Free electron gas in three dimensional box

Let us consider that the electron is confined to remain inside a cubical box of edge L. The potential energy of the electron inside the box every where is taken as zero. The wave function $\psi_k(r)$ is described by the Schrödinger equation of the form

$$\nabla^2 \psi_k(r) + \frac{2m}{\hbar^2} E_k \psi_k(r) = 0 \quad \text{--(1)}$$

where E_k is the total energy of the electron. Here it is kinetic energy of the electron in the state k.

It can be shown that the normalized wave function satisfying the eqn.(1) is given by

$$\psi_k(r) = \left(\frac{8}{L^3}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right) \quad \text{--(2)}$$

Where n_x, n_y, n_z are positive integers. This is a standing wave solution. However it is more convenient to work with a plane travelling wave solution of the form

$$\psi_k(r) = A e^{i \vec{k} \cdot \vec{r}}$$
$$= A e^{i(k_x x + k_y y + k_z z)}$$

Where $k^2 = \left(\frac{2m}{\hbar^2}\right) E_k$ and A is an arbitrary constant.

Such wave solution must satisfy the following periodic boundary conditions:

$$\left.\begin{aligned} \psi(x+L, y, z) &= \psi(x, y, z) \\ \psi(x, y+L, z) &= \psi(x, y, z) \\ \psi(x, y, z+L) &= \psi(x, y, z) \end{aligned}\right\} \quad (3)$$

These conditions obviously make the wave function

to be periodic in x, y, z with period L. Applying the first boundary condition, we have

$$\exp i[K_x(x+L)+K_y y+K_z z] = \exp i[K_x x+K_y y+K_z z]$$

or $\exp iK_x L = 1$

or $K_x = 0, \pm\frac{2\pi}{L}, \pm\frac{4\pi}{L}, \ldots, \pm\frac{2\pi n_x}{L}$

Similarly,

$$K_y = \pm 2\pi n_y/L$$

and $K_z = \pm 2\pi n_z/L$ (4)

Where n_x, n_y, n_z are integers including zero.

$$\therefore K^2 = K_x^2+K_y^2+K_z^2 = \left(\frac{2\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2)$$

$$= \left(\frac{2\pi}{L}\right)^2 n^2, \qquad n^2 = n_x^2+n_y^2+n_z^2.$$

Thus the energy eigen values are given by

$$E_K = \frac{\hbar^2}{2m}K^2 = \frac{\hbar^2}{2m}(K_x^2+K_y^2+K_z^2) \quad -(5)$$

Where K_x, K_y, K_z are obtained according to conditions (4). Evidently, the energy spectrum consists of discrete energy levels which usually be very close together ($\sim 10^{-15}$ eV apart). Such energy levels are said to be quasi-continuous. This energy separation depends upon the size of the box.

To obtain the expression for A, we have

$$\int_0^V \psi^*(r)\,\psi(r)\,dv = 1$$

whence, we get

$$A = \left(\frac{1}{V}\right)^{\frac{1}{2}}$$

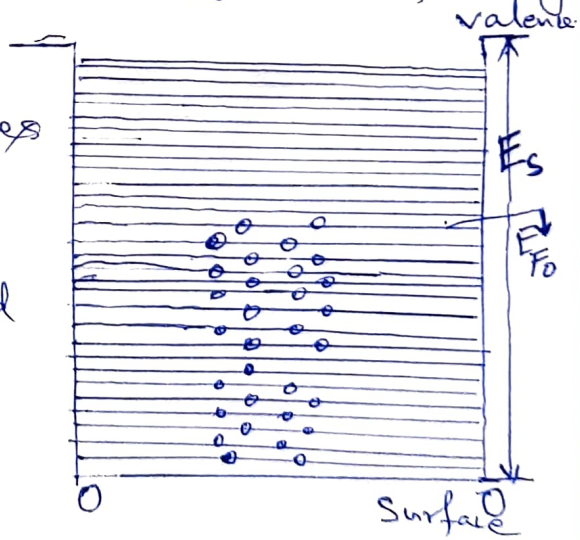
Thus the normalized wave function is

$$\psi_K(r) = \left(\frac{1}{V}\right)^{\frac{1}{2}} e^{i\vec{K}\cdot\vec{r}}$$

Obviously $\vec{K}$ is a wave-vector and K_x, K_y, K_z are the components of $\vec{K}$. The set of values of K_x, K_y, K_z define a state of energy. If m_s be the spin quantum number of the electron, then K_x, K_y, K_z, m_s define the energy state of electron. The state ~~numbers~~ of the system is defined by the quantum numbers K_x, K_y, K_z and m_s. The electron can have only two spins $(\pm \frac{1}{2})$ corresponding to two possible orientations.

Fermi-energy level

Let there be N(even) electrons available to be filled in a box. Each energy state corresponding to a set of values of K_x, K_y, K_z will accommodate two electron having opposite spins according to Pauli's exclusion principle. Thus the first N/2 available energy states will be filled by the available electrons. The highest filled energy level will be known as Fermi energy level and the energy corresponding to this level is called Fermi energy. Thus discussion assumes that the system is in the ground state (T=0). The Fermi energy in the ground state is designated by E_{F0}.



Fermi distribution function

The probability that a particular quantum state at energy E is filled is given by the Fermi function

$$f(E) = \frac{1}{\exp[(E-E_F)/k_BT]+1}$$