Chapter

1 Theory of Metal

Elementary Quantum Mechanical Ideas

Quantum mechanics is the generalized form of mechanics applicable to very small object like electrons and nuclei of atoms. It can be applied large entities but most of the large system are well described by the much simpler classical mechanics. Quantum mechanics deals with the mathematical description of the motion and interaction of elementary particles, incorporating the concepts of quantization of energy, wave particle duality, the uncertainty principle and the correspondence principle. In fact, phenomena which occur on a very small (atomic or sub atomic) scale cannot be explained outside the frame work of quantum physics. For example, the existence and properties of atoms, the chemical bond and the propagation of an electron in a crystal cannot be understood by classical physics. Even when we are concerned only with macroscopic physical objects it is necessary to study the behaviour of their constituent atoms, ions, electrons in order to arrive at a complete scientific description.

It can be said that quantum mechanics is the basis of our present understanding of all natural phenomena.

Wave Particle Duality: de-Broglie's Equation

The successful explanation of Compton Effect, Photoelectric effect and Black body radiation shows that electromagnetic radiation travels not only in the form of continuous stream of energy but in the form of tiny packets or bundles of energy. These packets of energy were called "*quanta*" (singular form - quantum). For electro magnetic radiation these were called "*photon*".

On the other hand the phenomena like Interference, Diffraction and Polarization cannot be explained unless wave nature of electro magnetic radiation is assumed.

It was discovered that particles of atomic dimensions some times behave more like waves than discrete particles. It was also observed that electromagnetic waves eg. x -rays, gamma rays, visible light etc sometimes exhibit properties similar to properties of discrete particles of matter.

Louis de- Broglie in 1924 suggested his hypothesis that there is wave - particle dualism. The wave associated with material particles is called "matter waves".

To show the wave particle dualism he made the use of Planck's theory of quantum radiation and Einstein's theory of relativity.

According the Planck's theory of quantum radiation energy of photon is given by.

$$E = hf = \frac{hc}{\lambda} \qquad ...(1)$$

Where, c = velocity of electromagnetic radiation

h = 6.62×10^{-34} JS is the Planck's constant

f = frequency of em radiation

Again from Einstein's mass energy relationship, Energy of photon is given by

$$E = mc^2 \qquad ...(2)$$

Comparing (1) and (2)

$$\frac{hc}{\lambda} = mc^2$$

$$\lambda = \frac{h}{mc} = \frac{h}{p} \text{ [where } p = mc = \text{momentum of photon]}$$

According to de-Broglie, the wave length 'λ' of the wave associated with a moving particle having momentum p = mv, is given by

$$\lambda = \frac{h}{mv} \qquad ...(3)$$

Experiment (1): [particle showing wave nature]

It is observed that beam of electrons can diffracted from a crystal in a manner similar to the diffraction of x-rays, which are electro magnetic waves.

If an electron of mass 'm' is accelerated through the potential 'V' and velocity 'v' then

$$\frac{1}{2}mv^2 = eV$$

$$v = \sqrt{\frac{2eV}{m}}$$

Therefore, $\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}$

The wave associated with this wave length is called de-Broglie electron wave.

Experiment: 2 [Wave showing particle nature]

When a beam of electro magnetic radiation is incident an a solid or gas, it ejects electron from the material. For each material a characteristic energy called the work function is required to remove electrons from the material. It is given by. $\phi = hf$.

Comparison of this equation with E = hf indicates that electro magnetic radiation behaves like particles.

Quantum mechanics does not distinguish between wave and particles. Although it can predict circumstances for which one type of behavior will dominate.

Wave Function

In quantum mechanics there exists an expression in the form of equation that is used to represent wave - particle duality called wave function (ψ).

A simple harmonic wave is represented by the equation $y = a \sin(\omega t - kx)$. In such type of wave motion there is only the transfer of energy. But incase of matter wave, there is transfer of momentum (particle) in addition to the energy. The suitable function to represent wave function for matter wave is.

$$\psi(x, t) = Ae^{-i(\omega t - kx)} \qquad \ldots (1)$$

Where A is called normalizing constant

$$\text{Since, } E = hf = \frac{h}{2\pi} \cdot 2\pi f = \hbar\omega$$

$$\Rightarrow \omega = \frac{E}{\hbar}$$

$$\text{And } P = \frac{h}{\lambda} = \frac{h}{2\pi} \frac{2\pi}{\lambda} = \hbar k$$

$$\Rightarrow k = \frac{P}{\hbar}$$

Therefore, equation (1) can also be represented as

$$\psi(x, t) = Ae^{-i/\hbar (Et - Px)} \qquad \ldots (2)$$

The wave function ψ has no meaning in itself. When it is operated by Schrödinger wave equation, it describes the motion of the particle associated with it as done by second law of motion in classical mechanics.

In quantum mechanics, energy, momentum and position of the particle are called observables and the wave function ψ is used to describe these observables.

The only quantity having the physical meaning is the square of its magnitude. The quantity $p = \psi\psi^* = |\psi|^2$ evaluated at a particular point at a particular time is proportional to the probability of finding the particle at that time. [Here, ψ^* is the complex conjugate of ψ]

The probability of finding a particle in the volume element dx dy dz is $|\psi|^2$ dx dy dz or $|\psi|^2$ dv.

Since the total probability of finding the particle in the entire space is unity.

$$\int |\psi|^2 \, dv = 1 \qquad \ldots (3)$$

The wave function satisfying this condition is called *normalized wave function.* Every acceptable wave function can be normalized by multiplying it with an appropriate constant called *normalizing constant.*

Characteristics of wave function

1. It must be normalized
2. It must be single valued and continuous
3. If $\psi_1(x)$, $\psi_2(x)$ ..... $\psi_n(x)$ are the solution of Schrödinger wave equation, then their linear combination $\psi(x) = a_1\psi_1(x) + a_2\psi_2(x) + ... + a_n\psi_n(x)$ must be solution of Schrödinger wave equation.
4. The wave function $\psi(x)$ must approaches zero as $x \rightarrow \pm\infty$

Schrödinger Wave Equation

Time Independent Schrödinger Wave Equation

Schrödinger wave equation describes the motion of quantum mechanical particle as Newton's second law in classical mechanics. It has been observed that in many situations, potential (V) acting on the particle does not depend upon time and varies only with its position only. For such conditions time independent form of Schrödinger's equation is applicable.

The wave function associated with quantum mechanical particle is given by

$$\psi = A\, e^{-i(\omega t - kx)} = A\, e^{-i/\hbar\,(Et - Px)}$$

Differentiating with respect to x.

$$\frac{d\psi}{dx} = \left(-\frac{i}{\hbar}\right)(-P)\, Ae^{\frac{-i}{\hbar}(Et - Px)}$$

$$= \frac{iP}{\hbar}\psi$$

Again differentiating with respect to x.

$$\frac{d^2\psi}{dx^2} = \left(\frac{iP}{\hbar}\right)^2\psi$$

$$\frac{d^2\psi}{dx^2} = \frac{-P^2}{\hbar^2}\psi$$

$$\Rightarrow P^2\psi = -\hbar^2\frac{d^2\psi}{dx^2} \qquad ...(1)$$

The total energy of a particle is given by, E = KE + PE

$$E = \frac{1}{2}mv^2 + V = \frac{1}{2}\frac{(mv)^2}{m} + V = \frac{P^2}{2m} + V$$

$$E = \frac{P^2}{2m} + V$$

Multiplying both sides by ψ

$$\left(\frac{P^2}{2m} + V\right)\psi = E\psi$$

$$\frac{P^2\psi}{2m} + V\psi = E\psi$$

Using equation (1)

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\,\psi = E\psi \qquad ...(2)$$

$$\frac{d^2\psi}{dx^2} + \frac{2m\,(E-V)}{\hbar^2}\,\psi = 0 \qquad ...(3)$$

This is the *time independent Schrödinger wave equation.*

In three dimensions it can be expressed as

$$\nabla^2\psi + \frac{2m\,(E - V)}{\hbar^2}\,\psi = 0 \;...(4)$$

Where, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is called Laplacian operator.

The equation (2) is

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi$$

$$\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V\right)\psi = E\psi$$

The Hamiltonian operator is given by, $\hat{H} = \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]$

Therefore time independent Schrödinger wave equation takes the form,

$$\hat{H}\psi = E\,\psi \qquad ...(5)$$

Time Dependent Schrödinger Wave Equation

The wave function associated with matter wave is

$$\psi = Ae^{-i/\hbar\,(Et - Px)}$$

Differentiating with respect to x, $\frac{d\psi}{dx} = \left(\frac{-i}{\hbar}\right)(-P)\,\psi = \frac{iP}{\hbar}\,\psi$

Again differentiating with respect to x,

$$\frac{d^2\psi}{dx^2} = \left(\frac{iP}{\hbar}\right)^2\psi = -\frac{P^2}{\hbar^2}\,\psi$$

$$\Rightarrow P^2\psi = -\hbar^2\frac{d^2\psi}{dx^2} \qquad ...(1)$$

Now, differentiating ψ with respect to t,

$$\frac{d\psi}{dt} = \frac{-iE}{\hbar}\psi \Rightarrow E\psi = \frac{-\hbar}{i}\frac{d\psi}{dt} = \frac{i^2\hbar}{i}\frac{d\psi}{dt}$$

Therefore, $E\psi = i\hbar\frac{d\psi}{dt}$ ...(2)

The total energy of a particle is given by, E = K.E. + P.E.

$$E = \frac{P^2}{2m} + V$$

Multiplying both sides by ψ,

$$E\psi = \frac{P^2\psi}{2m} + V\psi$$

Using equations (1) and (2)

$$i\hbar\frac{d\psi}{dt} = \frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi \quad ...(3)$$

This is the time dependent Schrödinger wave equation

Equation (3) can be re-written as

$$\frac{-\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = i\hbar\frac{d\psi}{dt}$$

The Hamiltonian operator is given by, $\hat{H} = \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]$

Therefore time dependent Schrödinger wave equation takes the form

$$\hat{H}\psi = i\hbar\frac{d\psi}{dt} \quad ...(4)$$

Applications of Schrödinger Wave Equation

Energy Well Model of Metal

(A particle confined in a one dimensional infinitely deep potential well)

Consider a particle (electron) restricted to move along the x-axis between x = 0 and x = L. The potential energy V of the particle is zero inside the box, but rises to infinity on the outside.

i.e. $V = 0$ for $0 < x < L$

$V = \infty$ for $x < 0$ and $x > L$

The Schrödinger wave equation for the particle with in the box is

$$\frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2}\psi = 0$$

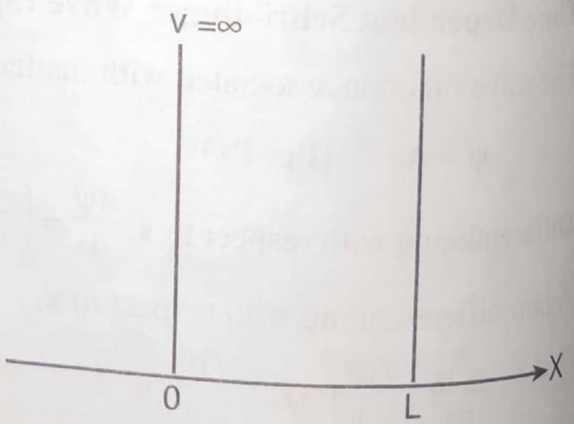

Figure 1: Electron in an infinite potential well

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \qquad ...(1)$$

Where, $k^2 = \frac{2mE}{\hbar^2} \qquad ...(2)$

The solution of equation (1) is,

$$\psi(x) = A \sin kx + B \cos kx \quad ...(3)$$

Where A and B are constants to be determined using boundary condition.

Since the particle cannot have infinite energy, it cannot exist outside the box. Therefore, the wave function ψ must be zero outside the box, so ψ must be zero at the walls i.e. at $x = 0$ and $x = L$

$$\psi(x) = 0 \text{ at } x = 0$$

From equation (3), $0 = 0 + B \Rightarrow B = 0$

From equation (3), $\psi(x) = A \sin k x$

Again, $\psi(x) = 0$ at $x = L$

$$0 = A \sin kL$$

$$\sin kL = 0$$

$$\sin kL = \sin n\pi,\ n = 0, 1, 2, 3, \ldots\ldots$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \qquad ...(4)$$

From equation (2) and (4), $\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2} \qquad ...(5)$$

This means the energy of particle in potential well is quantized. Each value of energy given by equation (5) is called eigen value and corresponding function ψ_n are called eigen functions.

Now substituting, $B = 0$ and $K = n\pi/L$ in equation (3), the allowed solution of Schrödinger equation are

$$\psi_n(x) = A \sin \frac{n\pi x}{L}$$

The coefficient A is called *Normalizing constant* and can be determined using Normalizing condition.

$$\int_0^L \psi\psi^* \, dx = 1$$

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

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

$$A^2 . \left[\frac{1}{2}\int_0^L dx - \frac{1}{2}\int_0^L \cos\frac{2n\pi x}{L} dx\right] = 1$$

$$A^2\left[\frac{L}{2} - 0\right] = 1$$

$$A^2 . \frac{L}{2} = 1$$

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

Hence, the Normalized wave function of the electron is

$$\psi_n = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$$

The first four eigen functions ψ_1, ψ_2, ψ_3 and ψ_4 together with the probability densities $(\psi_1)^2$, $(\psi_2)^2$, $(\psi_3)^2$ and $(\psi_4)^2$ are shown in figure below.

It is obvious that the Quantum mechanical result is very different from the classical result. Classical mechanics predicts the same probability for the particle being any where in the box. But quantum mechanics predicts that the probability is different at different point.

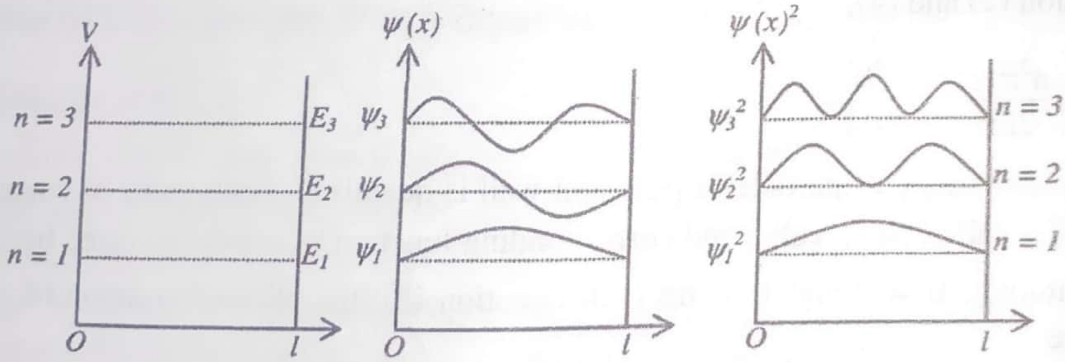

Figure 2: The energy eigen values, wave functions and probability distribution functions for an electron in an infinite potential well

For, particle in an infinite potential well the minimum energy that the electron possesses can be calculated by Heisenberg's uncertainty principle.

The particle is confined in potential well of width L, this means uncertainty in position is L, i.e. $\Delta x = L$

And the particle have momentum $+P_x$ while moving in +ve x direction and $-P_x$ while moving in -ve x direction.

Therefore, uncertainty in momentum, $\Delta Px = Px - (-Px) = 2Px = 2\hbar k$ for ground state, $K = \frac{n\pi}{L} = \frac{\pi}{L}$ for n = 1

Therefore, $\Delta P_x . \Delta x = 2\hbar k. L = 2. \frac{h}{2\pi} . \frac{\pi}{L} . L = h$

$$\Delta P_x . \Delta x = h \qquad ...(6)$$

Again, substituting the value of ΔP_x and Δx in equation (6)

$$2P_x. L = h \Rightarrow P_x = \frac{h}{2L}$$

The potential energy of electron inside the well is zero. Hence the total energy is given by

$$E = \frac{1}{2} mv^2 = \frac{P^2}{2m}$$

$$E = \frac{1}{2m}\left(\frac{h}{2L}\right)^2 = \frac{h^2}{8mL^2}$$

$$\left[E = \frac{h^2}{8mL^2}\right]$$

Tunneling Phenomena: Finite Potential Barrier

To understand tunneling phenomena, consider an example of roller coaster as shown in figure (1). When the roller coaster is released from rest at a height A, the conservation of energy means that the carriage can reach B at most C but certainly not beyond C and definitely not D and E. Classically there is no possible way that carriage will reach E. An extra energy of D-A is needed. Ignoring the frictional losses, the roller coaster will go back and forth between A and C.

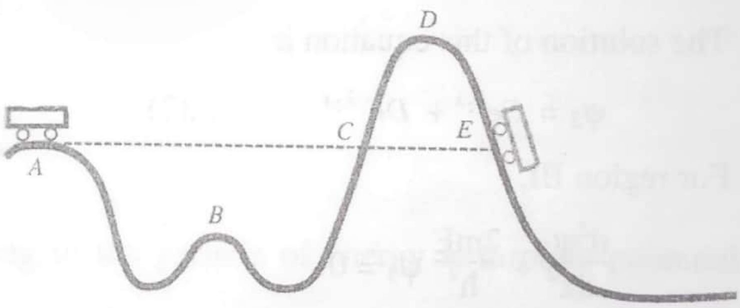

Figure 1: Path of roller coaster movement

Consider an analogous event on an atomic scale, when an electron of energy E is incident on the barrier of height 'V' which is greater than E. Classically region II and region III are forbidden to particle. How ever quantum mechanics predicts finite probability of finding the particle in region III. This effect of quantum mechanical particle is called "*quantum leak*" or "*barrier tunneling*". Remember except in the region of infinite potential (where $\psi = 0$), there will always be a solution $\psi(x)$ and there always will be some probability of finding the electron.

The potential function for the particle can be expressed as

$$V(x) = 0 \text{ for } x < 0 \text{ (for region I)}$$

$$V(x) = V \text{ for } 0 < x < l \text{ (for region - II)}$$

$V(x) = 0$ for $x > l$ (for region III)

The Schrödinger wave equation and their solutions for these regions are as follows.

For region I:

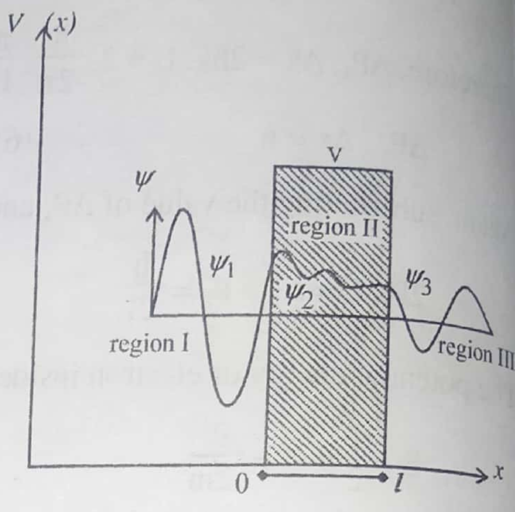

Figure 2: Electron wave functions in different regions

$$\frac{d^2\psi_1}{dx^2} + \frac{2mE}{\hbar^2}\psi_1 = 0$$

$$\frac{d^2\psi_1}{dx^2} + k_1^2\psi_1 = 0$$

where $k_1^2 = \frac{2mE}{\hbar^2}$

and the solution of this equation is,

$$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x} \qquad ...(1)$$

For region II,

$$\frac{d^2\psi_2}{dx^2} + \frac{2m(E-V)}{\hbar^2}\psi_2 = 0$$

$$\frac{d^2\psi_2}{dx^2} - \frac{2m\,(V-E)}{\hbar^2}\psi_2 = 0$$

$$\frac{d^2\psi_2}{dx^2} - k_2^2\psi_2 = 0, \text{ where } k_2^2 = \frac{2m\,(V-E)}{\hbar^2}$$

The solution of this equation is

$$\psi_2 = Ce^{k_2x} + De^{-k_2x} \qquad ...(2)$$

For region III,

$$\frac{d^2\psi_3}{dx^2} + \frac{2mE}{\hbar^2}\psi_3 = 0$$

$$\frac{d^2\psi_3}{dx^2} + k_1^2\,\psi_3 = 0 \text{ where } k_1^2 = \frac{2mE}{\hbar^2}$$

The solution of this equation is,

$$\psi_3 = Fe^{ik_1x} + Ge^{-ik_1x}$$

Since there is no reflected wave in region (III) so, $G = 0$

Therefore, $\psi_3 = Fe^{ik_1x}$ ...(3)

Using boundary condition at $x = 0$

$$\psi_1|_{x=0} = \psi_2|_{x=0}$$

$$A + B = C + D \qquad ...(4)$$

And $\psi'_1|_{x=0} = \psi'_2|_{x=0}$

$$ik_1A - ik_1B = k_2C - k_2D \qquad ...(5)$$

Again, using boundary conditions at x = l

$$\psi_2|_{x=l} = \psi_3|_{x=l}$$

$$Ce^{k_2 l} + De^{-k_2 l} = Fe^{ik_1 l} \quad ...(6)$$

And $\psi'_2|_{x=l} = \psi'_3|_{x=l}$

$$Ck_2e^{k_2 l} - Dk_2e^{-k_2 l} = ik_1Fe^{ik_1 l} \quad ...(7)$$

Solving equations (4), (5), (6) and (7) we get transmission probability or transmission coefficient as

$$T = \left|\frac{F}{A}\right|^2 = \frac{4E\,(V - E)}{4E\,(V - E) + V^2 \sin h^2 k_2 l} \quad ...(8)$$

If the width and height of potential are very large, the term 4E (V - E) in the denominator of equation (8) can be neglected in comparison to $V^2 \sin h^2 k_2 l$.

Also, $\sin h\, k_2 l = \dfrac{e^{k_2 l} - e^{-k_2 l}}{2} \approx \dfrac{e^{k_2 l}}{2}$ for large l

Therefore equation (8) can be written as.

$$T = \frac{4E\,(V - E)}{V^2\left(\dfrac{ek_2 l}{2}\right)^2}$$

$$\therefore T = \frac{16\,E\,(V - E)}{V^2}\, e^{-2k_2 l} \quad ...(9)$$

Where, $k_2 = \sqrt{\dfrac{2m\,(V\text{-}E)}{\hbar^2}}$

Equation (9) gives the probability of tunneling of the particle of energy E through potential barrier of width 'l' and height V.

This is the superiority of quantum mechanics over the classical mechanics which shows that there is finite probability of emission of electron (β-emission) from the nucleus of an atom even the electron has lower energy than the energy by which it is bounded.

The reflection coefficient or the probability of reflection of the particle at the barrier is given by.

$$R = \left|\frac{B}{A}\right|^2 = 1 - T$$

Heisenberg's Uncertainty Principle

A free electron corresponds to single wave length. This means the wave associated with free electron have single wave length. So the probability distribution function is uniform throughout the whole space. The electron can be found every where. This means the uncertainty in position of electron is infinite. At the same time the electron has a fixed well - defined wave length, which gives the exact value of momentum of particle. This corresponds to uncertainty in momentum being zero.

Heisenberg uncertainty principle states that "It is impossible to determine precisely and simultaneously the value of both members of physical variables which describe the motion of an atomic system". Such pairs of variables are called canonically conjugate variables. For example the position co-ordinate and momentum co-ordinate, energy and time, the angular momentum and angular position.

Let, Δx and ΔP_x are the uncertainty in measurement of position and momentum then, $\Delta x.\ \Delta Px \geq \hbar$

Similarly, $\Delta E.\ \Delta t \geq \hbar$

And $\Delta J.\ \Delta\theta \geq \hbar$

Where,

ΔE = Uncertainty in energy

Δt = uncertainty in time

ΔJ = uncertainty in angular momentum

$\Delta\theta$ = uncertainty in angular position

If the position co-ordinate x of a particle in motion is accurately determined at some instant so that $\Delta x = 0$, then at the same instant the uncertainty ΔP_x in determination of the momentum becomes infinite and vice-versa.

Similarly, in all of the above cases, if one quantity is measured accurately, the measurement in the other quantity becomes less accurate.

Application of Uncertainty Principle

The uncertainty principle can explain a large number of facts.

1. Non existence of electrons and existence of proton and neutron in nucleus.
2. Calculation of binding energy of an electron in an atom.
3. Determination of radius of hydrogen atom.
4. Determination of finite width of spectral lines.
5. To study the strength of nuclear force and stability of the atom.

Operator Notation

An equation of the form, $\hat{A}\,\psi = a\psi$ is called eigen value equation.

Here $\hat{A}$ is an operator

ψ is called eigen function

And 'a' is called eigen value.

An operator is a function over a space of physical states to another space of physical states. The operators must yield real eigen values, since they are values which may come up as the result of the experiment.

We have the wave function associated with quantum mechanical particle as:

$$\psi = A \exp\left(\frac{-i}{\hbar}(Et - Px)\right)$$

Differentiating with respect to 't'

$$\frac{\partial\psi}{\partial t} = \frac{-i}{\hbar} E\psi$$

$$E\psi = \frac{-\hbar}{i}\frac{\partial\psi}{\partial t}$$

$$E\psi = i\hbar\frac{\partial\psi}{\partial t}$$

$\hat{E} \rightarrow i\hbar\frac{\partial}{\partial t}$ is called Energy operator

Again differentiating ψ with respect to 'x'

$$\frac{\partial\psi}{\partial x} = \left(\frac{-i}{\hbar}\right)(-P)\psi = \frac{iP}{\hbar}\psi$$

$$P\psi = \frac{\hbar}{i}\frac{\partial\psi}{\partial \pi} = \frac{-i^2\hbar}{i}\frac{\partial\psi}{\partial x}$$

$\hat{P} \rightarrow -i\hbar\frac{\partial}{\partial x}$ is called momentum operator.

Similarly, $\hat{x} \rightarrow x$ is called position operator. All these operators are used to predict the respective parameters i.e. energy, momentum and position of the electron.

Expected Value

In quantum mechanics, the expectation value is the probabilistic expected value of the result (measurement) of an experiment. It is not the most probable value of a measurement; indeed expectation value may have zero probability of occurring.

For the position x, the expectation value is defined as

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x}\,\psi\,dx$$

$\hat{x} \rightarrow$ Position operator

This integral can be interpreted as the average value of x that we would expect to obtain from a large number of measurements. Alternatively it could be viewed as the average value of position for a large number of particles which are described by same wave function.

Similarly, expectation value for momentum is

$$<P> = \int_{-\infty}^{\infty} \psi^* \hat{P} \psi \, dx$$

$\hat{P} \rightarrow$ Momentum operator

In general, the expectation value for any observable quantity is found by putting the quantum the quantum mechanical operator for that observable in the integral of the wave function over space.

$$<G> = \int_{-\infty}^{\infty} \psi^* G_{operator} \psi \, dx$$

Note: Observable $\rightarrow$ any quantity that can be measured in physical experiment.

Pauli Exclusion Principle

It states that no two electrons within a given system may have all four identical quantum numbers n, l, m_l, and m_s. Each set of values of n, l, m_l, and m_s represent a possible electronic state and correspondingly a wave function ψ_{n,l,m_l,m_s}, where, n = principal quantum number, l = orbital angular quantum number, m_l = magnetic quantum number, m_s = spin magnetic quantum number.

Free Electron Theory of Metal

The free electron model is a simple model for the behaviour of valance electrons in a metallic solid. The metal form unique type of bonding known as metallic bonding and form lattice structure. In Ionic bonding and covalent bonding there is sharing of electrons between two atoms and the electrons remain localized where as in metallic bonding the bond is formed among all the atoms in the lattice and the free electrons from the each atom is shared by the whole lattice. These free electrons move freely throughout the lattice and hence are termed as electron gas. Neglecting the electron-electron interaction and the electron-ion interaction, it appears as ideal gas in a container.

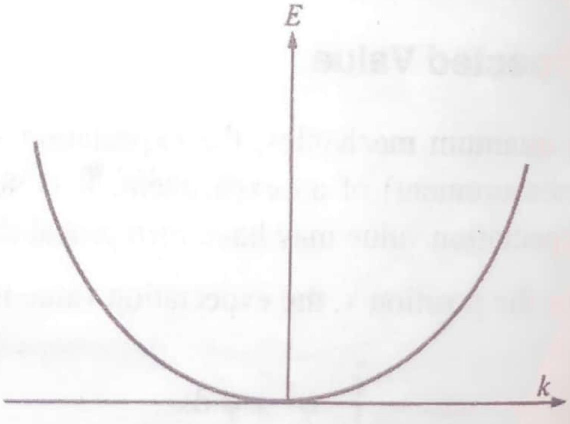

Figure : E-k diagram of free electron in metal

The cohesion in metallic crystal is due to the positive ion core and negative electrons passing between these ions. This is the reason for metallic bonds being weaker than ionic and covalent bonds. This indicates to ductile nature of metal.

According to this theory, the outer most electrons or valence electrons of an atom in metal are very loosely attached to the parent atom. These electrons are free to move throughout the metal.

So, if the electron has kinetic energy only.

$$E = \frac{1}{2}mv^2 = \frac{1}{2m}m^2v^2 = \frac{P^2}{2m}$$

$$\therefore E = \frac{\hbar^2k^2}{2m} \quad ..(1)$$

This equation represents the kinetic energy of the free electron with in the metal.

Equation (1) shows that the relationship between E and K is parabolic in nature as shown in figure.

Electron in Linear Solid (Metal)

Consider a copper wire of length L. There are many free electrons with in the copper rod. The wave length exhibited by electron in the wire depends upon kinetic energy.

For maximum wave length the kinetic energy of electron will be smallest and K.E. will progressively increases as the wave length decreases.

So, for greatest wavelength or minimum kinetic energy

$$L = \frac{\lambda}{2} \Rightarrow \lambda = 2L$$

Similarly for smaller wave length or larger value of kinetic energies, the relationship between length of wire and wave length of electron is given by

$$L = \frac{2\lambda}{2} \Rightarrow \lambda = \frac{2L}{2}$$

$$L = \frac{3\lambda}{2} \Rightarrow \lambda = \frac{2L}{3}$$

And so on up to n

$$L = n\frac{\lambda}{2} \Rightarrow \lambda = \frac{2L}{n}$$

for wave length in terms of length of wire, we will get

$$\lambda = 2L, \frac{2L}{2}, \frac{2L}{3}, \ldots\ldots \frac{2L}{n} \quad ...(1)$$

Here λ is decreasing so according to relation, $E = \frac{\hbar^2k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{\lambda}\right)^2$, kinetic energy is increasing.

Wave length and wave number are related as.

$$k = \frac{2\pi}{\lambda} \qquad \text{...(2)}$$

Substituting the value of wave length from equation (1), we will get,

$$k = \frac{2\pi}{\left(\frac{2L}{1}\right)}, \frac{2\pi}{\left(\frac{2L}{2}\right)}, \frac{2\pi}{\left(\frac{2L}{3}\right)} \ldots\ldots\ldots \frac{2\pi}{\left(\frac{2L}{n}\right)}$$

$$\text{or } k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \ldots\ldots\ldots \frac{n\pi}{L} \qquad \text{...(3)}$$

In normal condition, a solid is electrically neutral with no net flow of electrons in any direction. This means a free electron having a velocity in one direction must be matched by similar electron having same velocity in opposite direction. Since the velocity is related to momentum and momentum related to wave number. So wave number must have both positive and negative values.

$$\text{i.e. } k = \pm\frac{\pi}{L}, \pm\frac{2\pi}{L}, \pm\frac{3\pi}{L} \ldots\ldots\ldots \pm\frac{n\pi}{L} \qquad \text{...(4)}$$

$$\text{In general, } k = \pm\frac{n\pi}{L}, n = 1, 2, 3, 4, 5, 6, . \qquad \text{...(5)}$$

$$\text{We have, } E = \frac{\hbar^2k^2}{2m} \qquad \text{...(6)}$$

Using equation (5) in (6) we will get

$$E = \frac{n\pi^2\hbar^2}{2mL^2} \qquad \text{...(7)}$$

Degenerate States

Two or more different states of quantum mechanical system are said to be degenerate states if they give same value of energy upon measurement.

In a single dimension solid and for one dimensional potential well the energy of electron is expressed as.

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

In three dimension, $n^2 = n_x^2 + n_y^2 + n_z^2$

$$E_n = \frac{(n_x^2 + n_y^2 + n_z^2)\,\pi^2 \hbar^2}{2mL^2}$$

Where as in the earlier cases, n_x, n_y and n_z can only be integers i.e. 1, 2, 3, 4........

The set of values of n along different axes in three dimensional case will determine the energy associated with electron. Unlike in single dimension, the same n along x axis can represent different energies because this energy not only depends upon principle quantum number along x-axis but also upon along y-axis and z-axis. These degenerate states are all equally probable of being filled. The number of such states gives the degeneracy of particular energy level. For example (n_x, n_y, n_z) = (1,1, 2), (1, 2, 1,) and (2, 1, 1,) represent the same electron energy. These all three states are degenerate states.

Fermi Energy

In metal, Fermi energy is defined as the energy of highest filled energy level at temperature of absolute zero i.e. 0K. All the energy level up to Fermi level are filled at 0K and empty above it.

A Fermi gas is an ensemble of a large number of *fermions*. Fermions are the particles that obey Fermi-Dirac statistics. Free electrons inside a metallic conductor behave like an electron gas and obey Fermi-Dirac statistics.

If N is the total number of electrons to be accommodated on the line then for even N, because of Pauli exclusion principle, $n_f = \frac{N}{2}$.

Where n_f represents principal quantum number of the Fermi level i.e. number of top most filled level.

As, electron energy in linear solid metal is

$$E = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

For $n = n_f$ the Fermi energy is

$$E_f = \frac{n_f^2\pi^2\hbar^2}{2mL^2} = \frac{\hbar^2}{2m}\left(\frac{n_f\pi}{L}\right)^2$$

$$E_f = \frac{\hbar^2 k_f^2}{2m} \qquad ...(1)$$

Where $k_f = \left(\frac{n_f\pi}{L}\right)^2$ is the Fermi wave vector. And the sphere of radius k_f in E- k space is called Fermi sphere.

Equation (1) shows that E-k curve is parabolic as shown in figure.

At T = 0K, the electrons occupy the lowest quantum states to save energy. In other words, the quantum states $E \leq E_f$ are occupied while the states with $E > E_f$ are empty.

Since, $E_f = \frac{\hbar^2 k_f^2}{2m}$, this means the states with momentum. $k \leq k_f$ are occupied and states with $k > k_f$ are empty. In other words, in the k-space the occupied states form a sphere with radius k_f. This sphere is known as Fermi sphere (or the Fermi Sea).

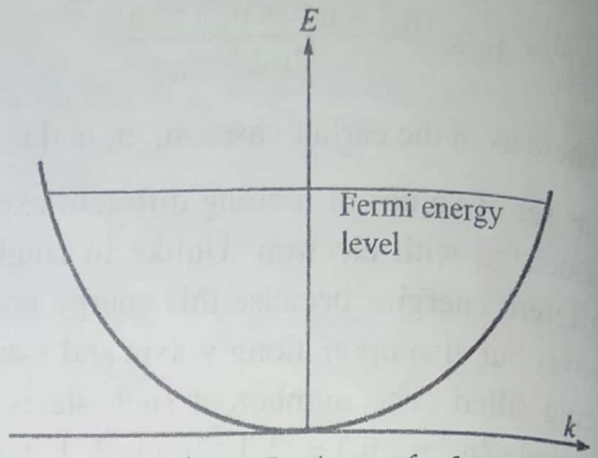

Figure : Fermi energy level

The total volume of the Fermi sphere is $\frac{4\pi}{3} k_F^3$.

Each quantum state occupies the volume $\left(\frac{2\pi}{L}\right)^3$, which comes from uncertainty relation.

So the total number of quantum states = $\dfrac{\frac{4\pi k_F^3}{3}}{\left(\frac{2\pi}{L}\right)^3} = \frac{Vk_F^3}{6\pi^2}$. [Here, $V = L^3$]

There are two electrons per state (because we have electrons with spin up and spin down). So the total number of occupied electrons in the sphere is.

$$N = 2 \times \frac{V k_F^3}{6\pi^2} = \frac{V k_F^3}{3\pi^2} \quad ...(2)$$

$$\Rightarrow k_F = \left(3\pi^2 \frac{N}{V}\right)^{1/3} \quad ... (3)$$

Thus k_F depends upon particle concentration i.e. number of electrons per unit volume.

$$\text{Fermi energy, } E_F = \frac{\hbar^2 k_F^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{3\pi^2 n}{V}\right)^{2/3} \quad ...(4)$$

This shows that E_f does not depend upon temperature and number of electrons but depends upon N/V only. As a result the Fermi energy does not change when two identical metals are joined together (since N/V is same)

If v_f is the velocity of the electron at the Fermi surface then,

$$mv_f = \hbar k_f$$

$$v_f = \frac{\hbar k_f}{m} = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad ... (5)$$

Density of States

The density of states function can be defined as number of electronic energy states per unit energy range. A high value of density of states function at a specific energy level means that there are many states available for occupation. A zero value of density of state function means that no states can be occupied at that energy level.

Density of states, $Z(E) = \frac{dN}{dE}$ ...(1)

We have $E = \frac{n^2\pi^2\hbar^2}{2mL^2} = \frac{n^2\pi^2}{2mL^2}\left(\frac{h}{2\pi}\right)^2 = \frac{n^2h^2}{8mL^2}$

$$n = \left(\frac{8mL^2E}{h^2}\right)^{1/2} \quad ...(2)$$

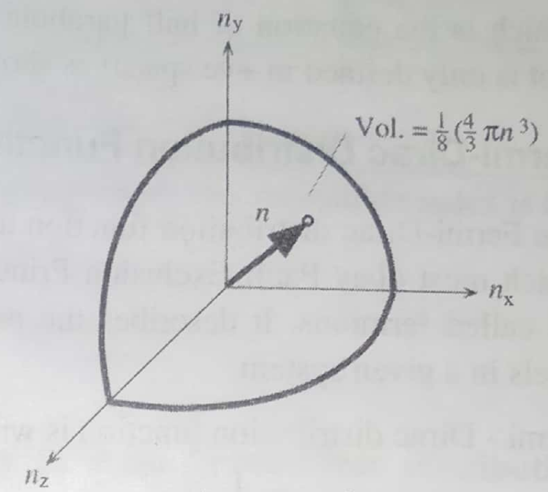

Figure 1: n-sphere

In three dimensional quantum space, n^2 can be written as, $n^2 = n_x^2 + n_y^2 + n_z^2$. A large number of states are associated with different value of n_x, n_y, n_z. for each set of quantum numbers n_x, n_y and n_z there exist a specific energy level called energy state. All these states lies with in the sphere of radius n. The principle quantum number n can take positive integers values only so the energy states are defined only in positive octant ($\frac{1}{8}$ th equal part of a sphere → octant) of the sphere made by the radius vector n.

So the number of energy states with in the sphere of radius n is given by,

$$N = \frac{1}{8}\frac{4\pi}{3}n^3 \quad ...(3)$$

Using equation (2) in (3)

$$N = \frac{1}{8}\frac{4\pi}{3}\left[\frac{8mL^2E}{h^2}\right]^{3/2}$$

$$N = \frac{\pi L^3}{6h^3}(8m)^{3/2}E^{3/2}$$

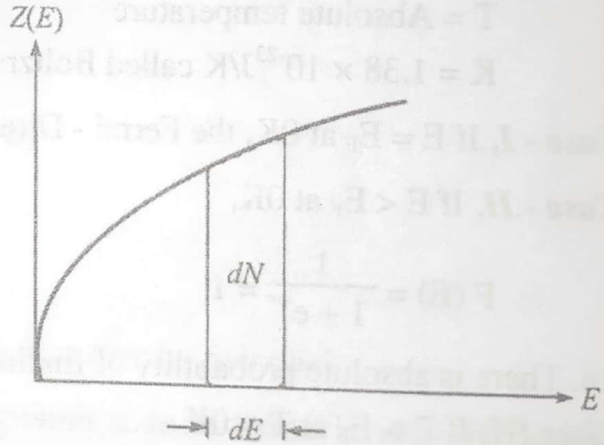

Figure 2: Density of states versus energy function

For an electron placed in three dimensional potential box with each side equal to L, the volume of the box is $V=L^3$.

$$N = \frac{\pi L^3}{6h^3}(2^2.\,2m)^{3/2}E^{3/2} = \frac{\pi L^3}{6h^3}2^3.\,(2m)^{3/2}E^{3/2}$$

$$N = \frac{4\pi V}{3h^3}(2m)^{3/2}E^{3/2}$$

The density of state function is given by

$$Z(E) = \frac{dN}{dE} = \frac{3}{2}\cdot\frac{4\pi V}{3h^3}(2m)^{3/2}E^{1/2}$$

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

$$Z(E) = CE^{1/2} \qquad ...(4)$$

Which is the equation of half parabola defined on first quadrant (since quantity under square root is only defined in +ve space) as shown in figure (2).

Fermi-Dirac Distribution Function

The Fermi-Dirac distribution function applies to non interactive particles with half integer spin which must obey Pauli Exclusion Principle. These particles which obey Fermi-Dirac statistics are called fermions. It describes the probability of occupancy of particle in available energy levels in a given system.

Fermi - Dirac distribution function is written as,

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{KT}\right)}$$

Where,

$F(E)$ = Occupation index or probability of occupation

E = Energy of electron

E_F = Fermi energy

T = Absolute temperature

$K = 1.38 \times 10^{-23}$ J/K called Boltzmann constant.

Case - I, If $E = E_F$ at 0K, the Fermi - Dirac distribution function becomes indeterminable.

Case - II, If $E < E_F$ at 0K,

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

i.e. There is absolute probability of finding the electrons below Fermi level at absolute zero.

Case III, If $E > E_F$ at $T = 0K$

$$F(E) = \frac{1}{1 + e^{\infty}} = 0$$

This shows that electrons cannot occupy a state higher than Fermi level at 0K.

Thus at $T = 0K$, Fermi distribution function becomes step function. This switches between 0 and 1, as shown in figure.

Case - IV, If $E >> E_F$ at $T \neq 0K$

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{KT}\right)} = e^{-\frac{(E - E_F)}{KT}}$$

Hence at higher temperature, the Fermi-Dirac distribution function approximates to Maxwell - Boltzmann classical distribution function.

The higher the temperature, the greater is the probability of higher energy states being occupied.

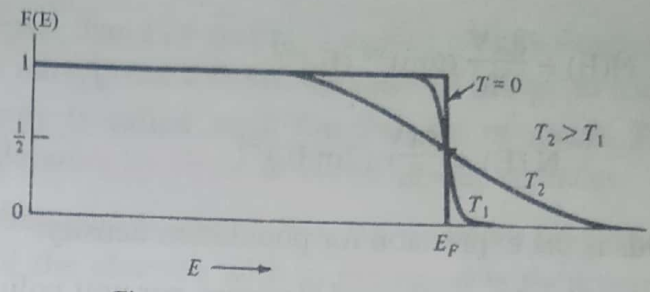

Figure : Fermi-Dirac distribution function

One interesting property of Fermi energy is that for any temperature the occupation index is 0.5 if the energy of electron is equal to Fermi energy.

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{KT}\right)} = \frac{1}{1+e^0} = \frac{1}{1+1} = \frac{1}{2} = 0.5 \text{ for } E = E_F.$$

To find population density N(E) and Fermi energy E_F from Fermi-Dirac distribution function

By using Fermi - Dirac distribution function we can calculate the number of energy states actually occupied by the electrons.

The number of energy states N(E) in an energy interval dE is given by the product of density of state function Z(E) and Fermi - Dirac distribution function F(E) i.e. d N (E) = Z (E) F (E) dE

According to Pauli Exclusion Principle, each state is occupied by two electrons with opposite spins.

$$dN(E) = 2\,Z(E)\,F(E)\,dE$$

The total number of electrons upto Fermi level is given by

$$N(E) = \int_O^{E_F} 2\,Z(E)\,F(E)\,dE$$

Here N (E) is also called "*population density*" or "*population density function*".

Since the probability of occupancy of electron from ground state to Fermi level is 100% i.e. F(E) = 1

$$\text{Therefore, } N(E) = \int_O^{E_F} 2\,Z(E)\,dE = 2\int_O^{E_F} CE^{1/2}\,dE$$

$$= \frac{2C\,E_f^{3/2}}{3/2} = \frac{4}{3}C\,E_f^{3/2}$$

$$\text{Since, } C = \frac{2\pi V}{h^3}(2m)^{3/2}$$

$$\therefore N(E) = \frac{8\pi V}{3h^3}(2m)^{3/2}(E_f)^{3/2}$$

$$N(E) = \frac{8\pi V}{3h^3}(2m E_f)^{3/2} \qquad ...(1)$$

This is the expression for population density.

Let, 'n' be the number of electrons per unit volume

$$n = \frac{N}{V} = \frac{8\pi}{3h^3}(2m E_f)^{3/2} \qquad ...(2)$$

$$\text{or, } (2m E_f)^{3/2} = \frac{3nh^3}{8\pi} \Rightarrow 2m E_f = \left(\frac{3nh^3}{8\pi}\right)^{2/3}$$

$$E_f = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} \qquad ...(3)$$

$$= \frac{h^2}{2m}\left(\frac{1}{8\pi}\right)^{2/3} . (3n)^{2/3}$$

$$= \frac{h^2}{2m}\left(\frac{1}{2^3\pi}\right)^{2/3}\left(\frac{3N}{V}\right)^{2/3}$$

$$= \frac{h^2}{2m}\frac{1}{4.\pi^{2/3}}\left(\frac{3N}{V}\right)^{2/3} = \frac{h^2}{8m\,\pi^{2/3}}\left(\frac{3N}{V}\right)^{2/3}$$

$$= \left(\frac{h}{2\pi}\right)^2 . \frac{4\pi^2}{8m\,\pi^{2/3}}\left(\frac{3N}{V}\right)^{2/3} = \frac{\hbar^2\,\pi^{4/3}}{2m}\left(\frac{3N}{V}\right)^{2/3}$$

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

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

By using equation (4) Fermi energy for any metal can be calculated if number of electrons per unit volume for that metal is known.

Thermionic Emission, Work Function

When a metal is heated, the free electrons become more energetic as the Fermi-Dirac statistics extends to higher temperature. Some of the electrons have sufficiently large energies to leave the metal and become free. This phenomenon is called *Thermionic emission.*

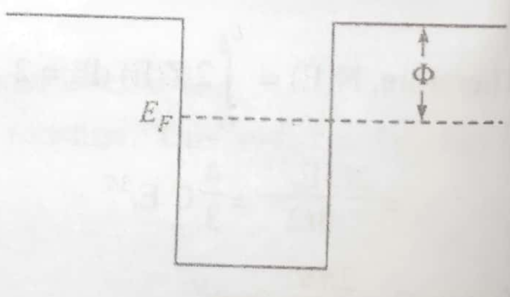

Figure : Fermi level and work function in metal

This situation is self limiting because as the electrons accumulate outside the metal, they prevent electrons from leaving the metal. Also the emitted electrons leave a net positive charge behind, which pulls the electron in. Only those electrons with energy greater than $E_f + \phi$ (Fermi energy + work function) can leave the metal. The electrons at Fermi level must given a threshold value of energy to leave the metal surface. This threshold value of energy is called work function (ϕ) of metal. The number of emitted electrons depends on the temperature by virtue of Fermi - Dirac statistics.

The conduction electrons behave as if they are free with in metal. We can therefore take PE to be zero with in the metal. The total energy E of the electron with in the metal is then purely kinetic i.e.

$$E = \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + \frac{1}{2} mv_z^2$$

Suppose that the surface of the metal is perpendicular to the direction of emission, say along x.

For an electron to be emitted from the surface of metal, it's K.E. $= \frac{1}{2} mv_x^2$ along x - direction must be greater than the potential energy barrier $E_F + \phi$

$$\text{i.e. } \frac{1}{2} mv_x^2 > E_F + \phi$$

The number of electrons per unit volume having momentum between P_x and $P_x + dP_x$ is given by $N(P_x)\, dP_x$

The number of electrons arriving at the surface of metal per unit time per unit volume = Velocity × $N(P_x)\, dP_x$

$$= \frac{P_x}{m} N(P_x)\, dP_x$$

Let r be the reflection coefficient i.e. probability that the electron will be reflected from the barrier into the metal.

Therefore, probability of emission (escape) = 1 - r

Number of escaping electrons = $[1-r] \frac{P_x}{m} N(P_x)\, d P_x$

Adding contribution by the entire electrons, which have momentum greater than P_{xo} (threshold momentum), the emission current density can be written as.

$$J = e \int_{P_{xo}}^{\infty} (1-r) \frac{P_x}{m} N(P_x)\, dP_x$$

$$J = \frac{e}{m} \int_{P_{xo}}^{\infty} (1-r) \frac{P_x}{m} N(P_x)\, dP_x \qquad \text{... (1)}$$

On calculation we get the number of electrons in the momentum range P_x to $P_x + dP_x$ as,

$$N(P_x)\,dP_x = \frac{4\pi m\,KT}{h^3}\exp\left(\frac{E_F}{KT}\right)\exp\left(\frac{-P_x^{\,2}}{2mKT}\right)dP_x \qquad ...(2)$$

Solving equation (1) and (2) using integral table we get

$$J = A_o\,(1 - r)T^2\exp\left(\frac{-\phi}{KT}\right) \qquad ...(3)$$

$$\text{Where, } A_o = \frac{4\pi mK^2}{h^3} = 1.2 \times 10^6\ \text{Am}^{-2}\ \text{K}^{-2}$$

Equation (3) is called *Richardson's equation*. This shows that the emission current density is heavily dependent upon both work function of material and its temperature. As temperature increases emission current density increases. As work function increases emission current density decreases.

Schottky Effect

When an electric field applied to a metal is increased, the work function is decreased and hence thermionic emission from the metal surface increases. This effect is called *Schottky effect.*

To study the lowering of barrier with increase in electric field we make the use of image charge method in electrostatics. It is a useful tool for solving some special classes of electrostatic problems that have some degree of mirror reflection symmetry. In thermionic emission an emitted electron from the metal surface leave an equivalent positive charge behind. In this way an image charge builds up in the metal behind.

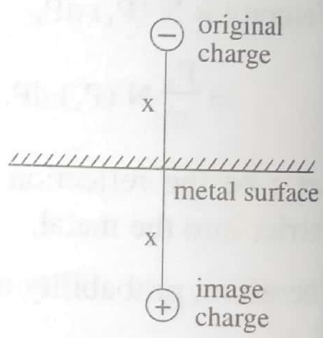

Figure : Metal surface with image charge

Image charge builds up in the metal electrode reduces the effective barrier height. This barrier reduction depends on the applied voltage.

The electrostatic force between the real and image charge can be calculated by Coulomb's law.

$$F = \frac{(-e).\,e}{4\pi\in_0(2x)^2} = \frac{-e^2}{16\pi\in_0 x^2} \qquad ...(1)$$

The potential energy can be found by integrating F from x to ∞

$$V(x) = \int_x^{\infty} F(x)\,dx = \frac{-e^2}{16\pi\in_0}\int_x^{\infty}\frac{dx}{x^2} = \frac{-e^2}{16\pi\in_0}\left[-\frac{1}{x}\right]_x^{\infty}$$

$$V(x) = \frac{-e^2}{16\pi\in_0 x} \qquad ...(2)$$

The application of image field does not make effective difference in the work function and potential energy barrier for electron at metal vacuum interface. The applied external electric field makes clear difference.

If E is the applied electric field, then the potential energy due to this field will be

$$V(x) = -e\,E\,x \qquad ...(3)$$

Now by adding contributions from image field and applied external field, the potential energy of the barrier will be

$$PE = E_f + \phi - \frac{e^2}{4\pi\epsilon_0 x} - eE\,x \qquad ...(4)$$

The reduction in work function (or barrier height) will be maximum if,

$$\frac{d}{dx}\left(-\frac{e^2}{16\pi\epsilon_0 x} - eEx\right) = 0$$

$$\Rightarrow \frac{e^2}{16\pi\epsilon_0 x^2} - eE = 0 \Rightarrow \frac{e^2}{16\pi\epsilon_0 x^2} = eE \Rightarrow E = \frac{e}{16\pi\epsilon_0 x^2}$$

$$x = \left(\frac{e}{16\pi\epsilon_0 E}\right)^{1/2} \qquad ...(5)$$

$$\text{Hence, } V_{max} = \frac{-e^2}{16\pi\epsilon_0 x} - eEx = \frac{-e^2}{16\pi\epsilon_0}\left(\frac{16\pi\epsilon_0 E}{e}\right)^{1/2} - eE\left(\frac{e}{16\pi\epsilon_0 E}\right)^{1/2}$$

$$V_{max} = -\frac{e^{3/2}E^{1/2}}{(16\pi\epsilon_0)^{1/2}} - \frac{e^{3/2}E^{1/2}}{(16\pi\epsilon_0)^{1/2}} = -2\frac{e^{3/2}E^{1/2}}{(16\pi\epsilon_0)^{1/2}}$$

$$V_{max} = -\left(\frac{4e^3E}{16\pi\epsilon_0}\right)^{1/2} = -\left(\frac{e^3E}{4\pi\epsilon_0}\right)^{1/2}$$

$$V_{max} = -\left(\frac{e^3E}{4\pi\epsilon_0}\right)^{1/2} \qquad ...(6)$$

Here, V_{max} is the maximum reduction in potential energy barrier after taking into account the effect of image field and applied external field.

The effective work function can now be written as,

$$\phi_{eff} = \phi + V_{max} = \phi - \left(\frac{e^3E}{4\pi\epsilon_0}\right)^{1/2} \qquad ...(7)$$

The reduced work function means the increase in emission current density. This is given as

$$J = A_o(1 - r)\,T^2 \exp\left(-\frac{\phi_{eff}}{KT}\right) \qquad ...(8)$$

This equation is called Richardson's equation for Schottky effect.

For simplicity we can omit the reflection coefficient considering negligible reflection into the metal. Then the equation (8) can be written as

$$J = A_oT^2\exp\left(-\frac{\phi_{eff}}{KT}\right), \text{ where, } A_o = \frac{4\pi mK^2}{h^3} = 1.2\times10^6\ Am^{-2}K^{-2}$$

Fermi Level at Equilibrium

Contact Potential

When two metals with different Fermi energy and work function are brought in contact, electron from metal with higher Fermi level will start crossing over to metal with lower Fermi level. Metal having lost electrons become positively charged where as metal having received electrons becomes negatively charged. Consequently a potential difference is developed at the junction called *contact potential*.

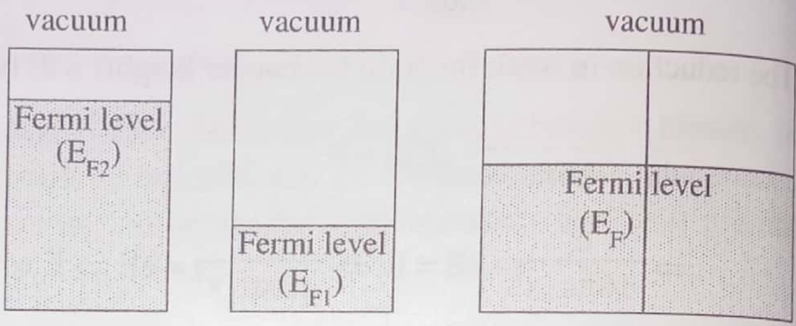

Figure 1: When metals are separate *Figure 2: When metals are in contact*

This electron transfer from one metal to another reduces the total energy of electrons in metal - metal system. This process continues till the contact potential is large enough to prevent further transfer of electrons. So the system reaches equilibrium. At equilibrium the Fermi levels of both atom will be same.

The contact potential (ΔV) is due to the difference in work functions of metal in contact.

i.e. $e\Delta V = \phi_2 - \phi_1$

$$\Delta V = \frac{\phi_2 - \phi_1}{e}$$

Seebeck Effect

The Seebeck effect is a phenomenon in which temperature difference between two dissimilar metal produces a voltage difference. When two metals one hot and other cold are brought together, more energetic electrons in the hot metal will diffuse to the cold metal. The electrons diffusing to cold side from hot side leave behind an equivalent positive charge. So there is net potential difference between hot metal and cold metal due to difference in temperature.

The ratio of the potential difference ΔV across metal - metal junction to temperature difference ΔT is called Seebeck coefficient.

$$\text{i.e. } S = \frac{\Delta V}{\Delta T} \qquad \text{...(1)}$$

The Seebeck coefficient for many metals is given by Mott and Jones equation

$$S = -\frac{\pi^2 K^2 T}{3eE_{Fo}} \qquad \text{...(2)}$$

Where E_{Fo} is Fermi energy at 0K

This effect is used in thermocouple. A thermo couple is a sensor used to measure temperature. Thermocouple consists of two wire legs made from different metals. The wire legs are wielded together at one end, creating a junction. When the junction experiences a change in temperature, a voltage is created. This change in voltage is calibrated to find temperature.

If V_H and V_C are the potential of hot and cold junction and S_H and S_C are the respective Seebeck coefficient, the potential difference between the two wires called *thermo emf* can be found as

$$V_{HC} = V_H - V_C = \int_{T_C}^{T_H} (S_H - S_C)\, dT \qquad ...(3)$$

Here, $S_{HC} = S_H - S_C$ is defined as *thermoelectric power* for the thermo couple pair.

Solving equations (2) and (3) and then integrating, leads to familiar thermocouple equation.

$$V_{HC} = a\,\Delta T + b\,(\Delta T)^2 \qquad ...(4)$$

Where a and b are called thermo couple coefficients and $\Delta T = T_H - T_C$

T_H = Temperature of hot junction

T_C = Temperature of cold junction

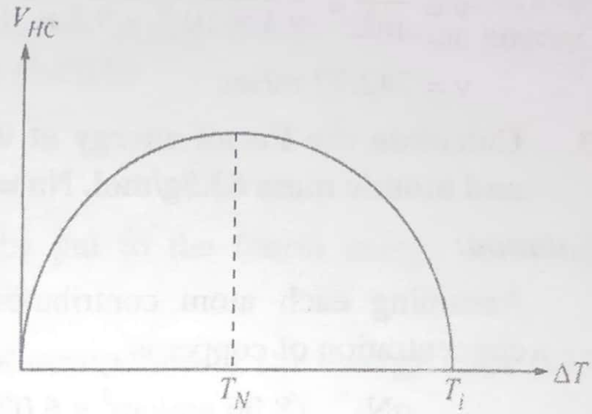

Figure : Variation in thermo-emf with change in temperature

According to equation (4) the variation of thermo emf (V_{HC}) with change in temperature is parabolic as shown in figure. Here T_N is called neutral temperature defined as the temperature at which thermo-emf is maximum. T_i is called inversion temperature defined as the temperature at which thermo-emf again falls to zero.

Solved Examples

1. Calculate the first and fifth energy levels for an electron in a potential well 0.2 mm wide.

Solution:

The energy of a particle inside in an infinite potential well is,

$$E_n = \frac{n^2h^2}{8ml^2}$$

For first energy level, $E_1 = \dfrac{1^2h^2}{8ml^2} = \dfrac{h^2}{8ml^2}$

$$= \frac{(6.62 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (0.2 \times 10^{-3})^2} = 1.5 \times 10^{-30} J$$

For fifth energy level, n = 5

$$E_5 = \frac{5^2h^2}{8ml^2} = 25 \times E_1 = 3.75 \times 10^{-29} J$$

2. **If de-Broglie wavelength of an electron is 980 nm. What is it's velocity?**

Solution:

Here, $\lambda = 980\text{nm} = 980 \times 10^{-9}\text{m} = 9.8 \times 10^{-7}\text{m}$

From de-Broglie relation, $\lambda = \dfrac{h}{mv}$

$$v = \frac{h}{m\lambda} = \frac{6.624 \times 10^{-34}}{9.1 \times 10^{-31} \times 9.8 \times 10^{-7}}$$

$$v = 742.77 \text{ m/sec}$$

3. **Calculate the Fermi energy at 0K (Kelvin) for Copper given it's density 8.96 g/cm^3 and atomic mass 63.5g/mol. Na = 6.022 × 10^{23}/mol**

Solution:

Assuming each atom contributes one electron to the conduction band, the electron concentration of copper is

$$n = \frac{\rho N_A}{M_{at}} = \left(\frac{8.96 \text{ gm/cm}^3 \times 6.022 \times 10^{23}/\text{mol}}{63.5 \text{ g/mol}}\right)$$

$$= 8.5 \times 10^{22} \text{ cm}^{-3}$$

$$= 8.5 \times 10^{28}/\text{m}^3$$

The Fermi energy at 0K is given by

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 \frac{N}{V}\right)^{2/3} = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

$$= \frac{(1.054 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}}(3 \times 3.14^2 \times 8.5 \times 10^{28})^{2/3}$$

$$= 1.13 \times 10^{-28} \text{ J}$$

4. **An electron is confined to an infinite potential well of size 8.5 nm. Calculate the ground state energy of the electron and radian frequency. How this electron can be put to the fourth energy level?**

Solution:

The energy of electron confined to an infinite potential well is,

$$E_n = \frac{n^2 h^2}{8ml^2}$$

For ground state, n = 1, $E_1 = \dfrac{h^2}{8ml^2} = \dfrac{(6.624 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (8.5 \times 10^{-9})^2}$

$$E_1 = 8.34 \times 10^{-22} \text{ J}$$

Radian frequency of electron associated with this energy is

$$\omega = \frac{E}{\hbar} = 8 \times 10^{12} \text{ rad/sec}$$

Energy of electron in fourth energy level is

$$E_4 = \frac{4^2h^2}{8ml^2} = 4^2.\ E_1 = 1.33 \times 10^{-20}\ J$$

The energy required to put electron into the fourth level is

$$E = E_4 - E_1 = 1.251 \times 10^{-20}\ J$$

This difference or short fall can be provided by a photon having exactly the same energy, no less, no more. The wave length of such photon is given by

$$\lambda = \frac{hC}{E} = \frac{6.624 \times 3 \times 10^8 \times 10^{-34}}{1.251 \times 10^{-20}} = 1.6 \times 10^{-5}m$$

Hence, the electron in ground state energy can be put to the fourth energy level by imparting it with a photon of wave length 1.6×10^{-5} m.

5. Find the temperature at which the probability of occupation of the energy state 0.75 eV above the Fermi level is 30 percentages.

Solution:

Here, $F(E) = 30\% = 0.3$

$$E = 0.75eV + E_F$$

We have, $F(E) = \dfrac{1}{\exp\left(\dfrac{E - E_F}{KT}\right) + 1} \Rightarrow 30\% = \dfrac{1}{\exp\left(\dfrac{0.75eV}{KT}\right) + 1}$

$$\exp\left(\frac{0.75eV}{KT}\right) + 1 = \frac{1}{0.3}$$

$$\exp\left(\frac{0.75eV}{KT}\right) = \frac{1}{0.3} - 1$$

$$\exp\left(\frac{0.75eV}{KT}\right) = 2.33$$

$$\frac{0.75eV}{KT} = ln\ (2.33)$$

$$T = \frac{0.75eV}{K \times ln\ (2.33)} = \frac{0.75 \times 1.6 \times 10^{-19}}{1.3 \times 10^{-23} \times ln\ (2.33)}$$

$$= 10280.15K$$

6. For an electron confined to an infinite potential well of width 0.1 nm, determine the uncertainty in momentum and kinetic energy.

Solution:

Heisenberg's uncertainty principle is expressed as

$$\Delta P_x\ .\ \Delta x \geq \hbar$$

$$\Delta P_x = \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34}}{0.1 \times 10^{-9}} = 1.054 \times 10^{-24} \text{ kg ms}^{-1}$$

Now, the uncertainty in kinetic energy is given by

$$\Delta E = \frac{\Delta P_x^2}{2m} = \frac{(1.054 \times 10^{-24})^2}{2 \times 9.1 \times 10^{-31}} = 6.1 \times 10^{-19} \text{ J}$$

$$\Delta E = 3.81 \text{ eV}$$

7. Derive the time independent Schrödinger's equation, starting with classical wave equation, $y = A \sin 2\pi \left(ft - \frac{x}{\lambda}\right)$, where notations have their usual meanings

Solution:

Here, $y = A \sin 2\pi \left(ft - \frac{x}{\lambda}\right)$

$$\text{or } y = A \sin \left(2\pi f.t - \frac{2\pi}{\lambda} . x\right)$$

$$y = A \sin (\omega t - kx) = A \sin \left(\frac{E}{\hbar} t - \frac{P}{\hbar} x\right)$$

Differentiating with respect to x,

$$\frac{dy}{dx} = \left(-\frac{P}{\hbar}\right) A \cos (\omega t - kx)$$

Again differentiating w.r.t. x

$$\frac{d^2y}{dx^2} = \left(\frac{-P}{\hbar}\right)^2 [- A \sin (\omega t - kx)]$$

$$\frac{d^2y}{dx^2} = -\frac{P^2 y}{\hbar^2}$$

$$P^2 y = - \hbar^2 \frac{d^2y}{dx^2}$$

The total energy is given by, $E = \frac{P^2}{2m} + V$

Multiplying both sides by y, $Ey = \frac{P^2 y}{2m} + Vy$

$$Ey = -\frac{\hbar^2}{2m} \frac{d^2y}{dx^2} + Vy$$

$$\frac{\hbar^2}{2m} \frac{d^2y}{dx^2} + Ey - Vy = 0$$

$$\frac{d^2y}{dx^2} + \frac{2m (E-V)}{\hbar^2} y = 0$$

Which is the required time independent Schrödinger's equation for given wave equation.

8. If the longest wave length required for photo electric effect from a certain metal is 2250 A°. Find i) Work function of the metal ii) The K.E. of electrons ejected from the metal surface if the same material is radiated with λ = 1800A°. iii) The velocity of ejected electrons

Solution:

i. At threshold, the photon energy just causes the photo emission, that is, the electrons just overcome the potential barrier φ.

$$\text{So, } \phi = hf = \frac{hC}{\lambda} = \left(\frac{6.624 \times 10^{-34} \times 3 \times 10^{8}}{2250 \times 10^{-10}}\right)$$

$$\phi = 8.832 \times 10^{-19} \text{ Joule} = 5.52 \text{ eV.}$$

ii. The energy of incident photon is

$$E = \frac{hc}{\lambda} = \left(\frac{6.624 \times 10^{-34} \times 3 \times 10^{8}}{1800 \times 10^{-10}}\right) = 1.104 \times 10^{-18} \text{ joule}$$

$$E = 6.9 \text{ eV}$$

Here, E > φ, so photo emission is possible. The excess energy, 6.9 - 5.52 = 1.38eV, will go to the ejected electron in the form of kinetic energy. Therefore, kinetic energy of ejected electron = 1.38eV

iii. The velocity of ejected electron is thus given by,

$$\frac{1}{2} mv^2 = 1.38 \text{ eV}$$

$$v = \sqrt{\frac{2 \times 1.38 \text{eV}}{m}}$$

$$v = \sqrt{\frac{2 \times 1.38 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}}$$

$$v = 6.97 \times 10^{5} \text{ m/sec}$$

9. In the photo electric experiment, green light with a wave length of 522 nm is the longest wave length radiation that can cause photo emission of electron from a clean sodium surface. Calculate the threshold value of energy required for photoemission from sodium. If ultraviolet radiation with wave length of 250 nm and another red light with wave length 700nm are incident to the sodium surface, is there emission of electrons justify. If emission calculate the velocity of photo emitted electrons.

Solution:

The minimum energy required for photo emission is,

$$\phi = hf = \frac{hC}{\lambda} = \left(\frac{6.624 \times 10^{-34} \times 3 \times 10^{8}}{522 \times 10^{-9}}\right) = 3.81 \times 10^{-19} \text{ Joule}$$

$$\phi = 2.38 \text{eV}$$

Case - I

Here, wave length of incident radiation, $\lambda = 250$nm

Therefore, energy, $E = \frac{hC}{\lambda} = \left(\frac{6.624 \times 10^{-34} \times 3 \times 10^{8}}{250 \times 10^{-9}}\right)$

$$E = 7.95 \times 10^{-19}\ J = 4.96\ eV$$

Here, $E > \phi$ so photoemission is possible. The velocity of photo emitted electron is given by the relation,

$$\frac{1}{2}mv^2 = (E - \phi)$$

$$\frac{1}{2}mv^2 = (4.96 - 2.38)\ eV$$

$$\frac{1}{2}mv^2 = 2.58\ eV$$

$$v = \sqrt{\frac{2 \times 2.58 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}}$$

$$v = 9.52 \times 10^{5}\ m/sec$$

Case II

Here, the wave length of incident radiation, $\lambda = 700$ nm

Therefore, $E = \frac{hC}{\lambda} = \left(\frac{6.624 \times 10^{-34} \times 3 \times 10^{8}}{700 \times 10^{-9}}\right)$

$$E = 2.84 \times 10^{-19}\ J = 1.77\ eV$$

Here, $E < \phi$ so photo emission is not possible.

10. Find the temperature at which there is 98% probability that a state 0.3eV below the Fermi energy level will be occupied by an electron

Solution:

Here, $F(E) = 98\% = 0.98$

$$E = E_f - 0.3eV$$

We have, $F(E) = \frac{1}{\exp\left(\frac{E - E_F}{KT}\right) + 1}$

$$0.98 = \frac{1}{\exp\left(\frac{E_F - 0.3eV - E_F}{KT}\right) + 1}$$

$$0.98 = \frac{1}{\exp\left(\frac{-0.3eV}{KT}\right) + 1}$$

$$\exp\left(\frac{-0.3eV}{KT}\right) + 1 = \frac{1}{0.98}$$

$$\exp\left(\frac{-0.3eV}{KT}\right) = 0.02$$

$$\exp\left(\frac{0.3eV}{KT}\right) = \frac{1}{0.02} \Rightarrow \exp\left(\frac{0.3eV}{KT}\right) = 50$$

$$\left(\frac{0.3eV}{KT}\right) = ln\,(50)$$

$$T = \frac{0.3eV}{K \times ln\,(50)} = \frac{0.3 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times ln(50)} = 889.12\ K$$

11. Calculate the uncertainty in the position of an electron moving with an uncertainty in speed of 2×10^6 m/sec.

Solution:

Given, uncertainty in speed (Δv) = 2×10^6 m/sec

We know from Heisenberg uncertainty principle.

$$\Delta x\,.\,\Delta p \geq \hbar$$

$$\Delta x.\ m.\ \Delta v \geq \hbar$$

$$\Delta x = \frac{\hbar}{m.\ \Delta v} = \frac{1.054 \times 10^{-34}}{9.1 \times 10^{-31} \times 2 \times 10^6}$$

$$\Delta x = 1.15 \times 10^{-9} m.$$

12. A transmitter type vacuum tube has a cylindrical Th-coated W cathode, which is 4cm long and 2mm in diameter. Estimate the saturation current if the tube is operated at 1600°C. The emission constant $A_o = 3 \times 10^4 Am^{-2}K^{-2}$. Work function for Th on W is 2.6 eV.

Solution:

Here, T = (1600 + 273)K = 1873K

Emission constant (A_o) = $3 \times 10^4\ Am^{-2}K^{-2}$

The surface area (A) = $2\pi rl = \pi dl$

$$= \pi \times 2 \times 10^{-3} \times 4 \times 10^{-2}$$

$$= 2.5 \times 10^{-4}\ m^2$$

The Richardson's equation is

$$J = A_o T^2 \exp\left(\frac{-\phi}{KT}\right)$$

$$= 3 \times 10^4 \times (1873)^2 \exp\left(-\frac{2.6 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 1873}\right)$$

$$= 1.08 \times 10^4\ Am^{-2}$$

The saturation current is given by,

$I = J.A = 1.08 \times 10^4 \times 2.5 \times 10^{-4}$

$I = 2.7$ A.

13. A transmitter type vacuum tube has a cylindrical Thorium (Th) coated Tungsten (W) cathode, which is 4cm long and 2mm in diameter. Calculate the saturation emission current if the cathode is separated from anode by 1mm and the anode voltage is 4 kV. Given, T = 1600°C, $A_o = 3 \times 10^4$ $Am^{-2}k^{-2}$ and $\phi = 2.6$ eV.

Solution:

The field at the cathode is,

$$E = \frac{V}{d} = \frac{4 \times 10^3}{1 \times 10^{-3}} = 4 \times 10^6 \text{ V/m}$$

The maximum reduction in work function due to image field and external field is,

$$V_{max} = -\left(\frac{e^3E}{4\pi\epsilon_o}\right)^{1/2}$$

The maximum reduction due to applied field only is

$$V_{max} = -\frac{1}{2}\left(\frac{e^3E}{4\pi\epsilon_o}\right)^{1/2} = -\left(\frac{e^3E}{16\pi\epsilon_o}\right)^{1/2}$$

$$\text{Therefore, } \phi_{eff} = \phi - \left(\frac{e^3E}{16\pi\epsilon_o}\right)^{1/2}$$

$$= 2.6 \times 1.6 \times 10^{-19} - \left(\frac{(1.6 \times 10^{-19})^3 \times 4 \times 10^6}{16 \times 3.14 \times 8.854 \times 10^{-12}}\right)^{1/2}$$

$$= 4.1 \times 10^{-19} \text{J}$$

$$= 2.562 \text{ eV}$$

The Richardson's equation is,

$$J = A_o T^2 \exp\left(-\frac{\phi_{eff}}{KT}\right)$$

$$= 3 \times 10^4 \times (1600 + 273)^2 \times \exp\left(-\frac{4.1\times10^{-19}}{1.38\times10^{-23}\times1873}\right)$$

$$= 1.36 \times 10^4 \text{ A/m}^2$$

Here, the emission surface area is, $A = 2\pi r\, l = \pi d l$

$$= \pi \times 2 \times 10^{-3} \times 4 \times 10^{-2}$$

$$= 2.5 \times 10^{-4} \text{ m}^2$$

The saturation current is, $I = J.A = 1.36 \times 10^4 \times 2.5 \times 10^{-4} = 3.4$ A

14. At what temperature we can expect a 10% probability that electrons in silver have energy, which is 1% above the Fermi level. E_F = 5.5eV for silver.

Solution:

Here, $F(E) = 10\% = \frac{10}{100} = 0.1$

$E_F = 5.5 \text{ eV} = 5.5 \times 1.6 \times 10^{-19} \text{ J} = 8.8 \times 10^{-19} \text{ J}$

$E = E_F + 1\% \text{ of } E_F = E_F + 0.01\, E_F = 1.01\, E_F$

$E = 1.01 \times 8.8 \times 10^{-19}\text{J} = 8.888 \times 10^{-19}\text{J}$

Now, $F(E) = \dfrac{1}{1 + e^{\frac{E-E_F}{KT}}}$

$$e^{\frac{E-E_F}{KT}} + 1 = \frac{1}{F(E)}$$

$$e^{\frac{E-E_F}{KT}} = \frac{1}{F(E)} - 1$$

$$e^{\frac{E-E_F}{KT}} = \frac{1}{0.1} - 1$$

$$e^{\frac{E-E_F}{KT}} = 9$$

$$\frac{E - E_F}{KT} = \ln(9)$$

$$T = \frac{E - E_F}{K.\ln(9)} = \frac{(8.888 - 8.8) \times 10^{-19}}{1.38 \times 10^{-23} \times \ln(9)}$$

$T = 290.22$ K

15. Normalize the wave function in 1-D.

$\phi(x) = e^{-\alpha x}$ **for x > 0**

$= e^{\alpha x}$ **for x < 0**

Solution:

Let, $\phi(x) = A e^{-\alpha x}$ for $x > 0$

$= A e^{\alpha x}$ for $x < 0$ be a normalized wave function.

Then, using normalizing condition,

$$\int_{-\infty}^{\infty} \phi\phi^* \, dx = 1$$

or, $$\int_{-\infty}^{0} \phi\phi^* \, dx + \int_{0}^{\infty} \phi\phi^* \, dx = 1$$

or, $\int_{-\infty}^{0} Ae^{\alpha x}.\, A e^{\alpha x}\, dx + \int_{0}^{\infty} Ae^{-\alpha x}.\, A e^{-\alpha x}\, dx = 1$

$$A^2 \left\{ \int_{-\infty}^{0} e^{2\alpha x}\, dx + \int_{0}^{\infty} e^{-2\alpha x}\, dx \right\} = 1$$

$$A^2 \left\{ \left[\frac{e^{2\alpha x}}{2\alpha}\right]_{-\infty}^{0} + \left[\frac{e^{-2\alpha x}}{-2\alpha}\right]_{0}^{\infty} \right\} = 1$$

$$\frac{A^2}{2\alpha} \left\{ \left[e^{2\alpha x}\right]_{-\infty}^{0} - \left[e^{-2\alpha x}\right]_{0}^{\infty} \right\} = 1$$

$$\frac{A^2}{2\alpha}\, [1 + 0 - 0 + 1] = 1$$

$$\frac{A^2}{\alpha} = 1$$

$$A = \sqrt{\alpha}$$

Hence, the Normalized wave function is,

$$\begin{aligned} \phi (x) &= \sqrt{\alpha}\, e^{-\alpha x} \text{ for } x > o \\ &= \sqrt{\alpha}\, e^{\alpha x} \text{ for } x < 0 \end{aligned}$$

16. A 3 nm thick oxide layer of CuO separates two copper conductors providing a barrier height of 10eV for the conduction of electrons in copper. Determine the transmission coefficient if the energy of electron is 5 eV. What will be the new transmission coefficient if the thickness of CuO was reduced to 1nm.

Solution:

Here, V = 10eV, E = 5eV

Case (I) :

T = ? For l = 3nm

We have, $T = \frac{16\, E\, (V - E)}{V^2}\, e^{-2k_2 l}$

Where, $k_2 = \sqrt{\frac{2m\, (V - E)}{\hbar^2}} = \sqrt{\frac{2 \times 9.1 \times 10^{-31} \times (10 - 5) \times 1.6 \times 10^{-19}}{(1.054 \times 10^{-34})^2}}$

$k_2 = 1.145 \times 10^{10}$

$$T = \frac{16 \times 5 \times (10 - 5)}{10^2}\, e^{-(2 \times 1.145 \times 10^{10} \times 3 \times 10^{-9})}$$

$= 4e^{-68.7}$

Case - II:

For $l = 1\text{nm} = 1 \times 10^{-9}\text{m}$

$$T = \frac{16\,E\,(V-E)}{V^2}\, e^{-2k_2 l}$$

$$= 4\, e^{-(2\times1.145\times10^{10}\times1\times10^{-9})}$$

$$= 4\, e^{-22.9}$$

17. Evaluate the probability of finding electron 1.5 KT above the Fermi level.

Solution:

Here, $E = E_F + 1.5\ KT$

We have,

$$F(E) = \frac{1}{\exp\left(\frac{E - E_F}{KT}\right) + 1} = \frac{1}{\exp\left(\frac{E_F + 1.5\ KT - E_F}{KT}\right) + 1}$$

$$F(E) = \frac{1}{e^{1.5} + 1} = 0.18$$

18. The normalized wave function for electron in infinite potential is $\psi_n = \left(\frac{2}{L}\right)^{1/2} \sin\frac{n\pi x}{L}$, where symbols have their usual meaning. Find the expected value of position and momentum for the electron

Solution:

Here, $\psi = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}$

1. The expect value of position is given by

$$<x> = \int_0^L \psi^* x \psi dx = \frac{2}{L}\int_0^L x \sin^2\frac{n\pi x}{L}\, dx$$

$$= \frac{2}{L}\int_0^L \frac{x}{2}\left[1 - \cos\left(\frac{2n\pi x}{L}\right)\right]dx$$

$$= \frac{1}{L}\left[\int_0^L x dx - \int_0^L x \cos\frac{2n\pi x}{L}\, dx\right] \qquad \left[\text{Since, } \int uv dx = u\int v dx - \int\left(\frac{du}{dx}\int v dx\right)dx\right]$$

$$= \frac{1}{L}\left[\int_0^L x dx - x\int \cos\frac{2n\pi x}{L}\, dx - \int\left(\frac{dx}{dx}\int \cos\frac{2n\pi x}{L}\, dx\right)dx\right]$$

$$= \frac{1}{L}\left[\frac{x^2}{2}\right]_0^L - \frac{1}{L}\left[\frac{x\sin\left(\frac{2n\pi x}{L}\right)}{\left(\frac{2n\pi}{L}\right)} - \left(\frac{-\cos\left(\frac{2n\pi x}{L}\right)}{\left(\frac{2n\pi}{L}\right)^2}\right)\right]_0^L$$

$$= \frac{1}{L}\cdot\frac{L^2}{2} - \frac{1}{L}\left[0 - 0 + \frac{L^2}{(2n\pi)^2}(\cos 2n\pi - 1)\right]$$

$$= \frac{L}{2} - \frac{1}{L}\left[\frac{L^2}{(2n\pi)^2}(1-1)\right] \text{ [Since, } \cos 2n\pi = 1, \text{ for } n = 0, 1, 2, 3..]$$

$$<x> = \frac{L}{2}$$

2. The expected value of momentum is given by,

$$<P> = \int_0^L \psi^* \hat{P} \psi dx = \int_0^L \psi^* (-i\hbar \frac{d\psi}{dx})\, dx$$

$$= -i\hbar \int_0^L \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \frac{d}{dx}\left(\sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L}\right) dx$$

$$= -i\hbar \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L}\cdot\cos\frac{n\pi x}{L}\cdot\left(\frac{n\pi}{L}\right) dx$$

$$= -i\hbar \frac{n\pi}{L^2}\int_0^L \sin\left(\frac{2n\pi x}{L}\right) dx \text{ [Since, } \sin 2A = 2\sin A\cos A]$$

$$= -i\hbar \frac{n\pi}{L^2}\left[\frac{-\cos\left(\frac{2n\pi x}{L}\right)}{\frac{2n\pi}{L}}\right]_o^L$$

$$= i\hbar \frac{n\pi}{L^2} \times \frac{L}{2n\pi}(\cos 2n\pi - 1)$$

$$= \frac{i\hbar}{2L}(1-1) \text{ [Since, } \cos 2n\pi = 1 \text{ for } n = 0, 1, 2, 3 ......]$$

Therefore, $<P> = 0$

19. For a given Fermi energy level E_F, show that the probability of emptying energy level KT below E_F is equal to probability of occupying energy level KT above E_F.

Solution:

The probability of emptying energy level KT below E_F:

$$P_1 = 1 - F(E) = 1 - \frac{1}{e^{\frac{E-E_F}{KT}}+1}$$

Here, $E = E_F - KT$

$$\text{Therefore, } P_1 = 1 - \frac{1}{e^{\frac{E_F-KT-E_F}{KT}}+1} = 1 - \frac{1}{e^{-1}+1} = 1 - \frac{1}{\frac{1}{e}+1}$$

$$P_1 = 1 - \frac{e}{1+e} = \frac{1+e-e}{1+e} = \frac{1}{1+e}$$

Now, the probability of occupying energy level KT above E_F is,

$$P_2 = F(E) = \frac{1}{e^{\frac{E-E_F}{KT}}+1}, \text{ Here } E = E_F + KT$$

$$\text{Therefore, } P_2 = \frac{1}{e^{\frac{E_F+KT-E_F}{KT}}+1} = \frac{1}{e+1} = \frac{1}{1+e}$$

Hence, $P_1 = P_2$

20. A macroscopic object of mass 100 gm is confined to move between two rigid walls separated by 1m. What is the minimum speed of the object? What should be the quantum number (n) if the object is moving six times this speed?

Solution:

Here, m = 100 gm = 0.1 kg, l = 1m

1. We have from uncertainty principle

$$\Delta P . \Delta x \geq \hbar \Rightarrow m\, \Delta v . \Delta x \geq \hbar$$

$$\Delta v \sim \frac{\hbar}{m. \Delta x} = \frac{1.054 \times 10^{-34}}{0.1 \times 1} = 1.054 \times 10^{-33} \text{m/sec}$$

2. We can write $\frac{1}{2}\, mv^2 = \frac{n^2h^2}{8ml^2}$

$$n^2 = \frac{4m^2\, l^2\, v^2}{h^2}$$

$$n = \frac{2mlv}{h} = \frac{2 \times 0.1 \times 1 \times 1.054 \times 10^{-33} \times 6}{6.624 \times 10^{-34}}$$

n = 2

21. Find the probability that an energy state 5KT above the Fermi level will not occupied by an electron.

Solution:

$$\text{We have } F(E) = \frac{1}{e^{\frac{E-E_F}{KT}}+1}$$

The probability that an energy state will not occupied by an electron.

$$1 - F(E) = 1 - \frac{1}{e^{\frac{E-E_F}{KT}} + 1}$$

Here, $E = E_F + 5\ KT$

$$\text{Therefore, } 1 - F(E) = 1 - \frac{1}{e^{\frac{E_F + 5KT - E_F}{KT}} + 1}$$

$$= 1 - \frac{1}{e^5 + 1}$$

$$= 0.99$$

$$= 99\%$$

22. What is the energy in electron volt of blue photon with a wave length of 450 nm?

Solution:

Here, $\lambda = 450\text{nm} = 450 \times 10^{-9}\text{m}$

$$\text{Therefore, } E = \frac{hC}{\lambda} = \frac{6.624 \times 10^{-34} \times 3 \times 10^8}{450 \times 10^{-9}}$$

$$= 4.416 \times 10^{-19} \text{ Joule}$$

$$= \frac{4.416 \times 10^{-19}}{1.6 \times 10^{-19}} \text{ eV}$$

$$= 2.76\text{eV}$$

23. The conductivity and drift mobility of copper conductor is 5.9×10^5 sm/cm and 43.4 cm^2/V.S. Calculate Fermi level for copper conductor.

Solution:

$$\text{Here, } \sigma = 5.9 \times 10^5 \text{ Sm/cm} = \frac{5.9 \times 10^5}{10^{-2}} \text{ Siemens/ m}$$

$$= 5.9 \times 10^7\ \Omega^{-1}\text{m}^{-1}\ [S \Rightarrow \Omega^{-1}]$$

And, $\mu = 43.4\ \text{cm}^2/\text{V.S.}$

$$= 43.4 \times 10^{-4}\ \text{m}^2\ \text{V}^{-1}\text{S}^{-1}$$

Since, $\sigma = ne\mu$

$$n = \frac{\sigma}{e\mu} = \frac{5.9 \times 10^7}{1.6 \times 10^{-19} \times 43.4 \times 10^{-4}}$$

$$n = 8.5 \times 10^{28}/\text{m}^3$$

Now, the Fermi energy is given by,

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}$$

$$= \frac{(1.054 \times 10^{-34})^2}{2 \times 9.1 \times 10^{-31}}(3 \times 3.14^2 \times 8.5 \times 10^{28})^{2/3}$$

$$= 1.1286 \times 10^{-18} \text{ Joule}$$

$$= 7.05 \text{ eV}$$

24. An electron is confined to a 1 micron thin layer of silicon. Assuming that the semiconductor can be adequately described by a one dimensional quantum well with infinite wall, calculate the lowest possible energy with in the material in units of electron volt. If the energy is interpreted as the kinetic energy of the electron, what is the corresponding electron velocity? (The effective mass of electrons in silicon is 0.26 m_o, where $m_o = 9.11 \times 10^{-31}$ kg is the free electron rest mass.)

Solution:

Here, $l = 1$ micron $= 1 \times 10^{-6}$m, for lowest possible energy, $n = 1$, $m = 0.26\ m_o$

We have, $E = \frac{n^2h^2}{8ml^2}$

$$E = \frac{1^2 \times (6.624 \times 10^{-34})^2}{8 \times 0.26 \times 9.11 \times 10^{-31} \times (1 \times 10^{-6})^2}$$

$$E = 2.32 \times 10^{-25} \text{ Joule} = 1.45 \times 10^{-6} \text{ eV}$$

Now, $E = \frac{1}{2}mv^2$

$$v = \sqrt{\frac{2E}{m}} = \sqrt{\frac{2 \times 2.32 \times 10^{-25}}{0.26 \times 9.11 \times 10^{-31}}}$$

$$v = 1400 \text{ ms}^{-1}$$

25. Calculate the density of states of 1mm^3 of copper at Fermi level with E_F = 7eV. Plank's constant (h) = 6.624×10^{-34} J-S, mass of electron (m_e) = 9.1×10^{-31} kg

Solution:

Here, $V = 1\text{mm}^3 = 1 \times 10^{-9}\ \text{m}^3$, $E_F = 7\ \text{eV} = 7 \times 1.6 \times 10^{-19}$J

The density of state is given by

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

$$= \frac{4 \times 3.14 \times 10^{-9}}{(6.624 \times 10^{-34})^3}(2 \times 9.1 \times 10^{-31})^{3/2}(7 \times 1.6 \times 10^{-19})^{1/2}$$

$$= \frac{3.264 \times 10^{-72}}{2.906 \times 10^{-100}}$$

$$= 1.123 \times 10^{28} \text{ states/Joule}$$

26. **An excited state of H-atom has life time of 2.0×10^{-14}S. Calculate the minimum error with which the energy of the state can be measured.**

Solution:

Here, $\Delta t = 2.0 \times 10^{-14}$ sec

From uncertainty principle, we have,

$$\Delta E . \Delta t \sim \hbar$$

$$\Delta E = \frac{\hbar}{\Delta t} = \frac{1.054 \times 10^{-34}}{2 \times 10^{-14}}$$

$$\Delta E = 5.27 \times 10^{-21} \text{ Joule}$$

$$= 0.033 \text{eV}.$$

27. **Calculate the kinetic energy of a neutron having de-Broglie wave length 1A°, (mass of neutron = 1.67×10^{-27} kg)**

Solution:

Here, $\lambda = 1A^{o} = 10^{-10}$m, $m = 1.67 \times 10^{-27}$ kg

Since, $\lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda}$

$$v = \frac{6.624 \times 10^{-34}}{1.67 \times 10^{-27} \times 10^{-10}} = 4 \times 10^{3} \text{m/sec}$$

The kinetic energy of neutron is given by,

$$E = \frac{1}{2} mv^2 = \frac{1}{2} (1.67 \times 10^{-27}) \times (4 \times 10^{3})^2$$

$$= 1.336 \times 10^{-20} \text{ Joule}$$

$$= 0.083 \text{ eV}$$

28. **X-rays of wave length 0.91 A° fall on a metal plate having work function 2eV. Find the wavelength associated with emitted photo electrons.**

Solution:

The energy of incident radiation is $E = hf$

$$E = \frac{hC}{\lambda} = \frac{6.624 \times 10^{-34} \times 3 \times 10^{8}}{0.91 \times 10^{-10}} = 2.18 \times 10^{-15} \text{ Joule}$$

$$E = 13648.35 \text{ eV}$$

Here, $E > \phi$ so photo emission is possible.

The excess energy, 13648.35 - 2 = 13646.35 eV will go to the ejected electrons in the form of kinetic energy.

Therefore kinetic energy of ejected electron = 13646.35 eV.

Since, $E = \frac{1}{2} mv^2$

$$v = \sqrt{\frac{2E}{m}}$$

Therefore, $\lambda = \frac{h}{mv} = \frac{h}{m\sqrt{\frac{2E}{m}}} = \frac{h}{\sqrt{2mE}}$

$$\lambda = \frac{6.624 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 13646.35 \times 1.6 \times 10^{-19}}}$$

$$\lambda = \frac{6.624 \times 10^{-34}}{6.3 \times 10^{-23}} = 1.05 \times 10^{-11} m$$

$$= 0.105\ A^o$$

29. Show that average kinetic energy per electron at 0K is $\frac{3}{5}$ E_F. Where E_F is the Fermi energy.

Solution:

The average kinetic energy per electron is given by

$$<E> = \frac{1}{N} \int_0^{E_F} E\, Z(E)\, F(E)\, dE$$

We have, density of state $Z(E) = \frac{2\pi V}{h^3} (2m)^{3/2} E^{1/2}$

Since, at 0K, all the electrons have energy less than E_F i.e. $E < E_F$.

So $F(E) = \frac{1}{\exp\left(\frac{E-E_F}{KT}\right) + 1} = \frac{1}{e^{-\infty} + 1} = 1$

Therefore,

$$<E> = \frac{1}{N} \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{E_F} E.\, E^{1/2}\, dE$$

$$= \frac{1}{N} \frac{2\pi V}{h^3} (2m)^{3/2} \int_0^{E_F} E^{3/2}\, dE$$

$$= \frac{1}{N} \frac{2\pi V}{h^3} (2m)^{3/2} \frac{2}{5} E_F^{5/2}$$

Since, $N = \frac{4\pi V}{3h^3} (2m)^{3/2} E_F^{3/2}$