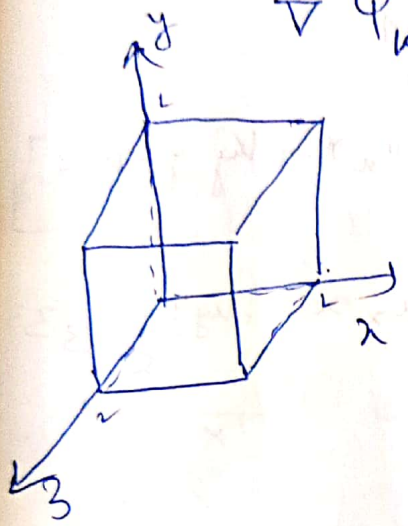
Free electron gas in Three dimensions

Let us consider metal as a cubical electron gas container of side L. The 3-D Schrodinger eqn for the electron of mass m is

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



the pot^l of electrons inside the crystal is constant and may be taken as zero whereas it has a large value outside the crystal.

E_k is the K-E of electron in K space. the sol^n of eqn (1) is (plane travelling wave)

$$\psi_k(\vec{r}) = A e^{i\vec{k}\cdot\vec{r}} \quad \text{---(2)} \qquad k^2 = \frac{2m}{\hbar^2} E_k \quad \text{---(3)}$$

$$\vec{k} = k_x \hat{i} + k_y \hat{j} + k_3 \hat{k} \quad \text{or} \quad |\vec{k}| = \sqrt{k_x^2 + k_y^2 + k_3^2}$$

$$\vec{r} = x\hat{i} + y\hat{j} + 3\hat{k} \quad \text{or} \quad |\vec{r}| = \sqrt{x^2 + y^2 + 3^2}$$

The f^n $\psi_k(\vec{r})$ is a periodic in x, y, 3 with period L such that

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

Applying the first boundary condition to the wave fn $\psi_k(\vec{r})$ we get

$$\psi_k(x+L, y, 3) = \psi(x, y, 3)$$

$$e^{i[k_x(x+L), y, 3]} = e^{i[k_x x + k_y y + k_3 3]}$$

or $e^{i k_x (x+L)}\, e^{i y k_y}\, e^{i 3 k_3} = e^{i k_x x}\, e^{i k_y y}\, e^{i k_3 3}$

or $e^{i k_x (x+L)} = e^{i k_x x}$

or $e^{i k_x x}\, e^{i k_x L} = e^{i k_x x}$

or $e^{i k_x L} = 1$, K

or $k_x = 0, \pm \frac{2\pi}{L}, \pm \frac{4\pi}{L} \cdots \frac{2n\pi}{L} \cdots$ ---(4)

For k_y & k_3 we get similar result

If m_s is the spin magnetic quantum number of electron, then its states can be represented by a set of four quantum numbers k_x, k_y, k_3 & m_s.

The value of A in equ^{n} (2) can be obtained from the cond^{n} of normalization i.e

$$\int_{0}^{V} \psi_k^*(\bar{r})\psi_k(\bar{r})\,dV = 1$$

or $$\int_0^L\int_0^L\int_0^L A^2 e^{-i(\bar{k}\cdot\bar{r})} \cdot e^{i(\bar{k}\cdot\bar{r})}\,dx\,dy\,dz = 1$$

or $$A^2 L^3 = 1$$

$$\therefore A = \left(\frac{1}{L^3}\right)^{1/2} = \left(\frac{1}{V}\right)^{1/2}$$

∴ The normalised wave f^{n} for the electron in the k^{th} state is

$$\boxed{\psi_k(\bar{r}) = \left(\frac{1}{V}\right)^{1/2} e^{i(\bar{k}\cdot\bar{r})}} \quad \text{—(4)}$$

The allowed eigen values of the state or orbital with wave vector k can be written as

$$E_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) \quad \text{(5)}$$

where magnitude of wave vector related to the W.L ↗ as

$$\boxed{k = \frac{2\pi}{\lambda}} \quad \text{—(6)}$$