Quantum theory of free electron

~~Due to this~~

These quantitative errors were removed by Sommerfield in 1928 by proposing quantum free electron theory of metal.

According to him free electron obey Fermi Dirac distribution f^n instead of Maxwell Boltzmann statistics.

He ~~considered that~~ assumed that the valence electrons travel in constant pot^l inside the metal and they are trapped in a constant pot^l well.

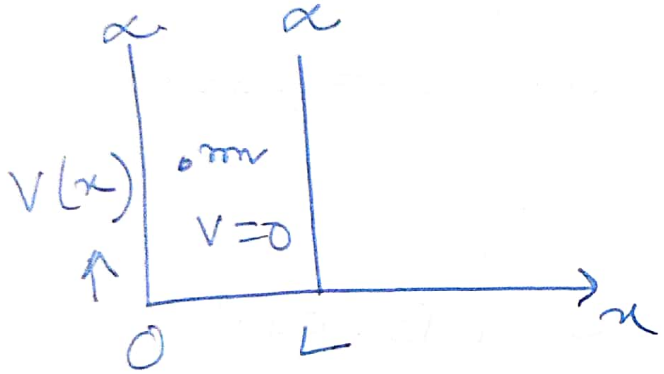
Sommerfield introduced Schrodinger's wave equ^n and its sol^n and by this he ~~fo~~ calculated the possible and permissible eng states for an electron to occupy in the potential box. ~~a~~ Applying F.D. statistics he explained

How are the very large no of free electrons distributed in the various permissible eng. states.

$$i\hbar \frac{\partial}{\partial t}\psi(r,t) = E\psi(r,t)$$
$$H\psi = E\psi$$

Free electron gas in 1-D box

Let us consider an electron of mass m confined in a 1-D potential box in a crystal of length L.



The boundary cond^{n}s are

$V(x) = 0$ for $0 < x < L$

$V(x) = \infty$ for $x \leq 0$ & $x \geq L$

The schrodinger eqn for the electron is

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2}(E_n - V)\psi_n = 0 \quad (1)$$

where ψ_n is the wave f^n for the electron in the nth state of eng E_n

$\because V = 0$ inside the well

$$\frac{d^2\psi_n}{dx^2} + \frac{2m}{\hbar^2}\psi_n E_n = 0 \quad \text{—— (2)}$$

$k = \sqrt{\frac{2mE}{\hbar^2}}$

$$\frac{d^2\psi_n}{dx^2} + k^2\psi_n = 0 \quad \text{—— (3)}$$

Let ~~to~~ $\psi_n(x)$ be the solⁿ of equⁿ (3)

$$\psi_n(x) = A\sin kx + B\cos kx \quad \text{—— (4)}$$

Applying boundary condⁿs:

$\psi_n(0) = 0$
$\psi_n(L) = 0$
at $x = 0$ & $x = L$

~~$\psi(x) = 0,\ 0 < x < L$~~

So
$$\psi_n(0) = 0 = A\sin 0 + B\cos 0$$
$$\text{or } 0 = 0 + B$$
$$\text{or } B = 0$$

equⁿ (4) $\Rightarrow$ $\psi_n(x) = A\sin kx$

Again $\psi_n(L) = 0$ at $x = L$

$$\psi_n(L) = A\sin KL = 0$$

as $A \neq 0$

$$\sin KL = 0$$

~~$\sin KL = n\pi$~~

$$\text{or } KL = n\pi$$

or $k = \frac{n\pi}{L}$

where $n = 1, 2, 3 \ldots\ldots$

So allowed wave f^n ~~are~~ is

$\psi_n(x) = A \sin kx$

$$\boxed{\psi_n(x) = A \sin\left(\frac{n\pi}{L}\right)x} \quad (5)$$

Eigen values of energy

as $\quad k = \sqrt{\frac{2mE}{\hbar^2}}$

or $\quad E_n = \frac{k_n^2 \hbar^2}{2m}$ $\qquad \boxed{E_n \propto k_n^2}$

$E_n = \left(\frac{n\pi}{L}\right)^2 \left(\frac{h}{2\pi}\right)^2 \frac{1}{2m}$

$$\boxed{E_n = \frac{n^2 h^2}{8mL^2}} \quad (6)$$

Thus $\boxed{E_n \propto n^2}$