

## Lecture 9 Quantum Free Electron Model (Sommerfeld Model)

**Simon: Chapter 4, p24-37; Kittel: Chapter 6, p132-141**

In contrast to the classical model the free electron model treats the electrons as quantum particles obeying Fermi-Dirac statistics and therefore the Fermi-Dirac distribution function. Electrons belong to a class of particles called Fermions.

The free electron model makes a number of assumptions:

1. As with the Drude model the valence (outer) electrons of each atom are assumed to move freely throughout the metal.
2. The effect of the ions and other electrons (+ve and -ve charges) cancel on average and can be ignored. This is the independent electron and free electron approximations discussed in the Drude model. (We will return to this later).

The introduction of a quantum theory provides the answer to the questions not answered by the classical Drude theory.

Q. How can a conduction electron apparently travel for enormous distances through a crystalline solid?

A1. The electrons behave as waves which can propagate freely through a periodic structure at certain wavelengths.

A2. A conduction electron does not interact with other conduction electrons because of the Pauli Exclusion Principle. It behaves as a free electron Fermi gas having a relatively low density of free electrons.

The free electron model describes our crystalline metal as an *empty box of the same dimensions as our crystal*. It assumes that there is *no potential* inside the box (hence the name of free electron model). It can be fully described by only one parameter

$\mathbf{L} = (L_x, L_y, L_z)$  the dimensions of the system. Inside this box the potential  $V(\mathbf{r}) = 0$  and outside the box the potential  $V(\mathbf{r}) = \infty$ . It is this potential which confines the electrons to a volume that has the same dimensions as our crystalline metal. As noted above the interaction between the electrons and the periodic potential produced by the atoms is ignored (this is the nearly-free electron approximation – which will be considered later in the course).

### Periodic Boundary Conditions

In solving the Schrödinger equation for this system it is convenient to use periodic boundary conditions such that the wavefunction  $\psi(\mathbf{r})$  is periodic with a period  $\mathbf{L}$ , the dimensions of the system in which the electrons are confined. This is another direct consequence of the periodic nature of crystals. The benefit of this boundary condition is that it removes any restrictions on the allowed values of  $\mathbf{r}$ .

The physical justification for this is that when considering an electron in a crystalline solid we can translate an electron by an amount equivalent to the dimensions of the crystal and the physical environment experienced by the electron is the same. Mathematically the advantage of doing this is that the values of  $\mathbf{r}$  are no longer required to be just positive, it removes all limitations on  $\mathbf{r}$ .

In 3D the **periodic boundary conditions** are written:

$$\psi(x, y, z) = \psi(x + L_x, y, z) = \psi(x, y + L_y, z) = \psi(x, y, z + L_z)$$

for all values of  $x, y, z$ . Note that in a cubic system  $|L| = |L_x| = |L_y| = |L_z|$ .

The application of these boundary conditions to the Schrödinger equation provides a straightforward set of solutions to the equation that are valid for these boundary conditions.

[Note, this applies even although there is no periodic potential in the free electron model. The next iteration of this model, the nearly-free electron model – covered in later lectures, does have a periodic potential.]

## Free Electron Wavefunction

The solid is defined by a potential such that  $V(x, y, z) = 0$  inside the crystal and  $V(x, y, z) = \infty$  outside the crystal.

We begin with the time-independent Schrödinger equation

$$\frac{-\hbar^2}{2m_e} \nabla^2 \psi(\mathbf{r}) + V(\mathbf{r})\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

where

$$\nabla^2 \psi \equiv \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2}$$

The solution of the Schrödinger equation in the solid where  $V(x, y, z) = 0$  is:

$$\psi(x, y, z) = A \exp i(k_x x + k_y y + k_z z)$$

where

$$k_x = \frac{2\pi l}{L}, \quad k_y = \frac{2\pi m}{L}, \quad k_z = \frac{2\pi n}{L}, \quad l, m, n = 0, \pm 1, \pm 2, \dots$$

The allowed values of wavevector come from the periodic boundary conditions – which are specified simply by the dimensions of the system  $L_x, L_y, L_z$

The energy of the solution is found by substituting the wavefunction into the Schrödinger equation:

$$E = \frac{\hbar^2}{m_e} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 k^2}{m_e}$$

The solution  $\psi$  is the “free electron wavefunction”. It is described by an electron wavevector  $k$ , whose quantum numbers  $l, m, n$  describes the allowed energy states of this system.

In the free electron model we are treating the metal as a container (dimensions  $L_x, L_y, L_z$ ) which contains a free electron gas. The electrons are quantum particles subject to the Pauli Exclusion Principle. They are described by Fermi-Dirac statistics.

There is no potential inside the container, in other words we are neglecting the effect of the atoms. This will change later when we introduce a periodic potential into the Schrodinger equation to allow for an interaction between the electron wavefunction and the atoms.

One consequence of the free electron model is that the electron states are stationary energy eigenstates obtained from the boundary conditions. This means that each electron wavefunction overlaps spatially with all other electron wavefunctions. The amplitude of the wavefunctions  $A$  is constant. This implies that the probability of finding an electron in the box, defined by the potential, is constant. The electron motion is not restricted within the box – as expected from the free-electron model.

The wavevector  $\underline{k}$  is related to the energy of the electron and is also a measure of the momentum and velocity of the free electron.

## k-space

Each allowed quantum state which can be occupied by an electron is labelled by the quantum numbers  $k_x, k_y, k_z$ . We can think of this as a point in  $k$ -space with coordinates  $k_x, k_y, k_z$ .

The allowed points form a regular mesh in this space with a separation of  $2\pi / L$  between the points in each direction. (Another consequence of the application of periodic boundary conditions.) Each  $k$ -state occupies a certain volume in  $k$ -space (or Energy space).

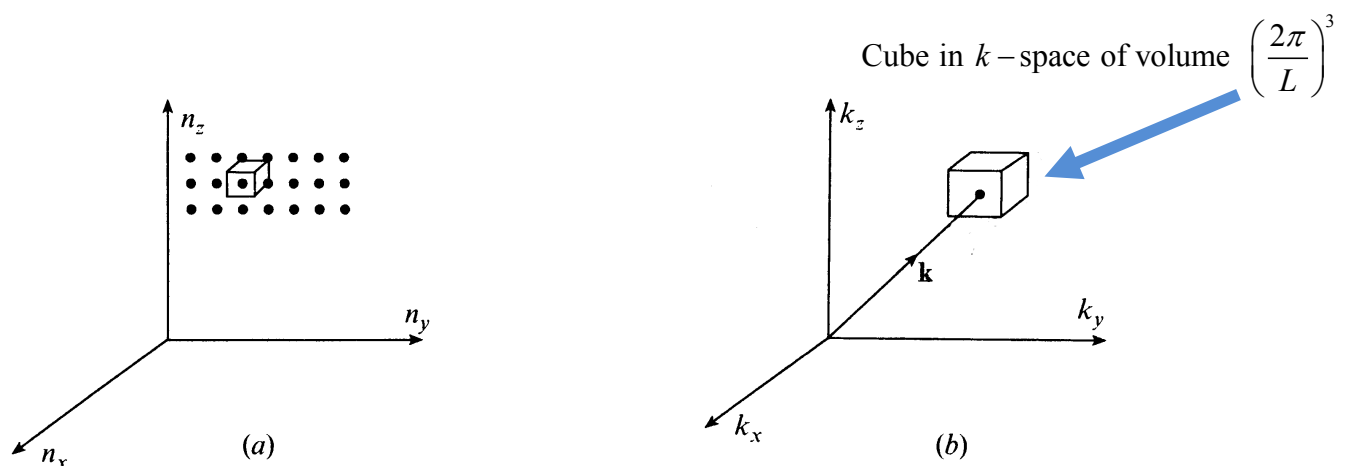


Fig. 2.7 (a) Coordinate system defining the allowed quantum states. (b) Equivalent diagram in reciprocal space showing the volume containing one allowed value of the wavevector.

Each point in  $k$ -space is surrounded by a volume of  $\left(\frac{2\pi}{L}\right)^3$  where there are no other  $k$ -states. This can be considered as an exclusion zone.

Allowing for spin up and spin down electrons (factor of 2) we then have:

$$2 \times \left(\frac{L}{2\pi}\right)^3 = \frac{L^3}{4\pi^3} \quad \text{electron energy states per unit volume of } k\text{-space.}$$

## The Fermi Energy and Fermi Surface

The Fermi energy  $E_F$  is defined as the energy of the highest occupied energy level in the *ground state* of an  $n$  electron system.

To obtain the lowest possible total energy the electrons are placed into the lowest possible energy states (this is described by Fermi Dirac statistics – more on this later).

We know that electrons are fermions therefore only two electrons (one with spin up, one with spin down) can occupy a given energy state. This is the Pauli Exclusion Principle which determines how electrons can be arranged in a system.

This is more correctly stated as no two fermions in a system can exist in identical quantum states and have the same quantum numbers. (Remember that one consequence of the free electron model is that all electron wavefunctions overlap and have the same spatial coordinates.)

We can determine the fermi energy at 0 Kelvin (equivalent to the ground state) with relative ease.

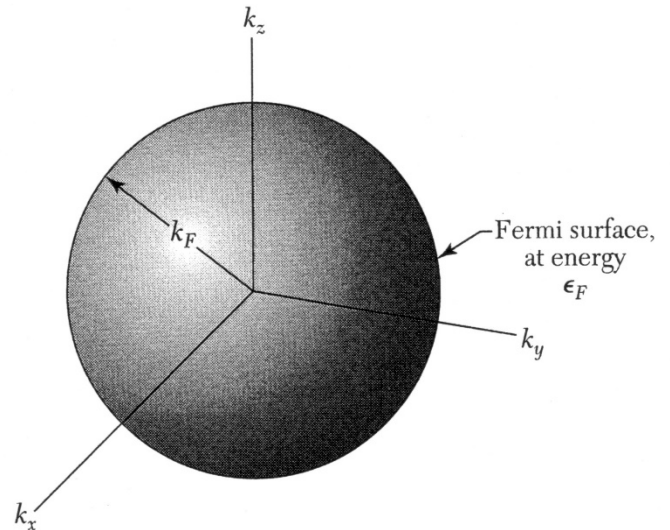
We choose to fill the electron states with the lowest energy.

All the points in  $k$ -space with a particular energy have a fixed value of energy equivalent to a fixed value of  $k^2 = k_x^2 + k_y^2 + k_z^2$  since we know that  $E = \frac{\hbar^2 k^2}{2m_e}$ . These points lie on a sphere in  $k$ -space with a radius  $k$ .

At 0 Kelvin all the energy states up to the surface of the sphere are occupied, all those outside the sphere are empty. The effect of temperature is to spread out the surface of the sphere in  $k$ -space (fuzzy boundary).

The spherical surface represents a surface of constant energy and is called a Fermi-sphere or Fermi-surface.

(Note: In general the Fermi-surface in crystals is more complex than a simple sphere.)



**Figure 4** In the ground state of a system of  $N$  free electrons the occupied orbitals of the system fill a sphere of radius  $k_F$ , where  $\epsilon_F = \hbar^2 k_F^2 / 2m$  is the energy of an electron having a wavevector  $k_F$ .

To obtain the total state of the system with the lowest possible energy we have to determine the  $N$  states with the lowest values of  $k^2$  which will therefore lie inside a sphere of radius  $k_F$  in  $k$ -space.

The radius  $k_F$  is determined by setting the volume of the sphere in  $k$ -space  $\times$  the number of electron energy states per unit volume equal to the total number of electrons  $N$ .

Recall there are  $\left(\frac{L^3}{4\pi^3}\right)$  electron energy states per unit volume of  $k$ -space.

From this we get:

$$\left(\frac{4}{3}\pi k_F^3\right)\left(\frac{L^3}{4\pi^3}\right) = N$$

$$k_F = \left(\frac{3N\pi^2}{L^3}\right)^{1/3} = (3\pi^2 n)^{1/3}$$

where  $n$  is the free electron density – number per unit volume.

The sphere surface separates the empty and filled states in 3D and is called the Fermi surface.

The Fermi energy is obtained from the Fermi wavevector,  $k_F$  :

$$E_F = \frac{\hbar^2 k_F^2}{2m_e} = \frac{\hbar^2}{2m_e} (3\pi^2 n)^{2/3}$$

The velocity of an electron at the Fermi surface is the Fermi velocity:

$$v_F = \frac{\hbar k_F}{m_e}$$

## The Density of States

This is an extremely important quantity. It describes the *number of energy states* which can be occupied by an electron in a given energy range. In the formalism of quantum mechanics an electron may only occupy an allowed or valid energy state (described by valid solutions to the Schrodinger equation). In the classical Drude model there is no such limitation when the electrons are considered as classical particles.

We can use the concept of the Fermi-sphere or Fermi-surface to derive the density of state function in 3D.

All points in  $k$ -space with a given value of  $k^2 = k_x^2 + k_y^2 + k_z^2$  lie on the surface of a sphere radius  $k$ .

The surface area of the sphere is  $4\pi k^2$ .

The volume of  $k$ -space between  $k$  and  $k+\delta k$  is  $4\pi k^2 \delta k$ . (Note this is an approximation based on the fact that  $\delta k$  is very small compared to the radius of the sphere.)

Multiplying by the number of  $k$  states per unit volume gives the total number of states between  $k$  and  $k+\delta k$ :

$$n(k)\delta k = \frac{L^3}{4\pi^3} 4\pi k^2 \delta k$$

$$n(k)\delta k = \frac{L^3}{\pi^2} k^2 \delta k$$

To calculate the density of states as a function of energy  $n(E)$  we express the density of states in terms of unit energy range (by definition the two expressions are equivalent):

$$n(k)\delta k = n(E)\delta E$$

Using

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

$$\frac{dk}{dE} = \frac{m_e^{1/2}}{\sqrt{2}\hbar} E^{-1/2}$$

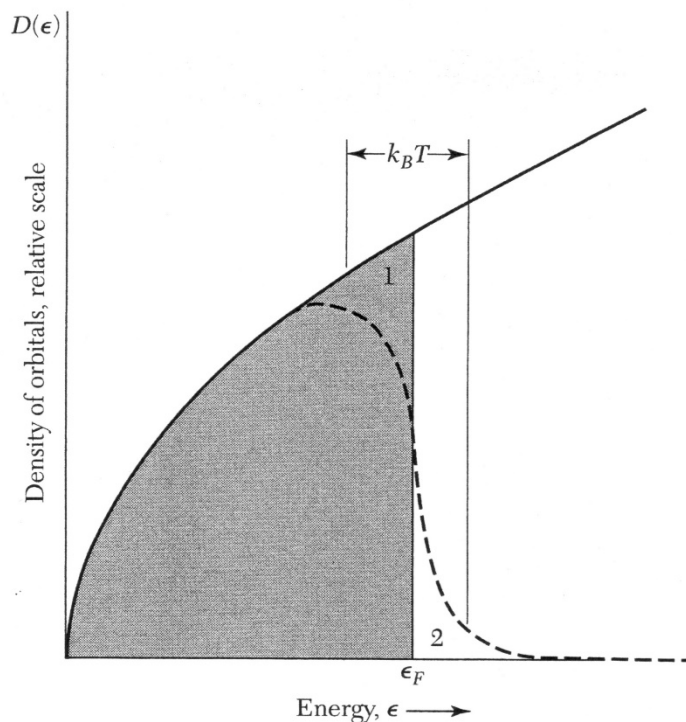
Finally, by setting  $\frac{\delta k}{\delta E} = \frac{dk}{dE}$  we have:

$$n(E)\delta E = \frac{L^3}{\pi^2} k^2 \delta k$$

$$n(E) = \sqrt{2} \frac{L^3}{\pi^2} \frac{m_e^{3/2}}{\hbar^3} E^{1/2}$$

This is the bulk 3D density of states and varies with energy as  $E^{\frac{1}{2}}$ . This is a key result in the electron properties of metals and other crystalline solids.

This is a very significant quantity in describing the properties of electrons in crystalline solids.



**Figure 5** Density of single-particle states as a function of energy, for a free electron gas in three dimensions. The dashed curve represents the density  $f(\epsilon, T)D(\epsilon)$  of filled orbitals at a finite temperature, but such that  $k_B T$  is small in comparison with  $\epsilon_F$ . The shaded area represents the filled orbitals at absolute zero. The average energy is increased when the temperature is increased from 0 to  $T$ , for electrons are thermally excited from region 1 to region 2.

The figure above shows the electron states increasing as  $E^{\frac{1}{2}}$  up to the Fermi energy with energy states above the Fermi energy being empty.

It tells us that as the energy of electrons increases the density of electron energy states per unit volume increases in proportion to  $E^{\frac{1}{2}}$ .

Also, the greater the volume ( $V = L^3$  in our cubic system) the more states are available up to the energy  $E$ .

The energy density of states function depends on the dimensions of the system. Confining the motion of the electrons (for example in low dimensional solids) results in a significant change in the density of states.

In a 2D system the density of states is constant with respect to energy. This has important consequences for devices and is explored in Example Workshop 4.