Unit 1: Quantum and Band Theory of electron

Quantum Free Electron Theory

Outlines:

1. Classical free electron theory and its draw back
2. Quantum Free Electron Theory
3. Particle in box
4. Fermi Dirac Distribution function

Classical free electron theory and its draw back

Classical Model:

- The valence electrons in a solid are free to move anywhere in the metal in a way similar to gas molecules in a container. Therefore, the assembly of free electrons in a metal is called electron gas.

- The electrical and thermal conductivities of the metals is solely due to free electrons

- The electrons move randomly in all directions with random velocities following the classical Maxwell Boltzmann distribution. The average kinetic energy of a free electron is thus given by

$$E = \frac{3}{2} k_B T$$

- Unlike gas molecules, the free electrons move in a background of immobile positive ions.

- The free electrons make collisions from time to time with fixed positive ions. Between these collisions, the electron-ion interaction is neglected. This is called free electron approximation. Further electron-electron interaction is also neglected. This is called independent electron approximation

Classical free electron theory and its draw back

Classical Model: contd…

- Collisions in Drude model (1900), as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron.

- An electron experiences a collision with a probability per unit time 1/τ. This means that on the average an electron travels for time τ after it undergoes a collision and before its next collision i.e. the average time between two successive collisions is τ .This time is known as **relaxation time (τ).** The average distance traversed by a free electron between two successive collisions with positive ions is called the **mean free path (λ)**.

- In absence of external electric field, the random motion of free electrons is equally probable in all directions. As a result, there is no net current in the absence of electric field. When an external electric field is applied, the electrons are accelerated in a direction opposite to that of electric field. Hence they acquire an average velocity in a direction opposite to that of electric field which is superimposed over the random motion. This velocity is known as the **drift velocity (v_d).**

Prerequisite/Recapitulations

Drawbacks of classical free electron theory

- From the classical free electron theory the value of specific heat of metals is given by 4.5*R*, where '*R*' is called the universal gas constant. But the experimental value of specific heat is nearly equal to 3*R*.
- With help of this model we can't explain the electrical conductivity of semiconductors or insulators.
- The theoretical value of paramagnetic susceptibility is greater than the experimental value.
- Ferromagnetism cannot be explained by this theory.
- At low temperature, the electrical conductivity and the thermal conductivity vary in different ways. Therefore $K/\sigma T$ is not a constant. But in classical free electron theory, it is a constant in all temperature.
- The photoelectric effect, Compton effect and the black body radiation cannot be explained by the classical free electron theory.

Objectives

After the completion of this lecture you will be able to:

- Understand the quantum free electron theory
- Explain Quantum mechanical model of Electron gas in solid
- Understand the Fermi Dirac distribution function and its variation with temperature

Basic assumptions of Quantum free-electron theory

- The energy values of electrons are quantized as various allowed energy levels.
- The distribution of electrons in these allowed levels takes place according to *Pauli exclusion principle*
- The electrons are treated as fermions and obeys Fermi-Dirac statistics
- The potential due to lattice ions is taken to be constant throughout the metal.
- The attractive force between core and the electron and the repulsion between the electron and electron is ignored.
- The metal contains a large number of conduction electrons which are completely free yet are bound to the metal as a whole. Thus a metal is said to be consisting of electron gas.
- Free electrons in a metal can be described as free particles confined in a box of certain volume. The possible electronics states and the distribution of electrons in these states can thus be determined using quantum mechanics.

Wave Function

The quantity with which quantum mechanics is concerned is the **wave function Ψ** of a body. While itself has no physical interpretation, the square of its absolute magnitude $|\Psi|^2$ evaluated at a particular place at a particular time is proportional to the probability of finding the body there at that time. The linear momentum, angular momentum, and energy of the body are other quantities that can be established from . The problem of quantum mechanics is to determine Ψ for a body when its freedom of motion is limited by the action of external forces.

since $|\Psi|^2$ is proportional to the probability density P of finding the body described by , the integration of $|\Psi|^2$ over all space must be finite—the body is *somewhere,* after all.

Normalization condition

$$\int_{-\infty}^{\infty} |\Psi|^2 \, dV = 1$$

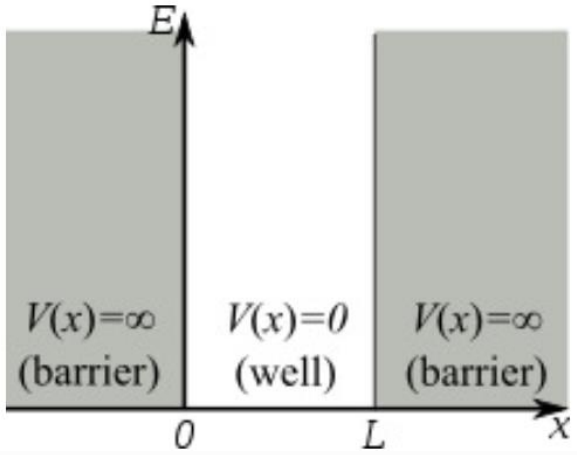
Well-Behaved Wave Functions

1 Ψ must be continuous and single-valued everywhere.
2 $\partial\Psi/\partial x$, $\partial\Psi/\partial y$, $\partial\Psi/\partial z$ must be continuous and single-valued everywhere.
3 Ψ must be normalizable, which means that Ψ must go to 0 as $x \to \pm\infty$, $y \to \pm\infty$, $z \to \pm\infty$ in order that $\int |\Psi|^2 \, dV$ over all space be a finite constant.

Free Electron Gas in One-Dimensional Box (Potential Well)

Consider an electron of mass 'm' which is bound to move in a one dimensional crystal of length 'L'. The electron is prevented from leaving the crystal by the presence of a large potential energy barrier at its surfaces.

Although the barriers extend over a few atomic layers near the surface, these are taken infinitely large for the sake of simplicity. The problem is identical to that of an electron moving in a one – dimensional potential box which is represented by a line and is bounded by infinite potential energy barriers as shown in figure



The potential energy within the crystal or box is assumed to be zero. Thus, we have

$V_{(x)} = 0$ for $o < x < L$

$V_{(x)} = \infty$ for $x \leq 0$ and $x \geq L$ ---------(1)

The wave function ψ_n of the electron occupying the nth state is determined from the solution of the Schrodinger equation, i.e.

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

Where E_n represents the kinetic energy of the electron in the nth state and V is its potential energy. Since V=0 inside the box Equation (2) becomes

$$\frac{d^2\psi_n}{dx^2} + \frac{2mE}{\hbar^2}\psi_n = 0 \text{ ----------} \quad (3)$$

Free Electron Gas in One-Dimensional Box

The general solution of this equation is

$$\psi_n = A\sin(kx) + B\cos(kx) \qquad \text{----------(4)}$$

Where A and B are arbitrary constants to be determined from the boundary conditions and k is given by

$$k = \sqrt{\frac{2mE_n}{\hbar^2}} \qquad (5)$$

The boundary conditions are, $\psi_n = 0$ when x = 0 and $\psi_n = 0$ when x = L

For x = 0 equation (4) gives B = 0 and the solution (4) becomes

$$\psi_n = A\sin(kx) \qquad (6)$$

Also $\psi_n = 0$ when x = L, therefore, equation (6) yields

$$A\sin(kx) = 0$$

Free Electron Gas in One-Dimensional Box

Since A cannot be zero as this will make the wave function zero everywhere. Therefore

$$\sin(kx) = 0\,; \text{ This gives } kx = \frac{n\pi}{L}$$

Where n = 1, 2, 3, 4, 5....Thus the expression (6) for the allowed wave function becomes

$$\psi_n = A\sin\left(\frac{n\pi}{L}\right)x \qquad (8)$$

The allowed energy can be obtained from equations (5) and (7) as

$$\boxed{E_n = \frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2} \qquad (9)$$

$$E_n \propto n^2$$

Free Electron Gas in One-Dimensional Box

For each value of n, there is an energy level and the corresponding wave function is given by equation (8). Each value of E_n is called an Eigen value and corresponding ψ_n is called Eigen function. Thus inside the box, the particle can only have the discrete energy values specified by equation (9). Note also that particle cannot have zero energy. The number n is called the quantum number. Hence energy spectrum consists of discrete energy levels where the spacing between the levels is determined by the values of n and L.

Expression for wave function:

It is certain that the particle is somewhere inside the box. The constant A in equation (8) is determined by using this information that the probability of finding an electron somewhere on the line is unity, i.e.

$$\int_0^L \psi_n^* \psi_n dx = 1$$

Expression for wave function

This is called as normalization condition. We get

$$A^2 \int_0^L \sin^2\left(\frac{n\pi}{L}x\right)dx = 1, \text{ or}$$

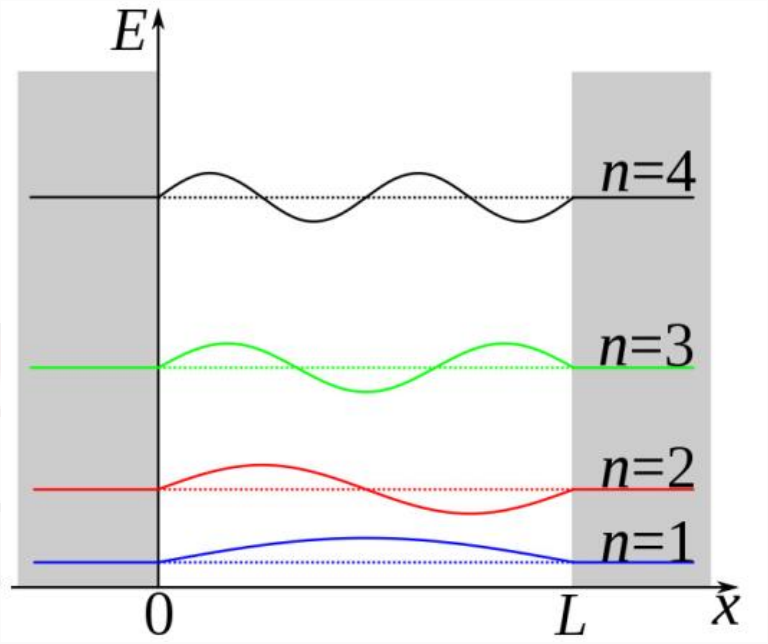
$$A^2 \int_0^L 1-\cos\left(\frac{2n\pi}{L}x\right)dx = 2, \text{ or } A^2 \int_0^L dx = 2, \text{ or}$$

$$A = \sqrt{\frac{2}{L}}$$

So, we get the normalized wave function as

$$\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi}{L}x\right)$$

The energy levels and the wave functions corresponding to n=1, 2, 3, and 4 are shown



Let us consider a situation when the electrons are moving inside a three dimensional potential box of side 'L'

$$\psi_n = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right)$$

the normalized wave function for cubical box becomes

$$E_n = \frac{h^2}{8mL^2}\left(n_x^{\,2} + n_y^{\,2} + n_z^{\,2}\right)$$

The corresponding form of energy is given by

$$\text{Or} \qquad E_n = \frac{h^2 n^2}{8mL^2} \quad \text{where}$$

$$n^2 = \left(n_x^{\,2} + n_y^{\,2} + n_z^{\,2}\right)$$

Thus in three dimensions, we have three quantum numbers nx, ny and nz which can take only positive integer values.
Thus each energy state is defined by a set of quantum numbers (nx, ny ,nz) and can contain a maximum of two electrons one spin up and other spin down in accordance to Pauli's exclusion principle.

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