QUANTUM FREE ELECTRON THEORY:

Somerfield applied quantum mechanics to explain conductivity phenomenon in metals. He has improved the Drude- Lorentz theory by quantizing the free electron energy and retaining the classical concept of force motion of electrons at random.

ASSUMPTIONS

1. The electrons are free to move with in the metal like gaseous molecules. They are confined to the metal due to surface potential.
2. The velocities of electrons obey Fermi-Dirac distribution because electrons are spin – half particles.
3. The electrons would go into different energy levels and obey Pauli's exclusion principle.
4. The motion of the electron is associated with a wave called matter wave, according to the deBroglie hypothesis.
5. The electrons can not have all energies but will have discrete energies according to the equation $E_{n=} \frac{n^2h^2}{8ma^2}$ where a is the dimension of the metals.

Derive an expression for electrical conductivity by using quantum free electron theory

According to Quantum theory

$$p = mv = \hbar K \text{ ---- } (1)$$

$$\text{Where } \hbar = \frac{h}{2\pi}, \quad K = \frac{2\pi}{\lambda}$$

Differentiating equation (1) w.r.t to t

$$a = \frac{dv}{dt} = \frac{\hbar}{m}\frac{dK}{dt}$$

At equilibrium the lorentz force $F = -eE$ acting on the electron is equal and opposite to the product of mass and acceleration of the electron
i.e.

$$eE = ma$$

$$\Rightarrow m\frac{\hbar\, dK}{m\, dt} = eE$$

$$\Rightarrow dK = \frac{eE}{\hbar}dt \text{ ---}(2)$$

Integrating (2) between the limits 0 and t

$$\int_0^t dK = \int_0^t \frac{eE}{\hbar}dt$$

$$K(t) - K(0) = \frac{eE}{\hbar}t$$

$$\Delta K = eE \; t \qquad \hbar \; ^{c}$$

where t_c

=men
collision
time.

But $J = ne\Delta v$ and $\Delta v = h\dfrac{\Delta K}{m}$

$$\Delta v = h\frac{\Delta K}{m} = \frac{h}{m}\frac{eE}{h}t = \frac{eEt}{m}$$

$$\therefore J = \frac{ne^2Et}{m^*}$$

From microscopic form of Ohm's law

$$J = \sigma E$$

$\therefore \sigma = \dfrac{ne^2t}{m^*}$ This is the expression for the electrical conductivity.

FERMI DIRAC DISTRIBUTION:

In quantum theory different electrons occupy different energy levels at O`K. Electrons obey Pauli's exclusion principle. As the electrons receive energy they are excited to higher levels which are unoccupied at O K. The occupation of electrons obeys Fermi-Dirac distribution law. The particles that obey Fermi-Dirac distribution law are called Fermions.

The Fermi-Dirac distribution function at a temperature T is given by

$$f(E) = \frac{1}{e^{(E-E_f)/KT}+1}$$

Where E_f = Fermi energy, $f(E)$ =the probability that a state of energy (E) is filled.

(I) At T=O K for $E > E_f$ $E = \frac{n^2h^2}{8ma^2}$

$$f(E) = \frac{1}{e^{\infty}+1} = 1$$

This means that all the energy state below E_f are filled.

For $E > E_f$

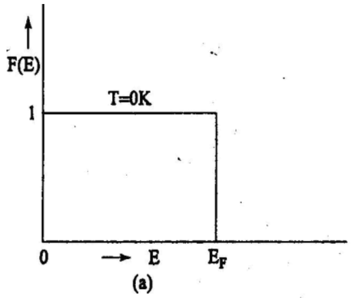
$f(E) = \frac{1}{e^{\infty}+1} = 0$ Means that all the energy levels above E_f are empty.

From this we define Fermi level as it is the level at 0K below which all the levels are filled and above which all the levels are empty or it is the highest occupied state at 0K

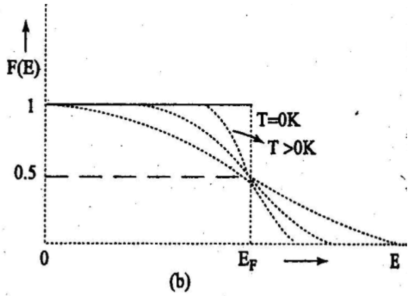
(2) At T>0 and $E = E_f$

$$f(E) = \frac{1}{1+1} = \frac{1}{2}$$

Fermi level is the state at which the probability of electron occupation is ½ at any temperature.



(a)



(b)

FERMI ENERGY:

The Fermi energy is a concept in quantum mechanics referring to the energy of the highest occupied quantum state in a system of Fermions at absolute zero temperature.

For the one dimensional infinite square well the energy of the particle is given by

$$E = \frac{n^2h^2}{8ma^2}$$

Suppose now instead of one particle in this box we haven particles in the box and that particles are fermions with spin ½ then only two particles can have the same energy.i.e. Two particles have the same energy of

$$E_1 = \frac{h^2}{8ma^2}$$

Two particles having energy

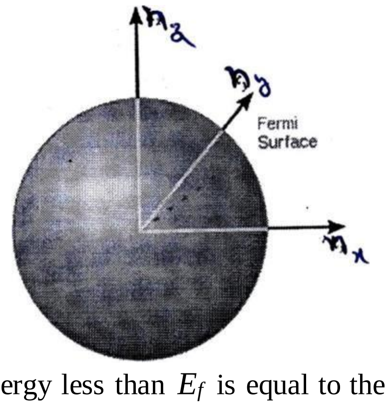
$$E_2 = \frac{4h^2}{8ma^2}$$

∴All the energy levels up to n=N/2 are occupied and all the higher levels are empty.

$$E_f = E_{N/2} = \frac{(N/2)^2 h^2}{8ma^2} = \frac{N^2h^2}{32ma^2}$$

$$\boxed{E_f = \frac{N^2h^2}{32ma^2}}$$

DENSITY OF STATES



The number of states with energy less than E_f is equal to the number of states that lie within a sphere of radius $|n_f|$ in a region of K–space where n_x , n_y and n_z are positive.

$$\therefore N = 2\times\frac{1}{8}\times\frac{4}{3}\pi n_f^3$$

$$\therefore N = 2\times\frac{1}{8}\times\frac{4}{3}\pi n_f^3 = \frac{3N}{\pi} \Rightarrow \boxed{n_f = \left(\frac{3N}{\pi}\right)^{\frac{1}{3}}}$$

So the Fermi energy

$$E_f = \frac{\hbar^2\pi^2 n_f^2}{2ma^2} = \frac{\hbar^2\pi^2}{2ma^2}\left(\frac{3N}{\pi}\right)^{\frac{2}{3}}$$

$$E_f = \frac{\hbar^2\pi^2}{2m\,a^2}\left(\frac{3N}{\pi}\right)^{\frac{2}{3}} = \frac{\hbar^2\,\pi^{\frac{4}{3}}(3N)^{\frac{2}{3}}}{2m\,(a^3)^{\frac{2}{3}}} = \frac{\hbar^2}{2m}\left(\frac{3N\pi^2}{a^3}\right)^{\frac{2}{3}} = \frac{\hbar^2}{2m}\left(\frac{3N\pi^2}{V}\right)^{\frac{2}{3}}$$

$$\therefore N^{\frac{2}{3}} = \frac{2m}{\hbar^2}\left(\frac{V}{3\pi^2}\right)^{\frac{2}{3}} E_f$$

$$\Rightarrow N = \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{V}{3\pi^2}\right)E_f^{\frac{3}{2}}$$

Therefore density of states: $D(E) = \frac{dN}{dE} = \frac{3}{2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\left(\frac{V}{3\pi^2}\right)E_f^{\frac{1}{2}}$

$$D(E) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{1}{2}}$$

Therefore the total number of energy states per unit volume per unit energy range

$$Z(E) = \frac{D(E)}{V} = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} E_f^{\frac{1}{2}} = \frac{1}{2\pi^2}\frac{(2m)^{\frac{3}{2}}}{h^3}8\pi^3 E_f^{\frac{1}{2}}$$

$$Z(E) = \frac{4\pi}{h^3}(2m)^{\frac{3}{2}} E_f^{\frac{1}{2}}$$

Therefore the number of energy states in the energy interval E and $E + dE$ are

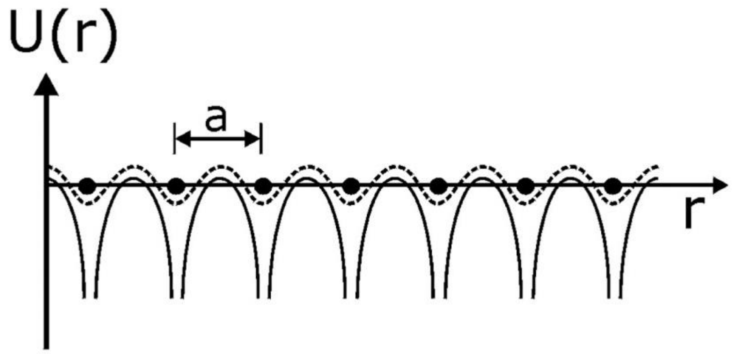
$$\boxed{Z(E)dE = \frac{4\pi}{h^3}(2m)^{\frac{3}{2}} E_f^{\frac{1}{2}} dE}$$

Important questions

1. a. Explain the salient features of classical free electron theory
   b. On the basis of classical free electron theory, derive the expressions for i) drift Velocity, ii) current density iii) mobility?
   c. What are drawbacks of classical free electron theory of materials?
2. a. Explain Fermi-Dirac distribution for electrons in a metal. Discuss its variation with temperature?
   b. Explain the terms 'Mean free path' 'Relaxation time' and 'Drift velocity' of an electron in a metal?
   c. Discuss the origin of electrical resistance in metals?
3. a. Derive the expression for electrical conductivity on the basis of quantum free electron theory?
   b. Explain i) Fermi energy?
   c. Evaluate the Fermi function for an energy KT above Fermi energy?

BAND THEORY OF SOLIDS

BLOCH THEORM:



Metals and alloys are crystalline in nature. When the electron move into the periodic ion core, it enters into the periodic potential i.e. potential is minimum at the positive ion sites and maximum between the two ions.

The one dimensional Schrödinger wave for this case is

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0$$

The periodic potential $V(x)$ may be defined as

$$V(x) = V(x+a)$$

Bloch has shown that the one dimensional solution of the form

$$\psi(x) = e^{ikx}.u_k(x) = e^{ika}.u_k(a)$$

Where $u_k(x) = u_k(x+a)$

$$\psi(x+a) = e^{ik(x+a)}.u_k(x+a)$$

$$= e^{ikx}e^{ika}.u_k(x+a)$$

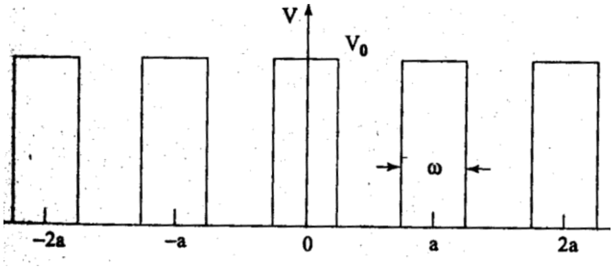
$$= e^{ika}e^{ikx}.u_k(x)$$

$$\boxed{\psi(x+a) = e^{ika}\psi(x)}$$

This is referred as Bloch condition.

KRONIG-PENNEY MODEL:

The free electrons in a metal move under a periodic potential due to regularly arranged positive ions. The nature of the energies of the electron is determined by solving Schrödinger wave equation. For simplicity, the periodic potential is taken in the form of regular o-ne dimensional array of square well potentials.



Within the wall the electron has potential energy

$$V = 0, 0 < x < a$$

Outside the wall the electron has the PE

$$V = V_0, -b < x < 0$$

$\therefore$ the Schrödinger wave equation for the two regions are

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 mE}{h^2} = 0, 0 < x < a \text{ ----------- } (1)$$

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m(E - V)\psi}{h^2} = 0, -b < x < 0 \text{--------------} (2)$$

$$\text{Let}\,\alpha^2 = \frac{8\pi^2 mE}{h^2}$$

$$\text{And}\;\beta^2 = \frac{8\pi^2 m(V_0 - E)}{h^2}$$

Then (1) and (2) becomes

$$\frac{\partial^2\psi}{\partial x^2} + \alpha^2\psi = 0, \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$$\frac{\partial^2\psi}{\partial x^2} - \beta^2\psi = 0, \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

On solving equations (3) and (4) and by applying Bloch Theorem we get

$$\boxed{P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a = \cos ka}$$

------------- (5)

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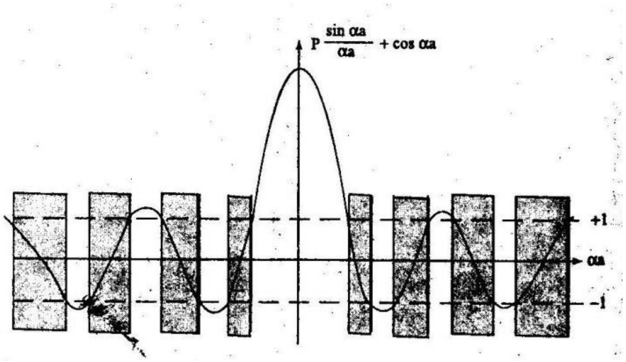
Where $P = \dfrac{mabV_0}{\text{h}^2}$

and $\alpha^2 = \dfrac{8\pi^2 mE}{h^2} \Rightarrow E = \dfrac{h^2\alpha^2}{8\pi^2 m}$

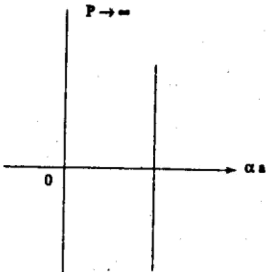
The nature of the equation is illustrated by the plot i.e. drawn between $P\dfrac{\sin\alpha a}{\alpha a} + \cos\alpha a$ and αa **and** at the same time the RHS having the value between +1 and -1



In the above graph only some of the range of αa **values are a**llowed indicating the a limiting range of energies are allowed. Allowed energy region is indicated by dark region and the forbidden region is indicated by dotted lines.

<u>Special cases:</u>

(i) If $P \to \infty$ the allowed band reduces to single energy level. This is the special case of electron trapped.



(ii) If $P \to 0$

$\cos\alpha a = \cos ka$

$k = \alpha$

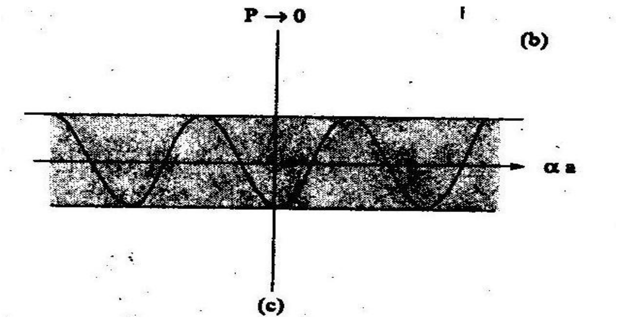
$k^2 = \alpha^2 = \dfrac{8\pi^2 mE}{h^2} \Rightarrow E = \dfrac{h^2k^2}{8\pi^2 m} = \dfrac{h^2 \quad 4\pi^2}{8\pi^2 m \quad \lambda^2}$

$\Rightarrow E = \dfrac{h^2}{2m}\dfrac{m^2v^2}{h^2} = \dfrac{1}{2}mv^2$

Therefore Total energy =KE+PE

$\Rightarrow$Potential Energy $V = 0$

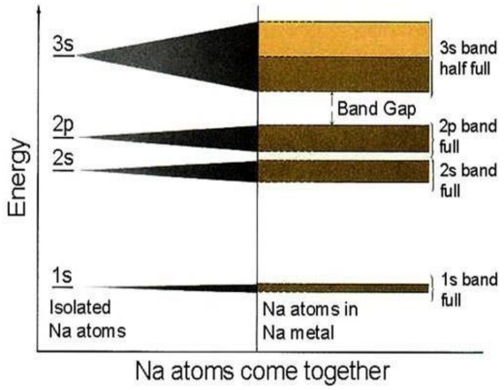
And this is the case of free electron.



Finally we conclude that

(i) Electrons insolids are permitted to be in allowed energy bands separated by forbidden energy gaps.
(ii) Allowed energy band width increases with αa
(iii) $P \to \infty$ is the case of electron trapped and
$P \to 0$ is the case of classical free particle

ORIGIN OF ENERGY BANDS:



In an isolated atom the electrons are tightly bound and have discrete sharp energy levels. When two identical atoms are brought closure the outermost orbit of these atoms overlaps and interacts. Then the energy levels corresponding to those atoms are split into two. If more atoms are brought together more levels are formed and for a solid of N atoms each of energy levels of an atom split into N levels of

Depends on the degree of overlap of electrons of adjacent atoms and is largest for outermost atomic electrons.

The electrons in the inner shells are strongly bound to their nucleus while the electrons in the outer most shells are not strongly bound to the nucleus. The electrons in the outermost shell are called valance electrons. The band formed by the energy levels containing the valance electrons is known as valence band.

Valence Band:

The band formed by the energy levels of valence electrons is called valence band. Or the band having highest occupied band energy. It may be partial or completely filled.

Conduction band:

This is the lowest unfilled energy band. This is empty or partially filled.

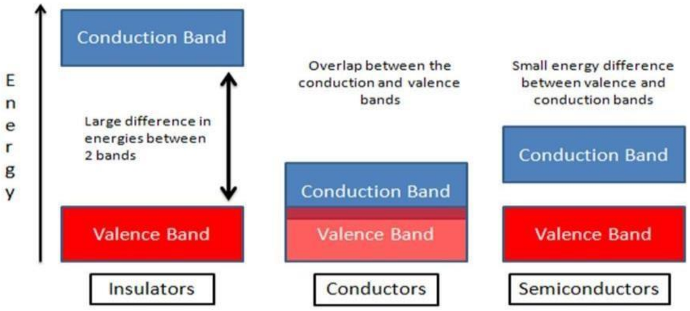
Forbidden Energy gap:

The conduction band and valence band are separated by a region or gap known as forbidden band. In this there is no electron exist.

CLASSIFICATION OF MATERIALS INTO CONDUCTORS, SEMICONDUCTORS AND INSULATORS:

INSULATOR:

In case of insulators the forbidden band is wide. Due to this free electrons cannot jump from valence band to conduction band. In insulators the energy gap between Valence and conduction band is of the order of 10eV.



CONDUCTORS:

In case of conductors there is no forbidden band the valence band and conduction band overlap each other. Here plenty of electrons are available for electronic conduction.

SEMICONDUCTORS:

In semiconductors there is small forbidden band exist between valence band and conduction band. In semiconductors forbidden band gap is between 0.7 to 1.1 eV. For semiconductors the electrical properties lie between insulators and good conductors.

EFFECTIVE MASS OF THE ELECTRON:

The effective mass of the electron is the mass of the electron when it is accelerated in a periodic potential and is denoted by m^*

When an electron is placed in a periodic potential and it is accelerated with the help of electric field. Then the mass of the electron is varied. That varied mass is called effective mass m^*.

Consider the free electron as a wave packet. The group velocity v_g corresponding to particle velocity is

$$v_g = \frac{d\omega}{dK}$$

Where K is wave vector and ω is angular velocity of the electron.

$$v_g = 2\pi \frac{d\nu}{dK} = \frac{2\pi}{h}\frac{dE}{dK} = \frac{1}{h}\frac{dE}{dK}$$

But acceleration $a = \frac{dv_g}{dt} = \frac{1}{h}\frac{d^2E}{dKdt} = \frac{1}{h}\frac{d^2E}{dK^2}\frac{dK}{dt}$

But $hK = p \Rightarrow \frac{dp}{dt} = h\frac{dK}{dt} = F$

$$\Rightarrow \frac{dK}{dt} = \frac{F}{h}$$

$$\therefore a = \frac{1}{h}\frac{d^2E}{dK^2}\frac{F}{h}$$

$$\Rightarrow F = \frac{h^2}{\frac{d^2E}{dK^2}}.a$$

But

$$m^* a = \frac{h^2}{\frac{d^2E}{dK^2}}.a \Rightarrow \boxed{m^* = \frac{h^2}{\frac{d^2E}{dK^2}}}$$

Special classes:

(1). If $\frac{d^2E}{dK^2}$ is positive then the effective mass is positive

(2) If $\frac{d^2E}{dK^2}$ is negative then the effective mass is negative.

(3) If $\frac{d^2E}{dK^2}$ =0 then the effective mass becomes ∞

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