{2}(-\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{e}}_x - \hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y - \hat{\mathbf{e}}_z) \quad (3.4)$$

3. Face-Centered Cubic:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_z), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y) \quad (3.5)$$

3.2.2 Hexagonal Cubic

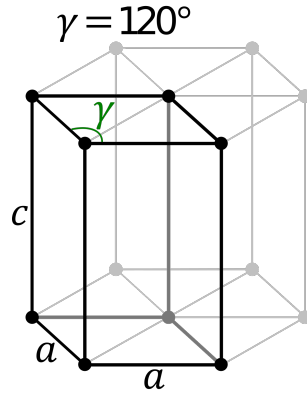


Figure 3.4: Hexagonal Cubic

The primitive vectors

$$\mathbf{a}_1 = a\hat{\mathbf{e}}_x, \quad \mathbf{a}_2 = \frac{a}{2}\hat{\mathbf{e}}_x + \frac{\sqrt{3}a}{2}\hat{\mathbf{e}}_y, \quad \mathbf{a}_3 = c\hat{\mathbf{e}}_z \quad (3.6)$$

3.3 Symmetric Properties of Crystal Structure

The crystal structure has the following three basic symmetric properties

1. **Rotation:** A rotation around a axis through a integer multiples of $2\pi/n$. Such an axis is called n -fold rotational axis.
2. **Reflection:** A reflection takes every point into its mirror image according to a plane, which is called the mirror plane.
3. **Inversion:** An inversion has a single fixed point. If that point is taken as origin, then every other point transferred from \mathbf{r} to $-\mathbf{r}$.

Remark

1. An important lemma: any 2-D Bravais lattice only has n -fold axes with $n = 1, 2, 3, 4, 6$.

Proof. Assume that \mathbf{a}_0 is the shortest primitive vector in its direction. Rotate \mathbf{a}_0 around the n -fold axis by $\theta = \frac{2\pi}{n}$ and $-\theta$, we obtain another two lattice vectors \mathbf{a}_1 and \mathbf{a}_2 . According to the definition of the lattice vectors we must have

$$\mathbf{a}_1 + \mathbf{a}_2 = m\mathbf{a}_0, \quad n \in \mathbb{Z} \quad (3.7)$$

so that

$$2a_0 \cos \frac{2\pi}{n} = ma_0, \quad n \in \mathbb{Z} \quad (3.8)$$

One can solve

$$m = 0, \pm 1, \pm 2 \quad (3.9)$$

m takes only 5 different values corresponding to 5 types of n -fold axes.

□

2. A crystal structure may have combined symmetry, for example, rotation-reflection and rotation-inversion.

3.4 The Reciprocal Lattice

The reciprocal lattice represents the Fourier transform of another lattice (usually a Bravais lattice). In normal usage, this first lattice (whose transform is represented by the reciprocal lattice) is usually a periodic spatial function in real-space and is also known as the direct lattice. Specifically, we consider a function in a Bravais lattice with periodicity

$$F(\mathbf{r}) = F(\mathbf{r} + \mathbf{R}_n) \quad (3.10)$$

Make the Fourier transform due to F , then we obtain

$$f(\mathbf{g}) = \frac{1}{\Omega} \int d\mathbf{r} F(\mathbf{r}) e^{-i\mathbf{g} \cdot \mathbf{r}} \quad (3.11)$$

Due to the periodicity of $F(\mathbf{r})$, so

$$f(\mathbf{g}) = \frac{1}{\Omega} \int d\mathbf{r} F(\mathbf{r} + \mathbf{R}_n) e^{-i\mathbf{g} \cdot \mathbf{r}} \quad (3.12)$$

Let $\mathbf{r}' = \mathbf{r} + \mathbf{R}_n$, such that

$$f(\mathbf{g}) = \frac{1}{\Omega} \int d\mathbf{r}' F(\mathbf{r}') e^{-i\mathbf{g} \cdot \mathbf{r}'} e^{-i\mathbf{g} \cdot \mathbf{R}_n} = f(\mathbf{g}) e^{-i\mathbf{g} \cdot \mathbf{R}_n} \quad (3.13)$$

Such \mathbf{g} satisfies $\mathbf{g} \cdot \mathbf{R}_n = 2\pi$. Naturally comes the definition of the reciprocal lattice

Definition 3.3 (The reciprocal lattice). *For all the vectors \mathbf{R}_n in a Bravais lattice, the set of all the vectors satisfying*

$$\mathbf{G}_l \cdot \mathbf{R}_n = 2\pi N, \quad N \in \mathbb{Z}, \quad l, n \in \mathbb{Z}^3 \quad (3.14)$$

is called the reciprocal lattice.

From equation (3.14) we find that any vectors in a reciprocal lattice can be written in the form of

$$\mathbf{G}_l = l_1 \mathbf{b}_1 + l_2 \mathbf{b}_2 + l_3 \mathbf{b}_3 \quad (3.15)$$

where

$$\mathbf{b}_i \cdot \mathbf{a}_j = 2\pi \delta_{ij} \quad (3.16)$$

Generally, the basis in the reciprocal lattice can be expressed in terms of the primitive vectors of the direct lattice

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3}, \quad \mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3}, \quad \mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{(\mathbf{a}_1 \times \mathbf{a}_2) \cdot \mathbf{a}_3} \quad (3.17)$$

And the volume of the primitive cell in the reciprocal lattice is inversely proportional to the volume of the primitive cell in the direct space

$$\Omega_{\text{rec}} = \frac{(2\pi)^3}{\Omega_{\text{dir}}} \quad (3.18)$$

Definition 3.4 (The first Brillouin zone). *The first Brillouin zone is the Wigner-Seitz primitive cell of the reciprocal lattice.*

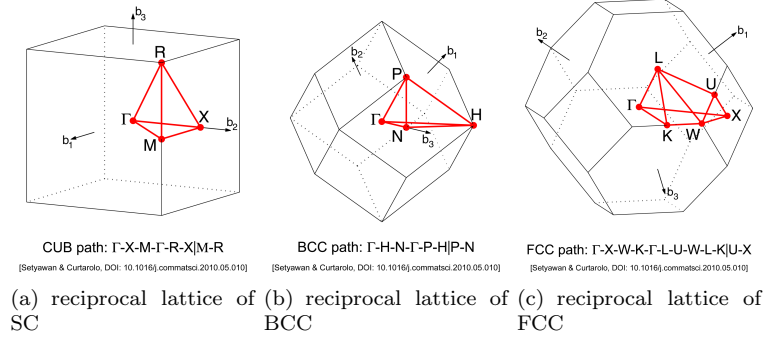


Figure 3.5: The reciprocal lattice of SC, BCC nad FCC.

Remarks

1. A reciprocal lattice itself also constitutes a Bravais lattice.
2. There are also second, third, etc., Brillouin zones, corresponding to a sequence of disjoint regions (all with the same volume) at increasing distances from the origin. Some critical points are conventionally illustrated in the first Brillouin zone, for example, Γ for the center point. The first Brillouin zones for SC, BCC and FCC are shown in figure 3.5.

3.5 Lattice Plane

Definition 3.5 (Lattice plane). *A lattice is any plane containing at least 3 noncollinear Bravais lattice points.*

Theorem 3.1. *For any family of lattice planes separated by a distance of d , there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length of $2\pi/d$. And vice versa.*

Proof. We let \hat{n} to be the unit vector perpendicular to the planes and define a vector $\mathbf{K} = 2\pi\hat{n}/d$. For any Bravais lattic point on any of the planes \mathbf{r} , it can be decomposed to $\mathbf{r} = r_{\perp}\hat{n} + r_{\parallel}\hat{t}$, where \hat{t} is a unit vector on any of the plane. which is perpendicular to \hat{n} . So that

$$e^{i\mathbf{K}\cdot\mathbf{r}} = e^{i\mathbf{K}\cdot r_{\perp}\hat{n}} e^{i\mathbf{K}\cdot r_{\parallel}\hat{t}} = 1 \quad (3.19)$$

So \mathbf{K} is indeed a reciprocal vector. Furthermore, for any given shorter vector parallel to \mathbf{K} corresponds to a greater distance d , contradicting the fact that d is the shortest. \square

Any lattice plane can be denoted by a set of number (n_1, n_2, n_3) , indicating the vector perpendicular to the plane. Miller indices and crystal

indices are two common indices applied to denote the plane lattice. The Miller indices illustrate a family of planes perpendicular to

$$\mathbf{n} = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \quad (3.20)$$

The crystal indices illustrate a family of planes perpendicular to

$$\mathbf{n} = n_1 \hat{\mathbf{e}}_x + n_2 \hat{\mathbf{e}}_y + n_3 \hat{\mathbf{e}}_z \quad (3.21)$$

One should notice that the plane determined by Miller indices is not always perpendicular to $n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$, because the lattice is not always orthogonal. Cases shown in figure 3.6

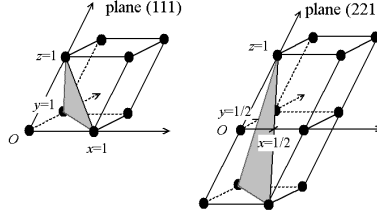


Figure 3.6: Examples to determining indices for certain planes in a unorthogonal lattice. Source: https://en.wikipedia.org/wiki/Miller_index

3.6 Determination of Crystal Structure

3.6.1 Bragg Condition

In 1913, W. H and W. L. Bragg explained the diffraction patterns of crystal through X-radiation by applying a simple model. Bragg stressed two conditions for crystalline diffraction

1. The X rays should be specularly reflected by the ions in any one plane.
2. The reflected rays from successive planes should interfere constructively.

Such that the condition for constructive interference writes

$$n\lambda = 2d \sin \theta \quad (3.22)$$

where d and θ are noted in figure 3.7.

3.6.2 Von Laue Condition

We regard the lattices as scatters. Let the displacement of two scatters is \mathbf{r} . The wave vectors of the incident wave and the scattering wave are separately \mathbf{k} and \mathbf{k}' . The condition for constructive interference is then

$$\mathbf{r} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m, \quad m \in \mathbb{Z} \quad (3.23)$$

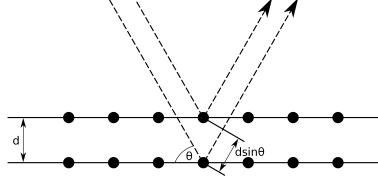


Figure 3.7: Bragg's law. Source: https://en.wikipedia.org/wiki/Bragg%27s_law

So we obtain

$$\mathbf{k} - \mathbf{k}' = \mathbf{G}_h \quad (3.24)$$

So the change of the wave vectors is a reciprocal vector, leading to a constructive interference along the direction \mathbf{k}' , which is called Laue condition. Laue condition can be equivalently written in the form of

$$\mathbf{k} \cdot \hat{\mathbf{G}}_n = \frac{1}{2} \mathbf{G}_n \quad (3.25)$$

where $\hat{\mathbf{G}}_n$ is the unit vector along \mathbf{G}_n .

3.7 Geometrical Structure Factor, Atomic Form Factor.

In a polyatomic Bravais lattice, the diffraction for electrons by different atoms vary significantly. Moreover, the number of atoms in a basis also influences the diffraction. Therefore we introduce geometric structure factor and atomic form factor to specify the electron diffraction in a polyatomic lattice. To begin with, we assume that the potential function is proportional to the density of electrons $V(\mathbf{r}) = cn(\mathbf{r})$. The scattering amplitude is related to the transitional matrix element of V , which writes

$$\langle \mathbf{k}' | V(\mathbf{r}) | \mathbf{k} \rangle = c \int n(\mathbf{r}) e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d\mathbf{r} \quad (3.26)$$

Separate the space into N cells in which there are p atoms, so that the integral becomes

$$\begin{aligned} \langle \mathbf{k}' | V(\mathbf{r}) | \mathbf{k} \rangle &= Nc \int_{\text{cell}} n(\mathbf{r}) e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}} d\mathbf{r} = Nc \int_{\text{cell}} n(\mathbf{r}) e^{-i\mathbf{G}_n \cdot \mathbf{r}} d\mathbf{r} \\ &= Nc \sum_{j=1}^p \int_{\text{cell}} n_j(\mathbf{r} - \mathbf{d}_j) e^{-i\mathbf{G}_n \cdot \mathbf{r}} d\mathbf{r} = A(\mathbf{G}_n) \end{aligned} \quad (3.27)$$

Where n_j and \mathbf{d}_j are the density and location attributed by the j^{th} atom. Make a substitution $\boldsymbol{\eta} = \mathbf{r} - \mathbf{d}_j$, then we obtain

$$A(\mathbf{G}_n) = Nc \sum_{j=1}^p e^{-i\mathbf{G}_n \cdot \mathbf{d}_j} \int_{\text{cell}} n_j(\boldsymbol{\eta}) e^{-i\mathbf{G}_n \cdot \boldsymbol{\eta}} d\boldsymbol{\eta} \quad (3.28)$$

Define the atomic form factor

$$f_j(\mathbf{G}_n) = \int_{\text{cell}} n_j(\boldsymbol{\eta}) e^{-i\mathbf{G}_n \cdot \boldsymbol{\eta}} d\boldsymbol{\eta} \quad (3.29)$$

and the geometrical structure factor

$$S(\mathbf{G}_n) = \sum_{j=1}^p e^{-i\mathbf{G}_n \cdot \mathbf{d}_j} f_j(\mathbf{G}_n) \quad (3.30)$$

Generally, the intensity of the diffraction wave is proportional to $|S(\mathbf{G}_n)|^2$. For example, there are two atoms (uniform or different) in single cell of a BCC lattice, locating separately at $\mathbf{d}_1 = 0$ and $\mathbf{d}_2 = a/2(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z)$ and with atomic form factors f_1 and f_2 . Thus the structure factor is

$$\begin{aligned} S(\mathbf{G}_n) &= f_1 + f_2 e^{-i\mathbf{G}_n \cdot \mathbf{d}_2} = f_1 + (-1)^{n_1+n_2+n_3} f_2 \\ &= \begin{cases} f_1 - f_2, & n_1 + n_2 + n_3 = \text{odd} \\ f_1 + f_2, & n_1 + n_2 + n_3 = \text{even} \end{cases} \end{aligned} \quad (3.31)$$

Especially, when $f_1 = f_2 = f$,

$$S(\mathbf{G}_n) = \begin{cases} 0, & n_1 + n_2 + n_3 = \text{odd} \\ 2f, & n_1 + n_2 + n_3 = \text{even} \end{cases} \quad (3.32)$$

Remarks

1. The atomic form factor is a Fourier transformation of $n(\mathbf{r})$.
2. Generally, Laue condition determines the direction of the diffraction wave; $|S(\mathbf{G}_n)|^2$ determines the intensity of the diffraction wave.
3. Equation (3.31) and (3.32) shows that there are both constructive and destructive interference through a polyatomic lattice.

Chapter 4

Theory of Energy Band

4.1 Bloch's Theorem

Theorem 4.1 (Bloch's theorem). *The eigenstates ψ of the one-electron Hamiltonian $H = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$, where $V(\mathbf{r}) = V(\mathbf{r} + \mathbf{R})$ for all \mathbf{R}_n in a Bravais lattice, can be chosen to have the form of a plane wave times a function with the periodicity of the Bravais lattice*

$$\psi_{n,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n,\mathbf{k}}(\mathbf{r}) \quad (4.1)$$

where

$$u_{n,\mathbf{k}}(\mathbf{r}) = u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) \quad (4.2)$$

for all \mathbf{R}_n in a Bravais lattice. The wavefunction can be written in another form

$$\psi_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k}\cdot\mathbf{R}} \psi_{n,\mathbf{k}}(\mathbf{r}) \quad (4.3)$$

4.2 Born-von Karman Boundary Condition

Born von-Karman boundary condition is applied to restrict that the wavefunction in a Bravais lattice is a periodic function. Suppose that there are $N = N_1 N_2 N_3$ Bravais points in the lattice, therefore we have

$$\psi(\mathbf{r} + N_i \mathbf{a}_i) = e^{-i\mathbf{k}\cdot N_i \mathbf{a}_i} \psi(\mathbf{r}) = \psi(\mathbf{r}) \quad (4.4)$$

so that

$$N_i \mathbf{k}_i \cdot \mathbf{a}_i = 2\pi l_i, \quad l_i \in \mathbb{Z} \quad (4.5)$$

Thus the Bloch vector writes

$$\mathbf{k} = \frac{l_1}{N_1} \mathbf{b}_1 + \frac{l_2}{N_2} \mathbf{b}_2 + \frac{l_3}{N_3} \mathbf{b}_3 \quad (4.6)$$

Allowed \mathbf{k} is a Bravais lattice in the reciprocal space with the primitive vectors \mathbf{b}_1/N_1 , \mathbf{b}_2/N_2 and \mathbf{b}_3/N_3 .

4.3 Energy Band

According to the form of Bloch wavefunction given by (4.1), the momentum operator acting on such function leads to

$$-i\hbar\nabla\psi_{\mathbf{k}}(\mathbf{r}) = \hbar\mathbf{k}\psi_{\mathbf{k}}(\mathbf{r}) - e^{i\mathbf{k}\cdot\mathbf{r}}i\hbar\nabla u_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}(-i\nabla + \mathbf{k})u_{\mathbf{k}}(\mathbf{r}) \quad (4.7)$$

The Schrödinger equation of the electron in Bravais lattice, according to (4.1), is thus

$$H_{\mathbf{k}}u_{n,\mathbf{k}}(\mathbf{r}) = [\frac{\hbar^2}{2m}(\mathbf{i}\nabla + \mathbf{k})^2 + V(\mathbf{r})]u_{n,\mathbf{k}}(\mathbf{r}) = \epsilon_{n,\mathbf{k}}u_{n,\mathbf{k}}(\mathbf{r}) \quad (4.8)$$

with the boundary condition

$$u_{n,\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n,\mathbf{k}}(\mathbf{r}) \quad (4.9)$$

and n indicates the energy level. Obviously we have

$$\psi_{n,\mathbf{k}+\mathbf{G}_m} = \psi_{n,\mathbf{k}} \quad (4.10)$$

and

$$\epsilon_{n,\mathbf{k}+\mathbf{G}_m} = \epsilon_{n,\mathbf{k}} \quad (4.11)$$

The result shown above displays that, for a certain n , the energy $\epsilon_{n,\mathbf{k}}$ is a periodic function with respect to \mathbf{k} . Thus the information of these functions is referred to as the band structure. Moreover, due to the periodicity of $\epsilon_{n,\mathbf{k}}$, all the bands can be drawn in the first Brillouine zone.

4.4 Electrons in A Weak Periodic Potential

4.4.1 Non-degeneracy Case

In this section, we discuss the case of electrons in the presence of a weak periodic potential. The electrons can be approximated as nearly-free electrons since the potential is weak enough to be regarded as a perturbation. For simplicity, we consider a 1D crystal with length $L = Na$. Hence the Hamiltonian for a single electron writes

$$H = H_0 + H' \quad (4.12)$$

where

$$H_0 = -\frac{\hbar^2}{2m}\nabla^2 = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \quad (4.13)$$

and $H' = V(x)$ is the weak potential that can be expanded by Fourier series

$$H' = V(x) = \sum_{n \neq 0} V_n e^{iG_n x} \quad (4.14)$$

According to the perturbation theory, the wavefunction to the first-order is

$$\psi_{\mathbf{k}}(x) = \psi_{\mathbf{k}}^0(x) + \psi_{\mathbf{k}}^1(x) = \psi_{\mathbf{k}}^0(x) + \sum_{\mathbf{k}' \neq 0} \frac{H'_{\mathbf{k}\mathbf{k}'}}{\epsilon_{\mathbf{k}}^0 - \epsilon_{\mathbf{k}'}^0} \psi_{\mathbf{k}'}^0(x) \quad (4.15)$$

where $\mathbf{k} = k$ for 1D case. And

$$\psi_k^0(x) = \frac{1}{\sqrt{L}} e^{ikx} \quad (4.16)$$

is the zeroth-order wavefunction and

$$H'_{kk'} = \langle k' | V(x) | k \rangle = \frac{1}{L} \int_0^L e^{-i(k'-k)x} V(x) dx \quad (4.17)$$

takes nonzero values only when $k' = k + 2n\pi/a$ ¹. So the wavefunction writes

$$\psi_k^0(x) = \frac{1}{\sqrt{L}} e^{ikx} + \sum_{n \neq 0} \frac{V_n}{\frac{\hbar^2}{2m} [k^2 - (k + 2n\pi/a)^2]} \frac{1}{\sqrt{L}} e^{i(k+2n\pi/a)x} \quad (4.20)$$

Correspondingly, the energy is

$$\epsilon_k = \epsilon_k^0 + \epsilon_k^2 = \epsilon_k^0 + \sum_{k' \neq 0} \frac{|H_{kk'}|^2}{\epsilon_k^0 - \epsilon_{k'}^0} = \frac{\hbar^2 k^2}{2m} + \sum_{n \neq 0} \frac{|V_n|^2}{\frac{\hbar^2}{2m} [k^2 - (k + 2n\pi/a)^2]} \quad (4.21)$$

4.4.2 Degeneracy Case

When $k = -2n\pi/a$ or $\epsilon_k^0 = \epsilon_{k'}^0$, the result given by non-degeneracy theory does not hold any more. This is because the last term in equation (4.21) diverges. So due to the degeneracy perturbation theory, the first-order energy approximation satisfies

$$\det(\langle k | H' | k' \rangle - \epsilon^1 \delta_{k,k'}) = 0 \quad (4.22)$$

So

$$\epsilon^1 = \pm |V_n| \quad (4.23)$$

So that the energy writes

$$\epsilon = \epsilon_k^0 + \epsilon^1 = \frac{\hbar^2 k^2}{2m} \pm |V_n| \quad (4.24)$$

¹Due to the periodicity of $V(x)$, we have

$$\int_0^L e^{-i(k'-k)x} V(x) dx = \int_0^L e^{-i(k'-k)(x+a)} V(x+a) dx = e^{-i(k'-k)a} \int_0^L e^{-i(k'-k)x} V(x) dx \quad (4.18)$$

So

$$(1 - e^{-i(k'-k)a}) \int_0^L e^{-i(k'-k)x} V(x) dx = 0 \quad (4.19)$$

So only when $k' = k + 2\pi n/a$ the integral takes nonzero values.

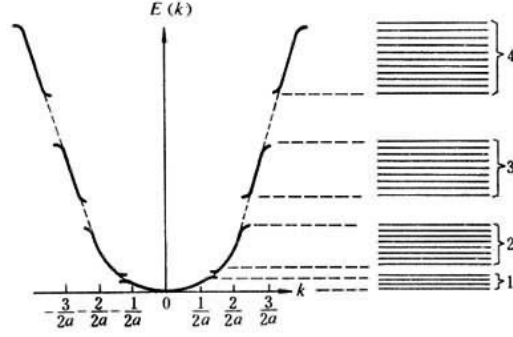


Figure 4.1: The band structure of nearly-free electrons.

From equation (4.24) we notice that some energy gaps are generated on the boundary of the Brillouine zones, as shown in figure 4.1. The width of the gaps are $2|V_n|$. Moreover, on the boundary of the Brillouin zone, the bands yield perpendicular to the vertical direction, that $\partial\epsilon/\partial k = 0$.

4.5 Tight-Binding Method

The tight-binding approximation deals with the case in which the overlap of atomic wave functions is enough to require corrections to the picture of isolated atoms, but not so much as to render the atomic description completely irrelevant. The approximation is most useful for describing the energy bands that arise from the partially filled d-shells of transition metal atoms and for describing the electronic structure of insulators.

4.5.1 Single Atomic Orbit

We first discuss the case that each atom has only one atomic orbital. We assume that in the neighbourhood of a single lattice point, the Hamiltonian can be approximated by the atom Hamiltonian of the atom located at this point. Thus the corresponding energy level and the eigenstate of the electron writes

$$H_{\text{at}}\phi_i = \epsilon_i\phi_i \quad (4.25)$$

We then assume that the wave function in the entire lattice is superposed by a set of atomic wave functions ψ_i . So

$$\psi = \sum_{m=1}^N a_m \phi_i(\mathbf{r} - \mathbf{R}_m) \quad (4.26)$$

The overlap of the atomic wave functions of different atoms is negligible, so we obtain the orthogonality

$$\langle \phi_i(\mathbf{r} - \mathbf{R}_n) | \phi_i(\mathbf{r} - \mathbf{R}_m) \rangle = \delta_{nm} \quad (4.27)$$

Since $\psi(\mathbf{r})$ is a Bloch function, the coefficients a_m writes in the form of

$$a_m = \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_m} \quad (4.28)$$

So (4.26) turns to

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}_m} \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_m} \phi_i(\mathbf{r} - \mathbf{R}_m) \quad (4.29)$$

which satisfies the Schrödinger equation

$$H\psi(\mathbf{r}) = \epsilon_{\mathbf{k}}\psi(\mathbf{r}) \quad (4.30)$$

Substitute ψ in equation (4.30) by (4.29) we obtain

$$\sum_{\mathbf{R}_m} e^{i\mathbf{k} \cdot \mathbf{R}_m} \left[-\frac{\hbar^2}{2m} \nabla^2 - \epsilon_{\mathbf{k}} + V(\mathbf{r}) \right] \phi_i(\mathbf{r} - \mathbf{R}_m) = 0 \quad (4.31)$$

Due to equation (4.25) we have

$$\sum_{\mathbf{R}_m} e^{i\mathbf{k} \cdot \mathbf{R}_m} [\epsilon_i - \epsilon_{\mathbf{k}} + V(\mathbf{r}) - V_{\text{at}}] \phi_i(\mathbf{r} - \mathbf{R}_m) = 0 \quad (4.32)$$

Dot both sides by $\phi_i^*(\mathbf{r})$ and integrate over \mathbf{r} we have

$$\epsilon_i - \epsilon_{\mathbf{k}} + \sum_{\mathbf{R}_m} e^{i\mathbf{k} \cdot \mathbf{R}_m} \int \Delta V \phi_i^*(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} = 0 \quad (4.33)$$

where $\Delta V = V(\mathbf{r}) - V_{\text{at}}$ is the potential difference of crystal potential and atomic potential. The summation can be divided into two parts for $\mathbf{R}_m = 0$ and $\mathbf{R}_m \neq 0$. Thus

$$\epsilon_i - \epsilon_{\mathbf{k}} + \int \Delta V |\phi_i(\mathbf{r})|^2 d\mathbf{r} + \sum_{\mathbf{R}_m \neq 0} e^{i\mathbf{k} \cdot \mathbf{R}_m} \int \Delta V \phi_i^*(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} = 0 \quad (4.34)$$

The last term on the left-hand side of equation (4.34) is called the overlap integrals. Since the overlap of different atomic wave functions is small, such integral is also small. Commonly we calculate the integrals for nearest neighbours of a atom. Consequently,

$$\epsilon_{\mathbf{k}} = \epsilon_i - J(0) - \sum_{\text{n.n.}} J(\mathbf{R}_m) e^{i\mathbf{k} \cdot \mathbf{R}_m} \quad (4.35)$$

where

$$J(0) = - \int \Delta V |\phi_i(\mathbf{r})|^2 d\mathbf{r} \quad (4.36)$$

$$J(\mathbf{R}_m) = - \int \Delta V \phi_i^*(\mathbf{r}) \phi_i(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} \quad (4.37)$$

4.5.2 Multiple Atomic Orbits

In analogy to the case of single atomic orbit, the Bloch function can be written as a superposition of a set of atomic wave functions. The atomic function is also a linear combination of different atomic orbital. Thus the Bloch function writes

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}_m} \sum_i \frac{1}{\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_m} b_i \phi_i(\mathbf{r} - \mathbf{R}_m) \quad (4.38)$$

where i indicates a set of quantum number corresponding to a same degenerated energy level, for example, $i = p_x, p_y, p_z$. Likewise the Shrödinger equation writes

$$\sum_{\mathbf{R}_m} \sum_i b_i e^{i\mathbf{k} \cdot \mathbf{R}_m} [\epsilon_i - \epsilon_{\mathbf{k}} + \Delta V] \phi_i(\mathbf{r} - \mathbf{R}_m) = 0 \quad (4.39)$$

Dot both sides by $\phi_j(\mathbf{r})$ and integrate over \mathbf{r} . Due to the orthogonality $\langle \phi_i | \phi_j \rangle = \delta_{ij}$ we obtain

$$\begin{aligned} & (\epsilon_i - \epsilon_{\mathbf{k}}) \delta_{ji} \delta_{\mathbf{R}_m, 0} + \sum_{\mathbf{R}_m} \sum_i e^{i\mathbf{k} \cdot \mathbf{R}_m} \int \Delta V \phi_j(\mathbf{r}) \phi_i(\mathbf{r} - \mathbf{R}_m) d\mathbf{r} \\ & = (\epsilon_i - \epsilon_{\mathbf{k}}) \delta_{ji} \delta_{\mathbf{R}_m, 0} - \delta_{\mathbf{R}_m, 0} \beta_{ji} - \sum_{\mathbf{R}_m \neq 0} e^{i\mathbf{k} \cdot \mathbf{R}_m} \gamma_{ji}(\mathbf{R}_m) = 0 \end{aligned} \quad (4.40)$$

where

$$\beta_{ji} = - \int d\mathbf{r} \Delta V \phi_j(\mathbf{r}) \phi_i(\mathbf{r}) \quad (4.41)$$

$$\gamma_{ji}(\mathbf{R}_m) = - \int d\mathbf{r} \Delta V \phi_j(\mathbf{r}) \phi_i(\mathbf{r} - \mathbf{R}_m) \quad (4.42)$$

4.5.3 p-Band in FCC Lattice

In dealing with cubic crystals, the most convenient linear combinations of three degenerate atomic p-levels have the form $x\phi(r), y\phi(r), z\phi(r)$, where the function $\phi(r)$ depends only on the magnitude of the vector \mathbf{r} . The primitive vectors of a FCC lattice are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{e}}_y + \hat{\mathbf{e}}_z), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_z), \quad \mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{e}}_x + \hat{\mathbf{e}}_y) \quad (4.43)$$

According to equation (4.40), the p-band structure in FCC lattice is determined by

$$\begin{vmatrix}
 \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^0 & -4\gamma_1 \sin \frac{k_x a}{2} \sin \frac{k_y a}{2} & -4\gamma_1 \sin \frac{k_x a}{2} \sin \frac{k_z a}{2} \\
 +4\gamma_0 \cos \frac{k_y a}{2} \cos \frac{k_z a}{2} & \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^0 & -4\gamma_1 \sin \frac{k_y a}{2} \sin \frac{k_z a}{2} \\
 -4\gamma_1 \sin \frac{k_x a}{2} \sin \frac{k_y a}{2} & +4\gamma_0 \cos \frac{k_x a}{2} \cos \frac{k_z a}{2} & \epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}}^0 \\
 -4\gamma_1 \sin \frac{k_x a}{2} \sin \frac{k_z a}{2} & -4\gamma_1 \sin \frac{k_y a}{2} \sin \frac{k_z a}{2} & +4\gamma_0 \cos \frac{k_y a}{2} \cos \frac{k_z a}{2}
 \end{vmatrix} = 0$$

(4.44)

where

$$\epsilon_{\mathbf{k}}^0 = E_p - \beta - 4\gamma_2 \sum_{\text{rev. } i, j, k} \cos \frac{k_i a}{2} \cos \frac{k_j a}{2} \quad (4.46)$$

$$\gamma_0 = - \int d\mathbf{r} (x^2 - y(y - a/2)) \phi(|\mathbf{r}|) \phi(|\mathbf{r} - \mathbf{a}_1|) \Delta V \quad (4.47)$$

$$\gamma_1 = - \int d\mathbf{r} x(y - a/2) \phi(|\mathbf{r}|) \phi(|\mathbf{r} - \mathbf{a}_3|) \Delta V \quad (4.48)$$

$$\gamma_2 = - \int d\mathbf{r} x(x - a/2) \phi(|\mathbf{r}|) \phi(|\mathbf{r} - \mathbf{a}_3|) \Delta V \quad (4.49)$$

Remarks

1. If $\mathbf{k} = 0$, then $k_x = k_y = k_z = 0$. So the matrix in equation (4.44) turns into a diagonal matrix with $\epsilon_{\mathbf{k}}$ solved by

$$\epsilon_{\mathbf{k}} = E_p = \beta - 12\gamma_2 - 4\gamma_0 \quad (4.50)$$

That the band structure has a triple-degeneracy at $\mathbf{k} = 0$.

2. If \mathbf{k} is directed along either ΓX or ΓL , likewise, there is a double-degeneracy.

² $\sum_{\text{rev. } i, j, k}$ indicates the revolving sum for indices i, j, k . Commonly,

$$\sum_{\text{rev. } i, j, k} f(i, j, k) = f(i, j, k) + f(j, k, i) + f(k, i, j) \quad (4.46)$$

Chapter 5

The Semiclassical Model of Electron Dynamics

5.1 Formalism

5.1.1 The Mean Velocity

The evolution of the position of the electron in a definite Bloch level is given by the mean velocity of the electron, which is defined by

$$\mathbf{v}_{n,\mathbf{k}} = \frac{1}{m} \langle \psi_{n,\mathbf{k}} | \mathbf{p} | \psi_{n,\mathbf{k}} \rangle = \frac{1}{m} \int u_{n,\mathbf{k}}^* (\mathbf{p} + \hbar \mathbf{k}) u_{n,\mathbf{k}} d\mathbf{r} \quad (5.1)$$

where $u_{n,\mathbf{k}}$ satisfies equation (4.8). Due to quasi-continuity of \mathbf{k} , we operate $\nabla_{\mathbf{k}}$ on both sides of (4.8). Thus

$$\frac{\hbar}{m} (\mathbf{p} + \hbar \mathbf{k}) u_{n,\mathbf{k}} + H \nabla_{\mathbf{k}} u_{n,\mathbf{k}} = (\nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}}) u_{n,\mathbf{k}} + \epsilon_{n,\mathbf{k}} \nabla_{\mathbf{k}} u_{n,\mathbf{k}} \quad (5.2)$$

Dot both sides by $u_{n,\mathbf{k}}^*$ and integrate over \mathbf{r} we have

$$\begin{aligned} & \frac{\hbar}{m} \int u_{n,\mathbf{k}}^* (\mathbf{p} + \hbar \mathbf{k}) u_{n,\mathbf{k}} d\mathbf{r} + \int u_{n,\mathbf{k}}^* H \nabla_{\mathbf{k}} u_{n,\mathbf{k}} d\mathbf{r} \\ &= (\nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}}) \int u_{n,\mathbf{k}}^* u_{n,\mathbf{k}} d\mathbf{r} + \epsilon_{n,\mathbf{k}} \int u_{n,\mathbf{k}}^* \nabla_{\mathbf{k}} u_{n,\mathbf{k}} d\mathbf{r} \end{aligned} \quad (5.3)$$

The second terms on both sides cancel each other due to the Hermitian of $H_{\mathbf{k}}$. So the mean velocity writes

$$\mathbf{v}_{n,\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \quad (5.4)$$

5.1.2 Description of The Model

The semiclassical model predicts how, the absence of collisions, the position \mathbf{r} and wave vector \mathbf{k} of each electron evolve in the presence of externally applied

electric and magnetic fields. Given the functions $\epsilon_{n,\mathbf{k}}$, the semiclassical model associates with each electron a position \mathbf{r} , a wave vector \mathbf{k} , and a band index n . In the course of time and in the presence of external electric and magnetic fields $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$ the position, wave vector, and band index are taken to evolve according to the following rules:

1. The band index n is a constant. The electron stays at the same band. The possibility of interband transition is ignored.
2. The evolution of the position of the electron is determined by equation (5.4)

$$\dot{\mathbf{r}} = \mathbf{v}_{n,\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \quad (5.5)$$

3. The evolution of the wave vector is determined by

$$\hbar \dot{\mathbf{k}} = -e(\mathbf{E} + \mathbf{v}_{n,\mathbf{k}} \times \mathbf{B}) \quad (5.6)$$

5.1.3 The Effective Mass

The acceleration of the electron, according to equation (5.4), is

$$\dot{\mathbf{v}} = \frac{\partial}{\partial t} \left[\frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \right] = \frac{1}{\hbar} \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \frac{\partial \mathbf{k}}{\partial t} = \frac{1}{\hbar^2} \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \cdot \mathbf{F}_{\text{ext}} \quad (5.7)$$

where \mathbf{F}_{ext} is the external force on the electron. Thus we can define the inverse effective mass tensor by

$$\bar{\bar{M}}^{-1} = \frac{1}{\hbar^2} \nabla_{\mathbf{k}} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \quad (5.8)$$

or in the form of matrix

$$\left(\frac{1}{m^*} \right)_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 \epsilon_{n,\mathbf{k}}}{\partial k_i \partial k_j} \quad (5.9)$$

Obviously, the inverse effective mass tensor is a symmetric tensor.

5.2 Motion in A Uniform Electric Field

5.2.1 Motion in A Uniform Electric Field

In a uniform electric field \mathbf{E} , the evolution of the wave vector and the velocity of the electron can be solved by

$$\mathbf{k}(t) = \mathbf{k}(0) - \frac{e\mathbf{E}t}{\hbar} \quad (5.10)$$

$$\mathbf{v} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{n,\mathbf{k}} \quad (5.11)$$

For simplicity, we consider a 1-D case and suppose that the band is written in the form of $\epsilon = \epsilon_0 + A \cos ka$. So the velocity evolves by

$$v(t) = \frac{1}{\hbar} \frac{\partial}{\partial k} (\epsilon_0 + A \cos ka) = -\frac{1}{\hbar} Aa \sin k(t)a \quad (5.12)$$

If we set $k(0) = 0$, then the position of the electron x is

$$x(t) = \int_0^t v(t') dt' = -\frac{A}{eE} \cos\left(\frac{AEa}{\hbar} t\right) + x(0) \quad (5.13)$$

The result shows that the electron oscillates in real space with a frequency $\omega = AEa/\hbar$. The oscillation is generated by a uniform electric field acting on the electron. From another perspective, an altering current is generated by direct current.

5.2.2 Holes

The current is thus contributed by the occupied electrons

$$\mathbf{J} = -e \int_{\text{occ}} \mathbf{v}_k \frac{1}{4\pi^3} d\mathbf{k} = -e \int_{\text{occ}} \frac{1}{\hbar} \nabla_k \epsilon_k \frac{1}{4\pi^3} d\mathbf{k} = -\frac{e}{4\pi^3 \hbar} \epsilon_k|_{\text{occ}} \quad (5.14)$$

Obviously, a fully occupied band carries no electric current because $\epsilon|_{\text{occ}} = 0$ due to the periodicity of the Brillouine zone. If the band is not completely filled, then the current can be equally given by

$$\mathbf{J} = +e \int_{\text{unocc}} \mathbf{v}_k \frac{1}{4\pi^3} d\mathbf{k} \quad (5.15)$$

Thus tire current produced by occupying with electrons a specified set of levels 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 parcles of charge $+e$ (opposite to the electronic charge).

Thus, even though the only charge carriers are electrons, we may, whenever it is convenient, consider the current to be carried entirely by fictitious particles of positive charge that fill all those levels in the band that are unoccupied by electrons. The fictitious particles are called Holes.

5.3 Motion in A Uniform Magnetic Field

In a uniform magnetic field \mathbf{B} along z -direction, the evolution of the wave vector and the velocity of the electron can be solved by

$$\dot{\mathbf{k}}(t) = -e \mathbf{v}_k \times \mathbf{B} \quad (5.16)$$

$$\mathbf{v} = \frac{1}{\hbar} \nabla_k \epsilon_{n,\mathbf{k}} \quad (5.17)$$

From equation (5.16) we find that the component of \mathbf{k} parallel to the magnetic field is a constant. The wave vector evolves only along the direction perpendicular to both the velocity and the magnetic field. Moreover, the energy $\epsilon_{\mathbf{k}}$ is conserved. This is because

$$\frac{\partial \epsilon_{\mathbf{k}}}{\partial t} = \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} \cdot \dot{\mathbf{k}} = -e\mathbf{v} \times (\mathbf{v} \times \mathbf{B}) = 0 \quad (5.18)$$

Thus, the electron will move along the curves on the contour surface of energy in k -space, as shown in figure 5.1.

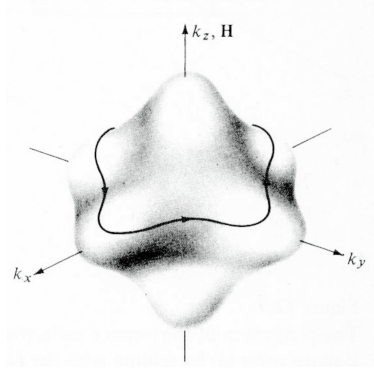


Figure 5.1: The trajectory of the electron on the contour surface of energy in k -space. A magnetic field along z -direction is subjected.

The period of the motion can be given by

$$T(\epsilon, k_z) = \oint \frac{d\mathbf{k}}{|\dot{\mathbf{k}}|} = \frac{\hbar^2}{eB} \oint \frac{d\mathbf{k}}{|\nabla_{\mathbf{k}} \epsilon_{\mathbf{k}}|} = \frac{\hbar^2}{eB} \oint \frac{\Delta \mathbf{k} d\mathbf{k}}{\Delta \epsilon} = \frac{\hbar^2}{eB} \frac{\partial A(\epsilon, k_z)}{\partial \epsilon} \quad (5.19)$$

where $A(\epsilon, k_z)$ is the area enclosed by the curve. Specifically, for a free electron, the curve is a circle. Thus the period is

$$T = \frac{2\pi m}{eB} \quad (5.20)$$

5.4 Experimental Measurement for Fermi Surface

5.4.1 Landau levels; Quantization of Bloch electrons

The energy level for an electron in a uniform magnetic field along z -direction is given by Landau level

$$\epsilon_{k_z, \nu} = \frac{\hbar^2}{2m} k_z^2 + \left(\nu + \frac{1}{2}\right) \hbar \omega_c, \quad \nu \in \mathbb{Z}^+ \quad (5.21)$$

where $\omega_c = eB/m$ is the cyclotron frequency. Thus the state of electron lies on the tubes, named by Landau tubes. The intersections of the Landau tubes are a series of enclosed curves, which are called Landau rings, shown in figure 5.2. The area between two neighbouring Landau rings is thus given by

$$\Delta A = \frac{2\pi eB}{h} \quad (5.22)$$

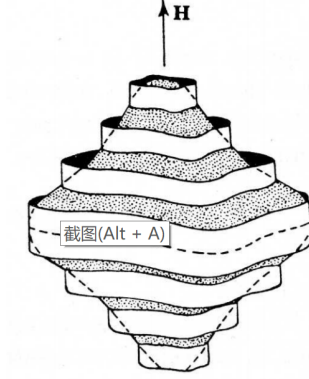


Figure 5.2: The Landau tubes.

Quantization of Bloch electrons, according to L. Onsager and E. M. Lifshitz, follows the Bohr-Sommerfeld condition

$$\oint \mathbf{p} \cdot d\mathbf{r} = (\nu + \lambda)2\pi\hbar \quad (5.23)$$

where $0 \leq \lambda \leq 1$ is a constant. Notice that

$$\hbar \mathbf{k} = -e(\mathbf{r} \times \mathbf{B}) \quad (5.24)$$

which equals to

$$\nabla \times \hbar \mathbf{k} = 2e\mathbf{B} \quad (5.25)$$

So

$$\oint \mathbf{p} \cdot d\mathbf{r} = \oint (\hbar \mathbf{k} - e\mathbf{A}) \cdot d\mathbf{r} = \int e\mathbf{B} \cdot d\mathbf{S} = eBA_r \quad (5.26)$$

where

$$A_r = \frac{2\pi\hbar}{eB}(\nu + \lambda) \quad (5.27)$$

is the area enclosed by the orbit of electron in real space. Correspondingly, the area enclosed by the orbit in k -space is simply multiplying A_r by a factor $(eB/\hbar)^2$

$$A_{\nu, k_z} = \frac{2\pi eB}{h}(\nu + \lambda) \quad (5.28)$$

5.4.2 The de Haas-van Alphen Effect

The de Haas-van Alphen effect, first discovered by W. J. de Haas and P. M. van Alphen, is a quantum effect in which the magnetic susceptibility of a pure metal crystal oscillates with the intensity of the external magnetic field. The period of the oscillation is inversely proportional to the intensity of the magnetic field.

As the magnetic field increases, the radius of the Landau tubes increase, thus causing the tubes constantly cross the Fermi surface. When the extremal orbit (shown in figure 5.2, plotted by the dotted lines) locates right in the middle of the adjacent tubes, the energy is relatively low; If the Fermi surface is tangent to some particular tube, the energy increases. Due to equation (5.28), if B_1 and B_2 correspond to the same energy, there should be

$$\begin{aligned}\frac{1}{B_1} &= \frac{2\pi e}{\hbar}(\nu + \lambda) \frac{1}{A_e(\epsilon_F, k_z)} \\ \frac{1}{B_2} &= \frac{2\pi e}{\hbar}(\nu + 1 + \lambda) \frac{1}{A_e(\epsilon_F, k_z)}\end{aligned}\tag{5.29}$$

where $A_e(\epsilon_F, k_z)$ is the area enclosed by the extremal orbit of the Fermi surface along the direction of the magnetic field. So the period is

$$\Delta\left(\frac{1}{B}\right) = \frac{1}{B_2} - \frac{1}{B_1} = \frac{2\pi e}{\hbar} \frac{1}{A_e(\epsilon_F, k_z)}\tag{5.30}$$

If period of the magnetic field can be experimentally determined, then the area of the extremal orbit can be determined. Thus the shape of the Fermi surface can be depicted by altering the orientation of the the magnetic field.

Chapter 6

The Semiclassical Model of Conduction in Metals

In this chapter we describe a more systematic method of calculating conductivities, applicable to general semiclassical motion in the presence of space- and time-dependent perturbing fields and temperature gradients.

The description of conduction is based on the nonequilibrium distribution function $f_n(\mathbf{r}, \mathbf{k}, t)$ and $f_n(\mathbf{r}, \mathbf{k}, t)$ represents the number of electrons in the n th band at time t in the phase space $d\mathbf{r}d\mathbf{k}$. In equilibrium the function reduces to Fermi-Dirac function

$$f_0(\epsilon_{\mathbf{k}}) = \frac{1}{e^{\epsilon_{\mathbf{k}} - \mu/k_B T} + 1} \quad (6.1)$$

The evolution of f_n is triggered by the external field, which is based on (a) the assumption that between collisions the electronic motion is determined by the semiclassical model, and (b) a particularly simple treatment of collisions, known as the relaxation-time approximation.

6.1 Relaxation-Time Approximation and Boltzmann Equation

The evolution of the distribution function of electrons in the presence of collision writes

$$f(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{r} - \dot{\mathbf{r}}dt, \mathbf{k} - \dot{\mathbf{k}}dt, t - dt) + \left(\frac{\partial f}{\partial t}\right)_{\text{coll}}dt \quad (6.2)$$

Expand the right hand side to the first order term of dt we obtain

$$\frac{\partial f}{\partial t} + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \quad (6.3)$$

where the left hand side are the drift terms and the right hand side is the collision term. For steady state $\partial f / \partial t = 0$, thus

$$\dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f + \dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}} \quad (6.4)$$

Equation (6.4) is Boltzmann equation for the electron system. The right hands side indicates the distribution of the electrons emerged form the collisions. We use the relaxation time approximation to deal with the collision term, that the changing rate of distribution function is inversely proportional to the relaxation time and proportional to the deviation to the equilibrium state. Thus

$$\left(\frac{\partial f_n}{\partial t} \right)_{\text{coll}} = -\frac{1}{\tau} (f_n - f_0) \quad (6.5)$$

where $\tau(\epsilon_n, \mathbf{k})$ is a function of energy. The solution can be written in form of

$$\begin{aligned} f_n(\mathbf{r}, \mathbf{k}, t) &= f_0 - \int_{-\infty}^t dt' \exp \left\{ - \int_{t'}^t \frac{dt''}{\epsilon_{n, \mathbf{k}(t'')}} \right\} \frac{df_0}{dt'} \\ &= f_0 - \int_{-\infty}^t dt' \exp \left\{ - \int_{t'}^t \frac{dt''}{\epsilon_{n, \mathbf{k}(t'')}} \right\} [\dot{\mathbf{k}} \cdot \nabla_{\mathbf{k}} f_0 + \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f_0] \\ &= f_0 - \int_{-\infty}^t dt' \exp \left\{ - \int_{t'}^t \frac{dt''}{\epsilon_{n, \mathbf{k}(t'')}} \right\} \\ &\quad \times \left[\frac{\partial f_0}{\partial \epsilon} \left(\frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{n, \mathbf{k}} \right) \cdot \frac{d\hbar \mathbf{k}}{dt'} + \dot{\mathbf{r}} \cdot \left(\frac{\partial f_0}{\partial \epsilon} \frac{\partial \epsilon}{\partial T} \nabla T + \frac{\partial f_0}{\partial \epsilon} \frac{\partial \epsilon}{\partial \mu} \nabla \mu \right) \right] \\ &= f_0 - \int_{-\infty}^t dt' \exp \left\{ - \int_{t'}^t \frac{dt''}{\epsilon_{n, \mathbf{k}(t'')}} \right\} \left(- \frac{\partial f_0}{\partial \epsilon} \right) \\ &\quad \times \mathbf{v}_n \cdot (e\mathbf{E} + e\mathbf{v}_n \times \mathbf{B} + \nabla \mu + \frac{\epsilon - \mu}{T} \nabla T) \end{aligned} \quad (6.6)$$

Where $-e\mathbf{E} - e\mathbf{v}_n \times \mathbf{B}$ is the force exerted by external field and $\nabla \mu + \frac{\epsilon - \mu}{T} \nabla T$ is contributed by temperature gradient and chemical potential gradient. Commonly, the relaxation time evolves by a relatively low rate, thus the integral in (6.6) can be approximated by

$$\int_{-\infty}^t dt' \exp \left\{ - \int_{t'}^t \frac{dt''}{\epsilon_{n, \mathbf{k}(t'')}} \right\} \approx \tau \quad (6.7)$$

So

$$f_n(\mathbf{r}, \mathbf{k}, t) = f_0 + \tau \left(\frac{\partial f_0}{\partial \epsilon} \right) \mathbf{v}_n \cdot (e\mathbf{E} + e\mathbf{v}_n \times \mathbf{B} + \nabla \mu + \frac{\epsilon - \mu}{T} \nabla T) \quad (6.8)$$

6.2 DC Electrical Conductivity

In the presence of only a uniform electric field \mathbf{E} , equation (6.8) writes

$$f_n = f_0 + \tau \left(\frac{\partial f_0}{\partial \epsilon} \right) \mathbf{v}_n \cdot (e\mathbf{E}) \quad (6.9)$$

Thus the electric current density writes

$$\begin{aligned}
 \mathbf{j} &= -e \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n f_n \\
 &= -e \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{v}_n f_0 + e^2 \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \left(-\frac{\partial f_0}{\partial \epsilon}\right) \mathbf{v}_n \mathbf{v}_n \cdot \mathbf{E} \\
 &= e^2 \tau \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \left(-\frac{\partial f_0}{\partial \epsilon}\right) \mathbf{v}_n \mathbf{v}_n \cdot \mathbf{E} \\
 &= \sum_n \bar{\sigma}_n \cdot \mathbf{E}
 \end{aligned} \tag{6.10}$$

where

$$\bar{\sigma}_n = e^2 \tau \int \frac{d\mathbf{k}}{4\pi^3} \left(-\frac{\partial f_0}{\partial \epsilon}\right) \mathbf{v}_n \mathbf{v}_n \tag{6.11}$$

is electrical conductivity tensor with 9 components

$$\sigma_n^{\mu\nu} = e^2 \tau \int \frac{d\mathbf{k}}{4\pi^3} \left(-\frac{\partial f_0}{\partial \epsilon}\right) v_n^\mu v_n^\nu, \quad \mu, \nu = x, y, z \tag{6.12}$$

and

$$j^\mu = \sigma_n^{\mu\nu} E_\nu, \quad \mu, \nu = x, y, z \tag{6.13}$$

Remarks The conductivity tensor has the following properties:

1. **Anisotropy.** In free electron, the current is parallel to the external electric field, thus the tensor is diagonal. In a general structure, however, the current need not to be parallel to the external field and the tensor need not to be diagonal.
2. **Irrelevance of filled bands.** If the band is filled, then no current is contributed.
3. **Recovery of free electron result.** In free electrons, the result can be reduced to

$$\sigma = \frac{ne^2\tau}{m^*} \tag{6.14}$$

6.3 Thermal Conductivity

The rate at which heat appears in the region is just T times the rate at which the entropy of the electrons within the region changes ($dQ = TdS$). Thus the thermal current density is T times the entropy current density

$$\mathbf{j}^q = T\mathbf{j}^s \tag{6.15}$$

The changes of heat are also related to the changes of internal energy and the numbers of particles flowing through the region ($dQ = TdS = dU - \mu dN$), thus

$$\mathbf{j}^q = T\mathbf{j}^s = \mathbf{j}^u - \mu\mathbf{j}^n \tag{6.16}$$

where \mathbf{j}^u and \mathbf{j}^n are given, in analogy to the form of electrical current density, by

$$\mathbf{j}^u = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \epsilon_{n,\mathbf{k}} \mathbf{v}_n f_{n,\mathbf{k}} \quad (6.17)$$

$$\mathbf{j}^n = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \mathbf{1} \cdot \mathbf{v}_n f_{n,\mathbf{k}} \quad (6.18)$$

Thus the thermal current density is

$$\mathbf{j}^q = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} [\epsilon_{n,\mathbf{k}} - \mu] \mathbf{v}_n f_{n,\mathbf{k}} \quad (6.19)$$

According to equation 6.6, the distribution function writes

$$\begin{aligned} f_n &= f_0 - \tau \left(-\frac{\partial f_0}{\partial \epsilon} \right) \mathbf{v}_{n,\mathbf{k}} [e\mathbf{E} + \nabla\mu + \frac{\epsilon - \mu}{T} \nabla T] \\ &= f_0 + \tau \left(-\frac{\partial f_0}{\partial \epsilon} \right) \mathbf{v}_{n,\mathbf{k}} [-e\epsilon + \frac{\epsilon - \mu}{T} (-\nabla T)] \end{aligned} \quad (6.20)$$

where

$$\epsilon = \mathbf{E} + \frac{\nabla\mu}{e} \quad (6.21)$$

Thus the thermal current density is

$$\mathbf{j}^q = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \tau \left(-\frac{\partial f_0}{\partial \epsilon} \right) (\epsilon_{n,\mathbf{k}} - \mu) \mathbf{v}_n \mathbf{v}_n [-e\epsilon + \frac{\epsilon - \mu}{T} (-\nabla T)] \quad (6.22)$$

Similarly, the electric current density is given by

$$\mathbf{j} = \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \tau \left(-\frac{\partial f_0}{\partial \epsilon} \right) (-e) \mathbf{v}_n \mathbf{v}_n [-e\epsilon + \frac{\epsilon - \mu}{T} (-\nabla T)] \quad (6.23)$$

We can thus construct a matrix formation for current density induced by external field and temperature gradients

$$\begin{pmatrix} \mathbf{j} \\ \mathbf{j}^q \end{pmatrix} = \begin{pmatrix} L^{11} & L^{12} \\ L^{21} & L^{22} \end{pmatrix} \begin{pmatrix} \epsilon \\ -\nabla T \end{pmatrix} \quad (6.24)$$

where

$$L^{(\alpha)} = e^2 \sum_n \int \frac{d\mathbf{k}}{4\pi^3} \tau \left(-\frac{\partial f_0}{\partial \epsilon} \right) \mathbf{v}_n \mathbf{v}_n (\epsilon_{n,\mathbf{k}} - \mu)^\alpha \quad (6.25)$$

$$L^{11} = L^{(0)}, \quad L^{12} = -\frac{1}{eT} L^{(1)}, \quad L^{21} = -\frac{1}{e} L^{(1)}, \quad L^{22} = \frac{1}{e^2 T} L^{(2)} \quad (6.26)$$

Now we try to verify the Wiedemann-Franz law. In order to deal with the thermal conductivity, we consider the current density in the absence of electric field. Thus

$$\begin{aligned} \mathbf{j} &= L^{11} \epsilon + L^{12} (-\nabla T) = 0 \\ \mathbf{j}^q &= L^{21} \epsilon + L^{22} (-\nabla T) = -\kappa \nabla T \end{aligned} \quad (6.27)$$

Therefore

$$\kappa = -L^{21}(L^{11})^{-1}L^{12} + L^{22} \approx L^{22} = \frac{\pi^2}{3e^2}k_B^2T\sigma \quad (6.28)$$

or

$$\frac{\kappa}{\sigma T} = \frac{\pi^2}{3e^2}k_B^2 = \text{const.} \quad (6.29)$$

which is the Wiedemann-Franz law.

6.4 Thermoelectric Effect

6.4.1 Seebeck Effect

When a temperature gradient is maintained in a metal and no electric current is allowed, there will be a steady-state electric potential difference between the high- and low- temperaturw ends of the specimen, which is called the Seebeck effect. Due to equation (6.24), when the electric current is zero

$$\mathbf{j} = L^{11}\boldsymbol{\epsilon} + L^{12}(-\boldsymbol{\nabla}T) = 0 \quad (6.30)$$

Thus the thermoelectric power Q , defined by the proportionality of the electric field to the temperature gradient, is

$$Q = \frac{L^{12}}{L^{11}} \quad (6.31)$$

So

$$\boldsymbol{\epsilon} = Q\boldsymbol{\nabla}T \quad (6.32)$$

6.4.2 Peltier Effect

Likewise, when the current flows through a bimetallic specimen at a uniform temperature(no temperature gradient), then heat will evolved at one junction and absorbed at another. This effect is called Peltier effect. Due to equation (6.24), by forcing $\boldsymbol{\nabla}T = 0$ we obtain

$$\mathbf{j}^q = \Pi\mathbf{j} = \frac{L^{11}}{L^{21}}\mathbf{j} \quad (6.33)$$

where Π is called the Peltier coefficient. A simple relationship between Q and Π is given by Kelvin relation, named after Lord Kelvin,

$$\Pi = QT \quad (6.34)$$

Chapter 7

Classical Theory of Harmonic Crystal

7.1 Harmonic Approximation

In order to describe the oscillation of the crystal lattice, we have the following basic assumptions.

1. The equilibrium point of each ion is a Bravais lattice \mathbf{R}_n .
2. The excursion of each ion from its equilibrium point is small compared with the interionic spacing.

Due to the validity of the assumptions above, the time-dependent position of each ion can be written as the sum of its Bravais site and a small deviation

$$\mathbf{R}(\mathbf{R}_n) = \mathbf{R}_n + \mathbf{u}(\mathbf{R}_n) \quad (7.1)$$

Thus the total potential energy between all the ions is sum of the contribution between all different pairs

$$V = \frac{1}{2} \sum_{n,n'} \phi(\mathbf{R}(\mathbf{R}_n) - \mathbf{R}(\mathbf{R}_{n'})) = \frac{1}{2} \sum_{n,n'} \phi(\mathbf{R}_n - \mathbf{R}_{n'} + \mathbf{u}(\mathbf{R}_n) - \mathbf{u}(\mathbf{R}_{n'})) \quad (7.2)$$

Since we have $|\mathbf{u}(\mathbf{R}_n) - \mathbf{u}(\mathbf{R}_{n'})| \leq |\mathbf{R}_n - \mathbf{R}_{n'}|$, the potential can be expanded by Taylor series

$$\begin{aligned} V = & \frac{1}{2} \sum_{n,n'} \phi(\mathbf{R}_n - \mathbf{R}_{n'}) + \frac{1}{2} \sum_{n,n'} (\mathbf{u}(\mathbf{R}_n) - \mathbf{u}(\mathbf{R}_{n'})) \cdot \nabla \phi(\mathbf{R}_n - \mathbf{R}_{n'}) \\ & + \frac{1}{4} \sum_{n,n'} ((\mathbf{u}(\mathbf{R}_n) - \mathbf{u}(\mathbf{R}_{n'})) \cdot \nabla)^2 \phi(\mathbf{R}_n - \mathbf{R}_{n'}) + O(u^3) \end{aligned} \quad (7.3)$$

The first term on the right hand side is a constant that can commonly be ignored in many problems. The second term on the right hand side must

vanish because the net force on the on any atom must be zero. Thus the only term left is the third term, hence

$$V = \frac{1}{4} \sum_{n,n'} ((\mathbf{u}(\mathbf{R}_n) - \mathbf{u}(\mathbf{R}_{n'})) \cdot \nabla)^2 \phi(\mathbf{R}_n - \mathbf{R}_{n'}) \quad (7.4)$$

7.2 Normal Mode of 1D Bravais Lattice

7.2.1 Monatomic Lattice

Consider the case that a set of ions with mass M distributed on a line and separated by distance a , so the Bravais lattice sites are $\mathbf{R}_n = na\hat{\mathbf{e}}_x$. Due to equation (7.4), the harmonic potential is

$$V = \frac{1}{2} K [u(na) - u((n+1)a)]^2 \quad (7.5)$$

where

$$K = \frac{\partial^2 \phi}{\partial x^2} \Big|_{x=a} \quad (7.6)$$

Thus the equations of the motion for all the ions are

$$M\ddot{u}(na) = -K \frac{\partial V}{\partial u(na)} = K [u((n+1)a) + u((n-1)a) - 2u(na)] \quad (7.7)$$

Due to the translational invariance of the equation, the solutions should satisfy Bloch theorem

$$u(na, t) = u(na, 0) e^{iqna} = A e^{i(qna - \omega t)} \quad (7.8)$$

Hence we can find that

$$\omega(q) = \sqrt{\frac{2\beta(1 - \cos qa)}{M}} \quad (7.9)$$

which is the dispersion relation of lattice wave. Born-von Karman condition requires q to have the form of

$$q = \frac{l}{N} \frac{2\pi}{a} \quad (7.10)$$

7.2.2 Diatomic Lattice

Consider the case that a set of two types of ions with masses M_1 and M_2 , respectively distributed at $x = na$ and $x = na + a/2$. Only the potential between neighbouring ions is considered. So, likewise, the equations of the motion for the ions are

$$M_1 \ddot{u}_{n,1} = K [u_{n,2} + u_{n-1,2} - 2u_{n,1}] \quad (7.11)$$

$$M_2 \ddot{u}_{n,2} = K[u_{n+1,1} + u_{n,1} - 2u_{n,2}] \quad (7.12)$$

Similarly we have

$$\omega_{\pm}^2 = K \frac{M_1 + M_2}{M_1 M_2} \left\{ 1 - \left[1 - \frac{4M_1 M_2}{(M_1 + M_2)^2} \sin^2\left(\frac{qa}{2}\right) \right] \right\}^{1/2} \quad (7.13)$$

The dispersion relation has two branches instead of one. ω_- , with lower frequency, is called the acoustic branch and ω_+ , with higher frequency, is called the optic branch.