

Contents

<i>Preface</i>	vii
<i>Foreword</i>	ix
1. Theory of Metals	1
1.1 Elementary Quantum Mechanical Ideas	1
1.1.1 Wave particle duality: De Broglie's equation	1
1.1.2 Wave function: Schrödinger's equation	2
1.1.3 Wave function ψ	5
1.2 Energy Well Model of Metal	7
1.2.1 Further application of Schrödinger's equation	7
1.2.2 Heisenberg's uncertainty principle	10
1.2.3 Operator notation	11
1.2.4 Finite potential barrier	13
1.2.5 Tunneling phenomenon, narrow potential barrier	16
1.2.6 Pauli exclusion principle	17
1.3 Free Electron Theory of Metal	18
1.3.1 General concepts	18
1.3.2 Electron in a linear solid (metal)	19
1.3.3 Fermi energy	20
1.3.4 Degenerate state	21
1.4 Density of States Function	22
1.4.1 Definitions of number of states, density of states	22
1.5 Fermi-Dirac Distribution Function	24
1.6 Thermionic Emission, Work Function	27
1.6.1 Schottky effect	29
1.7 Fermi Level at Equilibrium, Contact Potential	32
1.7.1 Contact potential	32
1.7.2 Seebeck effect	33
1.8 Solved Numerical Examples	33
Exercise	39

4.5.1 Ferroelectricity	87
4.5.2 Piezoelectricity	89
4.6 Properties of Some Dielectric Materials	90
4.7 Solved Numerical Examples	92
<i>Exercise</i>	94
 <i>XII</i>	
5. Magnetic Materials	95
5.1 Ferromagnetism, Ferrimagnetism and Paramagnetism	95
<i>5.1.1 Magnetic dipole moment</i>	95
<i>5.1.2 Atomic magnetic moments</i>	95
<i>5.1.3 Magnetization vector M</i>	96
<i>5.1.4 Magnetizing field or Magnetic field intensity</i>	97
<i>5.1.5 Magnetic permeability and susceptibility</i>	98
<i>5.1.6 Ferromagnetism</i>	99
<i>5.1.7 Antiferromagnetism</i>	99
<i>5.1.8 Ferrimagnetism</i>	100
<i>5.1.9 Paramagnetism</i>	100
<i>5.1.10 Diamagnetism</i>	101
5.2 Domain Structure	101
<i>5.2.1 Introduction</i>	101
<i>5.2.2 Domain walls</i>	102
<i>5.2.3 Magnetostriction</i>	103
5.3 Hysteresis Loop, Eddy Current Losses	103
5.4 Soft Magnetic Materials	106
5.5 Fe-Ni Alloys	107
5.6 Ferrites for High Frequency Transformers	108
5.7 Hard Magnetic Materials	109
5.8 Square Loop Magnetic Materials	110
5.9 Solved Numerical Examples	112
<i>Exercise</i>	113
 <i>XIII</i>	
6. Semiconductor Materials	115
6.1 Band Structure of Group IV Materials, Energy Gap	115
<i>6.1.1 Energy band in silicon crystal</i>	115
<i>6.1.2 Electron and hole</i>	116
<i>6.1.3 Electrical conduction in semiconductor</i>	117
6.2 Electron and Hole Concentrations in Intrinsic Semiconductor	119
6.3 Extrinsic Semiconductors	122
<i>6.3.1 n-type semiconductor</i>	123
<i>6.3.2 p-type semiconductor</i>	125
<i>6.3.3 Compensation doping</i>	127
6.4 Temperature Dependence of Carrier Concentration	128

6.5 Drift and Diffusion of Charge Carriers	129
6.5.1 Drift of charge carriers	129
6.5.2 Temperature dependence of mobility	131
6.5.3 Diffusion in semiconductor	133
6.5.4 Degenerate and Non-degenerate semiconductors	135
6.6 Einstein Relationship	135
6.7 Recombination and Generation	139
6.7.1 Direct Recombination and generation	139
6.7.2 Indirect thermal generation and recombination	139
6.7.3 Photogeneration	140
6.7.4 Continuity equations for carriers	142
6.8 PN Junction	144
6.8.1 Ideal abrupt junction	144
6.8.2 Forward biased pn junction	148
6.8.3 Reverse biased pn junction	152
6.9 Metal-Semiconductor Junction	154
6.9.1 Schottky junction	154
6.9.2 Ohmic contact	157
6.10 Solved Numerical Examples	157
7. Semiconductor Materials Processing	169
7.1 Crystal Growing	169
7.1.1 Floating zone method of crystal growth	169
7.1.2 Czochralski growth	170
7.2 Diffusion System	171
7.2.1 Diffusion	171
7.3 Ion Implantation Process	176
7.3.1 Ion implantation	176
7.3.2 Lattice damage and annealing	178
7.3.3 Chemical vapour deposition	178
7.3.4 Epitaxial growth	178
7.4 Monolithic IC Fabrication: Planar Process	179
7.5 Metallization, Contacts	183
8. Superconductivity	184
8.1 Introduction	184
8.2 Historical Background	184
8.3 Electric and Thermodynamic Properties	185
8.4 Magnetic Properties	187
8.5 Type I and Type II Superconductor	189
8.6 The BCS Theory	193
	194

8.7 Material Aspects	195
8.8 Examples	196
Exercise	197
Appendix-A Einstein's Equation	198
Appendix-B Collection of Particles	200
Appendix-C Some Typical Questions	202
Appendix-D Some Common Physical Constants	209
Appendix-E Bibliography	210
	211

Index

1

Chapter

Theory of Metals

1.1 Elementary Quantum Mechanical Ideas

Quantum mechanics is a generalized form of mechanics applicable to very small objects like electrons in the atom. Large systems can also be described by quantum mechanics but mostly a much simpler form of mechanics-classical mechanics is used to describe them. Many things that we have experienced throughout our life are not applicable to quantum mechanics. Rather some strange phenomena (in the sense of common man's understanding) are inherent to quantum mechanics. So when studying quantum mechanics it might seem during the course we may get lost out of realm but still will be forced, based upon immense works and results of these works by many scientist, to agree with these findings.

Various processes and phenomena that take place within a material cannot be explained without having good understanding of quantum mechanics. Although classical mechanics gives us information about various behaviors of different materials, but it fails to explain the material behaviors when it comes to microscopic level. This is the region where quantum mechanics fits the bill, i.e. quantum mechanics is able to explain this or that phenomenon.

1.1.1 Wave Particle Duality: De Broglie's Equation

During the early part of twentieth century scientists failed to explain number of phenomena by using Newton's laws of motion and Maxwell's electromagnetic theory. It was discovered that particles of atomic dimensions sometimes behave more like waves than discrete classical particles. It was also observed that electromagnetic waves, e.g., x-rays, gamma rays, visible light etc sometimes exhibit properties similar to properties of discrete particles of matter.

Experiments showed that particles like electrons, protons and neutrons exhibit an equivalent wavelength given by

$$\lambda = \frac{h}{p} \text{ De Broglie's Equation} \quad (1.1)$$

Where λ = equivalent wavelength exhibited by the particle

p = momentum of the particle

h = Planck's universal constant

$$= 6.624 \times 10^{-34} \text{ J.s}$$

Also, we can write the above equation in the following form

$$p = \hbar k \quad (1.2)$$

where $\hbar = h/2\pi$ and $k = 2\pi/\lambda$ wave number

Other experiments showed that electromagnetic radiation energy is sometimes contained in "packets" known as photons.

$$E = hf \quad (1.3)$$

Equation (1.3) is called Planck's equation.

Frequency of electromagnetic radiation f is related to radian frequency ω by

$$\omega = 2\pi f \quad \text{or} \quad f = \omega/2\pi$$

Putting the value of f in equation (1.3), we will get

$$E = h\omega \quad (1.4)$$

There were two famous experiments conducted early in the twentieth century that were unexplained by classical mechanics and so warranted the need for quantum mechanical ideas.

Experiment 1:

It was observed that beams of particle such as electrons were diffracted from a crystal in a manner similar to the diffraction of x-rays, which are electromagnetic waves.

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} \quad (1.5)$$

$$P = (2mE)^{1/2}$$

Experiment 2:

When electromagnetic radiation interacts with electrons in a solid or gas, a certain maximum wavelength of radiation is required to eject electrons from the surface of the material. By bombarding the material with photons of different energies it is found that for each material a characteristic energy is required to remove the electrons from the surface of the material. The minimum frequency (hence the maximum wavelength) of this electromagnetic radiation was found to be

$$f = \frac{\phi}{h} \quad (1.6)$$

where ϕ = characteristic energy known as work function of the material.

Comparing equations (1.3) and (1.6), we can conclude that the electromagnetic radiation behaves like particles with packets of energy when it collides with microscopic particles like electrons in the material.

From above discussed we can clearly see the duality of wave and particle. Particles like electrons sometimes behave like wave. And wave like electromagnetic radiation sometimes behaves like particles (photons with packets of energy). In quantum mechanics there are no clear distinctions between wave and particle – waves sometimes exhibiting particle-like properties and particles sometimes exhibiting wave-like properties. So, what is this- wave or particle? Till now there is not a single name that is commonly used to represent this wave-particle duality. Some say it "wavicle", some say it "particle-wave" and some say it "wave-particle". Whatever be the nomenclature used to represent this duality, the duality itself exists and is of utmost importance compared to its nomenclature.

1.1.2 Wave Function: Schrödinger's Equation

Since there is no clear distinction between wave and particle in quantum mechanics, there should be some clear representation (maybe in the form of mathematical expression) of what we call wave-particle duality.

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

Similar to ordinary wave, the displacement about its mean position is represented by wave-function ψ as

$$\psi = Ae^{-j(\omega t - \frac{2\pi}{\lambda}x)}$$

$$E = hf = 2\pi\hbar f = \frac{2\pi\hbar c}{\lambda}$$

$$\lambda = \frac{h}{p} = \frac{2\pi\hbar}{p}$$

$$\psi = Ae^{-j\left(\frac{E}{\hbar}(t) - px\right)} \quad (1.7)$$

where A = maximum displacement from mean position

λ = wave length

x = distance from origin

f = frequency of vibration

ω = radian frequency

$k = 2\pi/\lambda$ = wave number

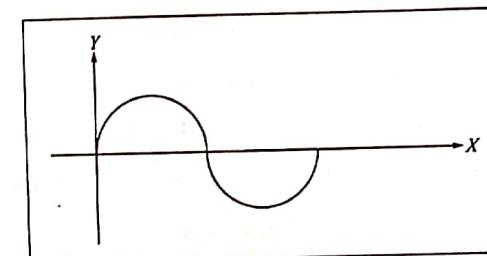


Fig. 1.1 Ordinary wave represented by equation (1.7)

Equation (1.7) is a mathematical description of the wave equivalent of an unrestricted particle with total energy E and momentum p moving in the $+x$ direction, and is correct only for freely moving particles.

Schrödinger's equation is the fundamental equation of quantum mechanics and is also wave equation in the variable ψ .

Differentiating equation (1.7) twice with respect to x , we will get

$$\frac{d\psi}{dx} = Aj\frac{2\pi}{\lambda}e^{-j(\omega t - \frac{2\pi}{\lambda}x)}$$

Then again differentiating w.r.t. x , we get

$$\frac{d^2\psi}{dx^2} = Aj^2k^2e^{-j(\omega t - \frac{2\pi}{\lambda}x)} = -\frac{p^2}{\hbar^2}\psi \quad (1.8)$$

And, differentiating equation (1.7) w.r.t. time, we get

$$\frac{d\psi}{dt} = -j \frac{E}{\hbar} A e^{-\frac{j}{\hbar}(Et - px)}$$

$$\frac{d\psi}{dt} = -j \frac{E}{\hbar} \psi$$

At speeds small compared to that of light, the total energy E of a particle is the sum of its KE ($p^2/2m$) and potential energy PE(V) where V is in general a function of position x and time t.

$$E = KE + PE$$

or,

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

Multiplying both sides by wave-function ψ , we get

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

Then from equations (1.8) and (1.9), we get

$$j\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$$

Equation (1.12) is the time-dependent form of Schrödinger's wave equation in one-dimension. In 3-dimension, the time dependent form of the above equation is given by

$$j\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi$$

It has been observed that in many situations, V of a particle does not depend on time and varies only with its position only. For such conditions, time-independent form of Schrödinger's equation is applicable which can be obtained as mentioned below. From equation (1.9) and (1.12), we get

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi$$

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

Equation (1.15) is the steady-state form of Schrödinger's equation in one-dimension. In 3-dimension, it can be expressed as

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

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.

Solving the above differential equations (1.12), (1.13), (1.15) and (1.16) we get a wave function ψ which fulfills the requirements for an acceptable wave-function, i.e., its derivatives be continuous, finite and single valued.

1.1.3 Wave Function ψ

The wave in classical mechanics can easily be understood and represented. There are numerous analogy to the wave in classical mechanics. Unlike in classical mechanics, the wave function does not enjoy the privilege of having similar analogies in quantum mechanics that will enable us to easily understand the wave function. Despite the difficulties in finding analogies to describe the wave function in quantum mechanics, it is used to describe what is called an "observable" in quantum 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. These observables which characterize the particle can not be measured at the same instant, i.e., only one can be measured at once.

The equation (1.15) and (1.16) were derived assuming that all the physical entities exhibit some wave properties, i.e., all the particles behave like waves. The wave function is extensively used to predict the probability that a particle would be found in a specified volume of space.

The wave function ψ is, in general, a complex three dimensional quantity (i.e., is the function of all three coordinates) and is dependent upon time. To be precise the wave function has both the real and imaginary components that will characterize the particle in quantum mechanical domain.

If $\psi(x, y, z, t)$ represents wave function, then $|\psi|^2$ is called probability amplitude.

Let $dxdydz$ be an elementary volume and the probability of the particle represented by wave function ψ being located in this incremental volume is to be assessed. The probability of finding the particle in given incremental volume is equal to the product of probability amplitude (also called probability density function) and the incremental volume, i.e.

$$|\psi(x, y, z)|^2 dxdydz$$

If we have to find out the probability of locating the particle between x and $x+dx$ in single dimensional case, then the probability will be equal to

$$|\psi(x)|^2 dx$$

But if the particle is located within the given interval (from x to $x+dx$ in single dimensional case), the sum of all probabilities that the particle is to be found in the above mentioned interval must be equal to 1. Mathematically, for a particle located somewhere in the universe, we can write

$$\int_{-\infty}^{+\infty} |\psi(x, t)|^2 dx = 1 \quad (1.17)$$

1.1.3.1 Hypothetical example

When we conducted various measurements in a system (fictitious not real), the probability amplitude vs. position of electron was found to be as shown in fig. 1.2 below. From the figure below it is clear that the electron is always found between x_1 and x_4 . So, the sum of all probabilities that the electron would be found between x_1 and x_4 is equal to unity. And, the probability of finding the electron beyond these limits is equal to zero.

Mathematically, we can write

$$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1 \quad (1.18)$$

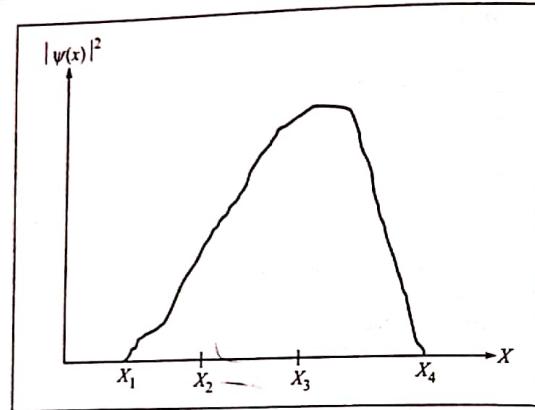


Fig. 1.2 Probability density vs. position of electron

From the Fig. 1.2 it can be said that the particle is most likely to be found in the vicinity of x_3 . The probability of finding the particle at x_2 is less than half of that of the probability of finding the same at x_3 . From the discussions to this point, we can make some important conclusions:

- Schrödinger's equation does not tell us about the position of the particle. Rather it only gives us the probability of finding the particle in the vicinity of a point.
- Statistical descriptions are inherent in quantum mechanics. We can not say much about an electron at a given time. We can only say what happens on average when we make number of observations on the same system. We can also say what happens on average by making many observations simultaneously on similar systems.
- A free particle is that which is not confined to any location. So by letting the value of potential energy $V=0$ in Schrödinger's equation for a particle in single dimensional case we have its solution in the form as given by equation (1.7) i.e.

$$\psi(x, t) = A \left[\exp j \left(kx - \frac{E}{\hbar} t \right) \right] \quad (1.19)$$

In the expression A can be found by what is called normalization.

But we know that

$$\begin{aligned} \psi \cdot \psi^* &= A \left[\exp j \left(kx - \frac{E}{\hbar} t \right) \right] \times A \left[\exp -j \left(kx - \frac{E}{\hbar} t \right) \right] \\ |\psi|^2 &= |A|^2 \end{aligned} \quad (1.20)$$

Equation (1.20) shows that a free particle can be found with equal probability anywhere, i.e., $|A|^2$ is independent of position. By equation (1.19), it is seen that a free particle does have precisely defined value of energy and hence momentum. But by Heisenberg's Uncertainty Principle, we can define only one of the observables at a time. So, a precisely defined energy or momentum implies an undefined momentum or energy.

A localized free particle must be described as a wave packet formed from superposition of wave functions with different momentum values (hence the k -vectors). This uncertainty in momentum allows spatial

In single-dimension we can write

$$\psi(x, t) = \int_{-\infty}^{+\infty} A(k) [\exp j(kx - \omega t)] dk \quad (1.21)$$

In equation (1.21) the wave function in the given integral represents wave packet formed by superimposing wave functions with different momentum (hence k) values.

We have,

$$\lambda = \frac{\hbar}{p} \quad \text{and} \quad k = \frac{2\pi}{\lambda}$$

$$p = \hbar k$$

So, momentum, which is related to the energy of the particle, is also related to k value. Energy E and wave number k are also related to each other.

1.2 Energy Well Model of Metal

1.2.1 Further Application of Schrödinger's Equation

Let an electron be confined to a certain region such that $0 < x < L$ where L represents the width of the confinement. Assume that the potential energy of the particle is zero inside the confined region and infinite outside it. The electron thus confined can not leave the region because to leave it requires infinite potential energy.

Let us solve the Schrödinger's equation for the electron confined in an infinite potential well as shown in the figure 1.3.

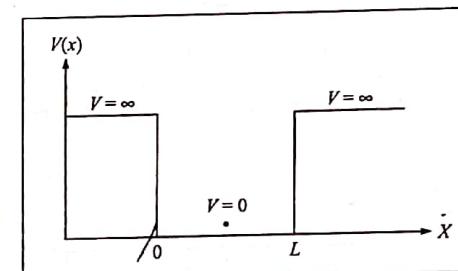


Fig. 1.3 Electron in infinite potential well

A general solution of the Schrödinger's equation (1.16) for single dimensional case is

$$\psi(x) = A \sin \beta x + B \cos \beta x \quad (1.22)$$

where A and B are some constants that are found from boundary conditions.

And

$$\beta^2 = \frac{8\pi^2 m}{h^2} (E - V)$$

Since the particle can not be found outside the potential well, the wave function representing the particle outside the well will be $\psi=0$. This condition should be extended to the boundary, i.e. at $x=0$ and $x=L$. So, applying boundary conditions, we will get

$$\psi(0) = A \sin 0 + B \cos 0$$

$$B = 0$$

$$\psi(L) = A \sin \beta L + B \cos \beta L$$

$$A \sin \beta L = 0$$

$$\sin \beta L = \sin(n\pi)$$

$$\beta L = n\pi, \text{ where } n = 1, 2, 3, \dots, \infty.$$

$$\beta^2 = \frac{n^2 \pi^2}{L^2}$$

$$\frac{n^2 \pi^2}{L^2} = \frac{8\pi^2 m E}{h^2}$$

Here E the total energy of the electron when potential energy is equal to zero (assumed for the electron in infinite potential well) will be given by

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (1.23)$$

$$E_n = \frac{\pi^2 n^2 \hbar^2}{2mL^2} \quad (1.24)$$

The energy of an electron that is confined in an infinite box (potential well) can not be arbitrary but must be defined by the parameter "n". Alternatively, the energy of an electron confined in an infinite potential well is quantized, i.e., can have only discrete sets of values. These quantized energy values are called "Eigen values" and the corresponding wave functions ψ_n are called Eigen functions.

It can be readily seen from figure 1.4 and equation (1.24) that the energy of a confined particle is quantized, so can have only discrete sets of values. The wave functions for the first three values of n in a single-dimensional case is shown below in figure 1.5.

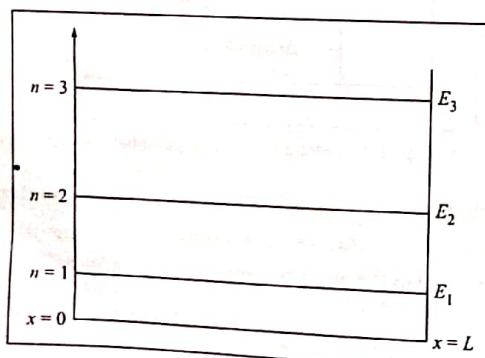


Fig. 1.4 Energy levels of an electron in an infinite potential well

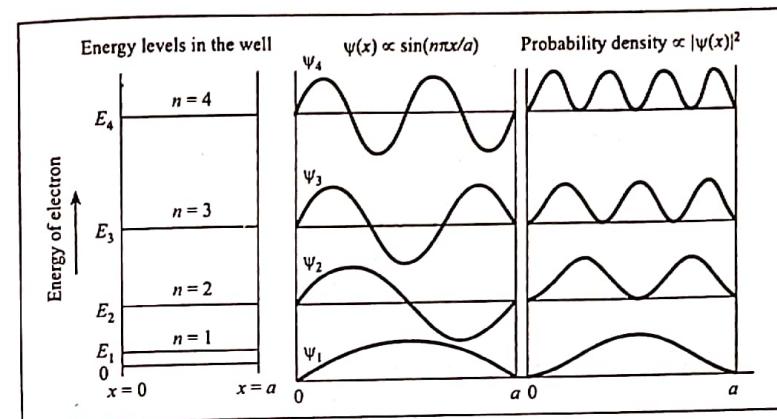


Fig. 1.5 Electron in a single dimensional infinite potential well of width L m. The energy of electron is quantized. The wave functions and probability distribution functions are also shown.

For a particle in infinite potential well the minimum energy that the electron can possess can be calculated by using Heisenberg's uncertainty principle (will be discussed later). Electron in the box at any instant can occupy any position between $x=0$ to $x=L$. At the same time, the electron can be heading to $+x$ direction with a momentum $+p_x$ or to $-x$ direction with momentum $-p_x$, the direction of momentum changing continuously due to collision with the wall of the well. Let Δx and Δp_x be uncertainty in position and uncertainty in momentum of the particle along x axis.

$$\Delta x \Delta p_x = L \cdot 2p_x (\Delta x = L - 0 = L)$$

$$p_x = \hbar/2L$$

Now the energy of the electron consists of only the kinetic one, the potential energy being assumed zero.

$$E = \frac{mv^2}{2} = \frac{p^2}{2m}$$

$$E = \frac{\hbar^2}{8mL^2} \quad (1.25)$$

Now the particle in the infinite potential well can be represented by wave function

$$\psi(x) = A \sin \beta x = A \sin \frac{n\pi}{L} x \quad (1.26)$$

In equation (1.26) A can be determined by normalization. We know that the particle is located within the potential well of width L m. So, we can write

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

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

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

$$\frac{A^2}{2} (x) \Big|_0^L = 1$$

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

greater than \hbar . Mathematically, this relationship can be expressed as

$$\Delta x \Delta p_x \geq \hbar \quad (1.31)$$

Because of the wave nature of quantum mechanics, we can not measure the position and momentum of the electron simultaneously. There will always be uncertainty in position of the electron given by Δx and uncertainty in momentum given by Δp_x . These uncertainties are related by Heisenberg's uncertainty relationship as expressed in (1.31).

These uncertainties are not in any way a consequence of the accuracy of a measurement or the precision of the measuring instrument. Rather, they are theoretical limits to our ability to explore a system and are the part of quantum nature of the universe. If we build the most perfect instrument to measure the position and momentum of the electron at any instant, there will always be uncertainties in momentum and position of the particle such that $\Delta x \Delta p_x \geq \hbar$.

The principle is also used to show for the following:

- the existence of protons and neutrons and non-existence of electrons in nucleus of an atom
- to find the binding energy of electrons in nucleus of an atom
- to find the radius of Bohr's first orbit as well as the finite width of the spectral lines.

Hence the normalized wave function of the electron is

$$\psi_n = [2/L]^{\frac{1}{2}} \sin \frac{n\pi}{L} x$$

(1.28)

1.2.2 Heisenberg's Uncertainty Principle

The wave function of a free electron corresponds to a traveling wave with a single wavelength. This means the traveling wave extends over all space with the same amplitude. So, the probability distribution function is uniform throughout the whole space. The electron can be found anywhere. This means the uncertainty in position of electron is infinite. At the same time the electron has a fixed well-defined wavelength, which gives the exact value of momentum of the particle. This corresponds to uncertainty in momentum being zero.

Let us recall the case of an electron confined in a single dimensional infinite potential well. The wave function of the particle extends from $x=0$ to $x=L$. So, the uncertainty in position is equal to the width L of the potential well. The momentum of the electron is either $p_x = \hbar k$ in $+x$ direction and $p_x = -\hbar k$ in $-x$ direction. The uncertainty in momentum is therefore difference between momentum in $+x$ direction and $-x$ direction and equal to $2\hbar k$. When the electron is in ground state, $n=1$ and $kL=\pi$. So, the uncertainty in momentum can be written as

$$\Delta p_x = \frac{2\hbar\pi}{L} \quad (1.29)$$

Now, the product of uncertainties in position and momentum of electron can be found.

$$\Delta x \Delta p_x = L \frac{2\pi\hbar}{L}$$

or,

$$\Delta x \Delta p_x = \hbar$$

So, the product of uncertainties in position and momentum is equal to Plank's universal constant \hbar . This is one of the fundamental relationships that puts a limit to our knowledge of the behavior of any system. We cannot exactly and simultaneously know or measure both the position and momentum of an electron along a given coordinate.

If Δ_x and Δp_x are the respective uncertainties in position and momentum of an electron during simultaneous measurement along x , then Heisenberg's uncertainty principle state that their product must be equal or

1.2.3 Operator Notation

We have, one of the solutions of Schrödinger's equation given in equation (1.19) as

$$\psi(x, t) = A \left[\exp j \left(kx - \frac{E}{\hbar} t \right) \right]$$

Differentiating w.r.t. t, we will get

$$\begin{aligned} \frac{\partial \psi}{\partial t} &= j \frac{E}{\hbar} A \left[\exp j \left(kx - \frac{E}{\hbar} t \right) \right] \\ &= -j \frac{2\pi E}{\hbar} \psi \\ E\psi &= j \frac{\hbar}{2\pi} \frac{\partial \psi}{\partial t} \end{aligned} \quad (1.32)$$

Thus,

$E \rightarrow j \frac{\hbar}{2\pi} \frac{\partial}{\partial t}$ is called "Energy Operator"

or,

$\hat{E} \rightarrow j\hbar \frac{\partial}{\partial t}$ (read energy operator corresponds to)

Similarly, taking partial derivative with respect to x in equation (1.19)

$$\frac{\partial \psi}{\partial x} = jkA \left[\exp j \left(kx - \frac{2\pi E}{\hbar} t \right) \right]$$

$$\frac{\partial \psi}{\partial x} = jk\psi \quad \text{But} \quad k = \frac{2\pi}{\hbar} p = \frac{p}{\hbar}$$

or,

$$\frac{\partial \psi}{\partial x} = j \frac{2\pi}{\hbar} p \psi$$

or,

$$p \psi = -j \frac{\hbar}{2\pi} \frac{\partial \psi}{\partial x} \quad (1.33)$$

$\hat{p} \rightarrow -j \frac{\hbar}{2\pi}$ is called momentum operator

(Read: momentum operator corresponds to)

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.

Let us consider an example, which will help us establish the use of these operators in quantum mechanics and also gives us analogy in statistics so as to understand these operators more clearly.

There are 40 students in the class. And the following is the result of test conducted by the class teacher.

Table 1

Serial No, i	No of students with score S_i	Score S_i
1	1	20
2	4	19
3	4	18
4	4	17
5	6	16
6	6	15
7	5	14
8	3	12
9	3	11
10	2	10
11	2	08
12	0	00

The average score of the class can be calculated as

$$S_{av} = \frac{\sum N_i S_i}{\sum N_i}$$

$$= \frac{1 \times 20 + 4 \times 19 + 4 \times 18 + 4 \times 17 + 6 \times 16 + 6 \times 15 + 5 \times 14 + 3 \times 12 + 3 \times 11 + 3 \times 10 + 2 \times 8 + 0 \times 0}{1 + 4 + 4 + 6 + 6 + 5 + 3 + 3 + 2 + 2 + 0} \\ = 14.935$$

In statistics, S_{av} is called "Expectation value" or "Expected value". In quantum mechanics, we have to find "expected average value" of one of the observables – energy, position or momentum.

The equivalent of S_{av} in quantum mechanics is given by

$$\langle G \rangle = \frac{\int_{-\infty}^{+\infty} \psi^* G \psi dx}{\int_{-\infty}^{+\infty} \psi^* \psi dx} \quad (1.34)$$

In the above equation (1.34), G is one of the operators (e.g. position operator or momentum operator or energy operator).

$$\text{We have, } \int_{-\infty}^{+\infty} \psi^* \psi dx = 1$$

Then the equation (1.34) becomes

$$\langle G \rangle = \int_{-\infty}^{+\infty} \psi^* G \psi dx \quad (1.35)$$

1.2.4 Finite Potential Barrier

We have established that the electron confined to an infinite potential well has its energy quantized by virtue of relationship given by equation (1.23) and (1.24). Now let us consider a free electron traveling in $+x$ direction and encountering a barrier whose potential energy is V_0 . The energy of the electron E is less than the barrier potential energy also known as "Barrier height". But, unlike in previous case, the potential energy of the barrier is finite.

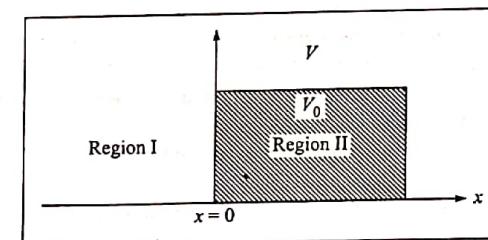


Fig. 1.6 Finite potential barrier

When applying Schrödinger's equation for the electron here, we have to take into account the fact that there are two distinct regions where the behavior of electron will be different.

In region I, electron is free so its potential energy is set equal to zero. So the Schrödinger's equation for the wave function will be

$$\frac{d^2 \psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0 \quad (1.36)$$

In the region I, $x < 0$. For region II where $x > 0$, we can write the Schrödinger's equation as

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0 \quad (1.37)$$

The solution of equation (1.36) will be for region I

$$\psi_I = A \exp(j\beta x) + B \exp(-j\beta x) \quad (1.38)$$

For region II,

$$\psi_{II} = C e^{j\alpha x} + D e^{-j\alpha x} \quad (1.39)$$

$$\text{where } \beta^2 = \frac{2mE}{\hbar^2} \text{ and } \alpha^2 = \frac{2m}{\hbar^2}(E - V_0)$$

The constants A, B, C and D in the above equations (1.38) and (1.39) can be found by using boundary conditions.

In the region I the electron wave function will be as discussed before but in region II it will be different. α will be imaginary if V_0 is greater than E.

$$\text{Let } \gamma = j\alpha$$

Then,

$$\gamma = j\alpha = \left[\frac{2mE}{\hbar^2} (V_0 - E) \right]^{\frac{1}{2}} \quad (1.40)$$

The γ given by equation (1.40) is real, not imaginary.

So, the wave function in the region II can now be written as

$$\psi_{II} = C e^{\gamma x} + D e^{-\gamma x} \quad (1.41)$$

When $x \rightarrow \infty$,

$$\psi_{II} = C \cdot \infty + D \cdot 0$$

For ψ, ψ' not to exceed 1, C must be equal to zero.

$$\psi_{II} = D e^{-\gamma x} \quad (1.42)$$

The above equation of the electron wave function in region II implies that the amplitude of the wave decreases exponentially in the region.

Note that for larger values of γ , the decrease in amplitude of the wave function in the region II will be faster compared to its smaller values.

At $x = 0$, both the wave functions are continuous. So they must be equal to each other.

$$\begin{aligned} \text{or, } \psi_I(0) &= \psi_{II}(0) \\ A e^{j\beta 0} + B e^{-j\beta 0} &= D e^{-\gamma 0} \\ \text{or, } A + B &= D \end{aligned} \quad (1.43)$$

The second boundary condition is: the slope of both the wave functions at $x = 0$ are continuous. That means

$$\begin{aligned} \frac{d\psi_I}{dx} \Big|_{x=0} &= \frac{d\psi_{II}}{dx} \Big|_{x=0} \\ A j\beta e^{j\beta x} - B j\beta e^{-j\beta x} &= -\gamma D e^{-\gamma x} \\ A j\beta - B j\beta &= -\gamma D \end{aligned} \quad (1.44)$$

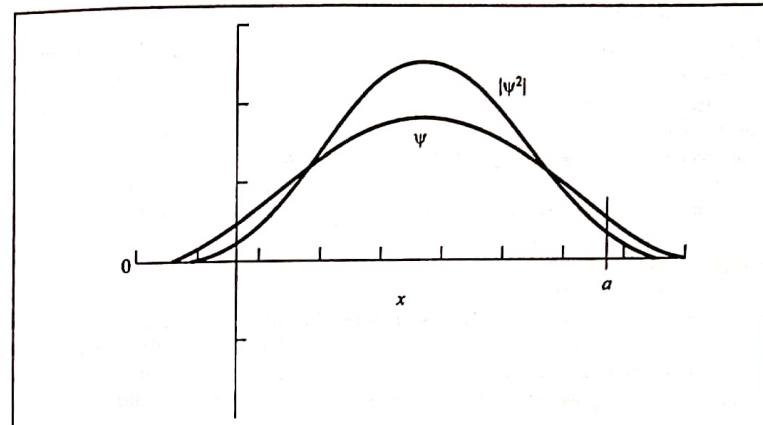


Fig. 1.7 Wave function of electron in the region of finite potential barrier

From equations (1.43) and (1.44) we will find

$$\begin{aligned} A &= \frac{D}{2} \left(1 + j \frac{\gamma}{\beta} \right) \\ B &= \frac{D}{2} \left(1 - j \frac{\gamma}{\beta} \right) \end{aligned} \quad (1.45)$$

So, an electron in any region where it is free or confined can be defined in terms of its amplitude. The same implies to the electron when it is within the finite potential barrier. Depending upon the width of the potential barrier, the amplitude of the electron wave function can be drastically reduced or completely wiped out. This phenomenon can be clearly seen from the figure shown below where the behaviors of wave functions in different regions and for different values of n are shown.

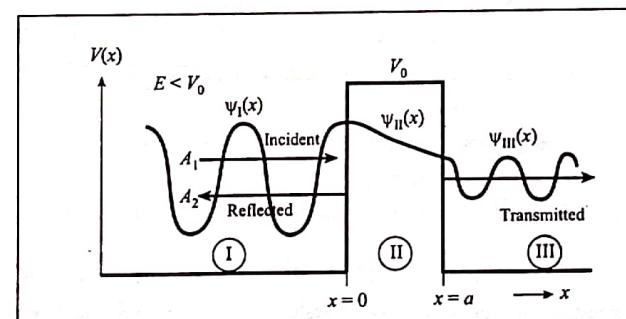


Fig. 1.8 Electron wave functions in different regions.

1.2.5 Tunneling Phenomenon, Narrow Potential Barrier

Let us consider the analogous system in atomic scale i.e. in quantum mechanical domain. As shown in the figure an electron moves with an energy E in the region $x < 0$ where for convenience the potential energy is set to zero. So, the total energy of the electron is solely contributed by kinetic energy. The electron when encountering a potential barrier of V_0 will be reflected back normally because the energy of the electron is less than the potential energy offered by the barrier. This is analogous to the phenomenon with roller coaster. But in quantum mechanics if the width of the potential barrier is small (narrow), then there is always probability that the electron can be found at the other side of the potential barrier. In this case the electron is said to have tunneled through the potential barrier. Such type of phenomena, in which electron tunnels through the barrier is known as tunneling or quantum leak. In classical mechanics such phenomena are impossible.

In figure 1.9 a roller coaster is placed at A is shown. When the roller coaster is released from position A based upon the theory of conservation of energy, it can reach at best to point C and can easily reach to point B . But in no condition can scale the height D and be found at E . To reach point E for the roller coaster the difference energy corresponding to $D-A$ is required. This is in classical mechanics.

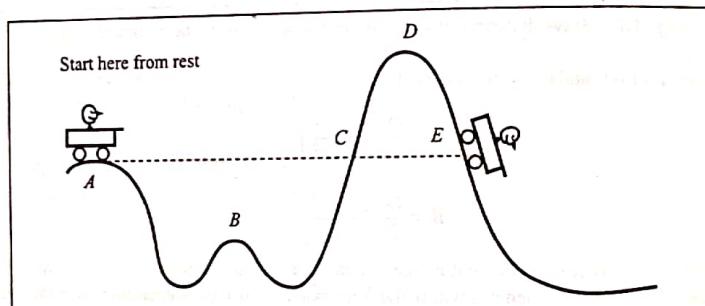


Fig. 1.9 Path of roller coaster movement

There are three distinct regions as shown in fig. 1.8 in which the electron wave function is different. In region I, the general solution of Schrödinger's equation is

$$\psi_I(x) = A_1 e^{i\beta x} + A_2 e^{-i\beta x} \quad (1.46)$$

In the region II, the general solution of the wave function is expressed as

$$\psi_{II}(x) = B_2 e^{-\gamma x} \quad (1.47)$$

Similarly in region III, the general solution of the Schrödinger's equation is

$$\psi_{III}(x) = C_1 e^{i\beta x} + C_2 e^{-i\beta x} \quad (1.48)$$

In equations (1.46), (1.47) and (1.48), the following notations have been used:

$$\beta^2 = \frac{2mE}{\hbar^2} \quad \text{and} \quad \gamma^2 = \frac{2m(V_0 - E)}{\hbar^2}$$

In above description, region I and III represent metals and region II the vacuum. In region I, the wave function is composed of both the incident and reflected waves whereas in region III it is only the incident

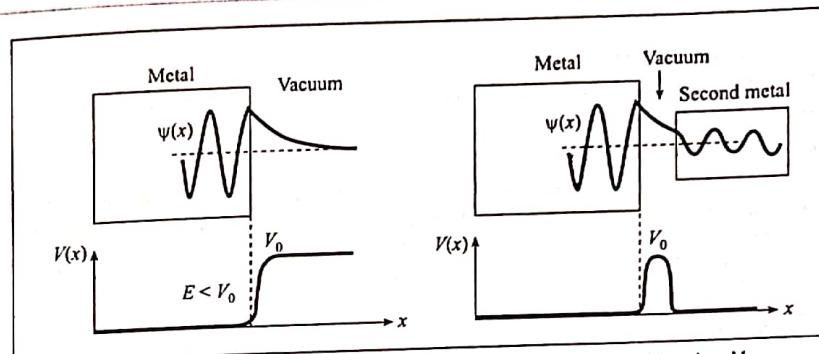


Fig. 1.10 Wave function of an electron incident on potential barrier V_0

wave that gives the wave function. In region II, the wave function decays exponentially given by the expression (1.47) derived earlier.

The relative probability that the electrons will tunnel from region I to the region III through region II is defined as transmission coefficient T which depends very strongly both on the relative potential barrier height ($V_0 - E$) and the width of the potential barrier. The final expression for the transmission coefficient is expressed as

$$T = \frac{|\psi_{III}(x)|^2}{|\psi_I(\text{incident})|^2} = \frac{C_1^2}{A_1^2} = \frac{1}{1 + D \sinh^2(\gamma L)} \quad (1.49)$$

$$\text{where } D = \frac{V_0^2}{4E(V_0 - E)} \quad (1.50)$$

and γ is the rate of decay of $\psi_{II}(x)$ as expressed above. For a wide or high barrier, using $\gamma L \geq 1$ in equation (1.49) and $\sinh(\gamma L) \approx \frac{1}{2} \exp(-2\gamma L)$, we can deduce

$$T = T_0 \exp(-2\gamma L) \quad (1.51)$$

The expression (1.51) gives the probability of tunneling through the potential barrier of width L and height V where T_0 is given by

$$T_0 = \frac{16E(V_0 - E)}{V_0^2} \quad (1.52)$$

The reflection coefficient R is given by

$$R = \frac{A_2^2}{A_1^2} = 1 - T \quad (1.53)$$

1.2.6 Pauli Exclusion Principle

This principle based on experimental observations 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 for 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 - principle quantum number
- l - orbital angular momentum quantum number
- m_l - magnetic quantum number
- m_s - spin magnetic quantum number.

If an electron is given by quantum numbers 2, 1, 1, 1/2, then there can not exist another electron with all four identical quantum numbers. There must be at least one of the quantum number other than those mentioned previously. Pauli exclusion principle is often used to determine the electronic structure of atoms with large numbers of electrons.

1.3 Free Electron Theory of Metal

1.3.1 General Concepts

To account in qualitative and quantitative way for the characterization of metallic properties, a theory was precluded. Drude (1900) constructed a theory of metal on the basis of highly successful kinetic theory of gases considering as a gas of electrons. But in gas one type of particles are present and in metal at least two, i.e., electrons and ions are present. In this theory interaction of electrons with ions and other electrons is rejected. Electrons are assumed to achieve thermal equilibrium with surroundings through collisions which are instantaneous events.

According to this theory, the outermost electrons known as valence electrons of an atom in metal are very loosely attached to the parent atom, so they are not bound to the parent atom. These electrons are free to move throughout the whole metal. These electrons are attached to different atoms at different instants. These freely roaming electrons within the metal form what is known as "Electron gas". When an atom loses its valence electron it becomes positively charged ion. So, the metallic bond is an unsaturated covalent bond due to electrostatic attraction between the positively charged ion core and negatively charged electron cloud.

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, which are called saturated bonds. This indicates to the ductile nature of metal.

In free electron theory it is assumed that the potential due to the ion cores is uniform throughout the metal. This means a free electron has the same potential energy everywhere within the metal. Although, strictly saying, the potential energy of an electron due to electrostatic attraction in the metal has a finite negative value, we assume it zero because we are concerned with change in potential energy rather than the potential energy itself.

So, if the electron has kinetic energy only

$$E = \frac{mv^2}{2} \quad (1.54)$$

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

But

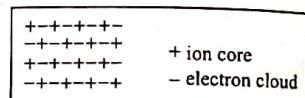


Fig. 1.11 Ion core and electron cloud

$$k = \frac{2\pi}{\lambda} \quad \text{and} \quad v = \frac{\hbar k}{m}$$

Substituting for λ and k in equation (1.54), we will have

$$E = \frac{m}{2} \left(\frac{\hbar^2 k^2}{m^2} \right)$$

$$E = \frac{\hbar^2 k^2}{2m} \quad (1.55)$$

The equation (1.55) represents the kinetic energy of the free electron within the metal. The relationship between E and k given by equation (1.55) is parabolic in nature as shown in figure 1.12.

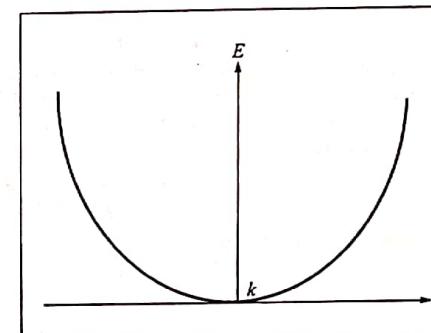


Fig. 1.12 E-k diagram of free electron in metal

1.3.2 Electron in a Linear Solid (Metal)

Consider a copper wire of length L . There are many free electrons within that linear solid. The wavelength exhibited by electron in the wire will depend upon their kinetic energy.

For minimum kinetic energy the wavelength of electron will be greatest and will progressively go down as the kinetic energy increases. So, for minimum kinetic energy

$$L = \frac{\lambda}{2} \quad (1.56)$$

And for higher values of kinetic energies, the relationship between wavelength and length of the wire is given by

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

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

And so on up to n

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

Now, arranging for wavelength in terms of length of the wire, we will get

$$\gamma = 2L, L \frac{2}{3}L, \frac{L}{2}, \frac{2}{5}L, \frac{1}{3}L, \dots \frac{2}{n}L \quad (1.57)$$

Wavelength and wave number are related as

$$k = \frac{2\pi}{\lambda}$$

Substituting the value of wavelength from equation (1.57) in the above expression, we will get

$$k = \frac{2\pi}{2L}, \frac{2\pi}{L}, \frac{2\pi}{\frac{3}{2}L}, \frac{2\pi}{\frac{5}{3}L}, \frac{2\pi}{\frac{7}{4}L}, \dots, \frac{2\pi}{\frac{2n}{n+1}L}$$

$$k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \frac{4\pi}{L}, \frac{5\pi}{L}, \frac{6\pi}{L}, \dots, \frac{n\pi}{L} \quad (1.58)$$

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, which in turn is related to wave number must have both the positive and negative values.

$$k = \pm \frac{\pi}{L}, \pm \frac{2\pi}{L}, \pm \frac{3\pi}{L}, \pm \frac{4\pi}{L}, \pm \frac{5\pi}{L}, \pm \frac{6\pi}{L}, \dots, \pm \frac{n\pi}{L} \quad (1.59)$$

Now substituting for k in equation (1.55) we will get

$$E = \frac{n^2 h^2 \pi^2}{2mL^2} \quad (1.60)$$

Above expression (1.60) shows that a free electron in a metal does not possess any arbitrary value of energy rather its energy is quantized by virtue of E being function of principle quantum number n .

1.3.3 Fermi Energy

In metals if to say in very few words Fermi Energy is defined as the highest filled energy level at a temperature of absolute zero, i.e., 0°K. All the energy levels up to the Fermi level are filled at 0°K and empty above it. In E-k diagram Fermi energy can be shown as in figure 1.13. The distribution of electrons among various energy levels in accordance with Pauli's exclusion principle. If N is the total number of electrons to be accommodated on the line, then for even n , we have $N = 2n_F$, where n_F is principle quantum number of the Fermi level. Thus, for $n=n_F$ from equation (1.60), we can rewrite the expression as

$$E_F = \frac{\hbar^2}{2m} \left(\frac{\pi n_F}{2} \right)^2 \quad (1.61)$$

Thus, the Fermi energy depends upon the length of the box and the number of electrons in the box.

$$E_F = \frac{\hbar^2}{2m} \left(\frac{\pi N}{2L} \right)^2 = \frac{\hbar^2}{2m} k_F^2 \quad (1.62)$$

where k_F is the Fermi wave vector and the sphere of radius k_F in E-K space is called Fermi sphere. The number of occupied electrons in the sphere is given by

$$N = 2 \times \frac{\text{Volume of sphere of radius } k_F}{\text{Volume of element of } k\text{-space}} = \frac{2 \frac{4}{3} \pi k_F^3}{(K_x)^3} = \frac{L^3 k_F^3}{3\pi^2}$$

$$\text{or, } N = \frac{V k_F^3}{3\pi^2} \quad \text{where } K_x = \frac{2\pi}{L}$$

$$\text{And, } n = \frac{N}{V} = \frac{k_F^3}{3\pi^2}$$

In the above expression, 2 comes from the two allowed values of the spin quantum number.

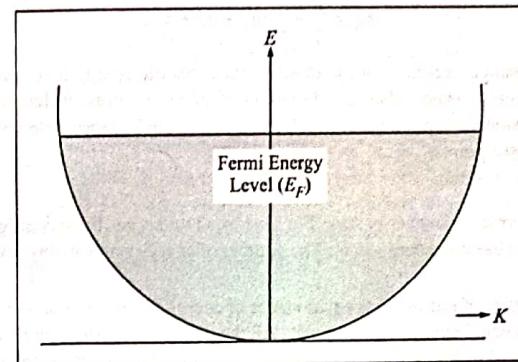


Fig. 1.13 The highest filled energy level at 0°K

1.3.4 Degenerate State

In a single dimensional solid the energy of the electron is expressed as

$$E = \frac{\pi^2 n^2 \hbar^2}{2mL^2} = \frac{n^2 \hbar^2}{8mL^2} \quad (1.63)$$

This expression is valid both for free electron and electron in a potential well.

In a three dimensional solid which is the general case, the above expression will be supplemented by the fact that in place of principle quantum number n is taken for single dimension and would be replaced by corresponding three-dimensional value.

$$n^2 = n_x^2 + n_y^2 + n_z^2 \quad (1.64)$$

And the energy expression becomes

$$E_n = \frac{\pi^2 \hbar^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (1.65)$$

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 n values along different axes in three-dimensional case will determine the energy associated with the electron. Unlike in single dimension, the same n along x axis can represent different energies

because of the fact that its energy is not only dependent upon principle quantum number along x-axis but also upon n along y and z axes also. When different combinations of principle quantum number represent same energy, these are called "degenerate states". For example $n(1,1,2)$, $n(1,2,1)$ and $n(2,1,1)$ will represent the same electron energy. These all three electronic states are degenerate states.

1.4 Density of States Function

1.4.1 Definitions of Number of States, Density of States

The quantized energy state of electron is expressed as

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) \quad (1.66)$$

For each set of quantum numbers n_x, n_y, n_z there exists a specific energy level called energy state. To determine how many energy states, also called number of states, are present, let us consider a quantum number in three dimensional quantum space. Each energy state can be represented by a vector n which is the radius from origin to a point n_x, n_y, n_z

$$n^2 = n_x^2 + n_y^2 + n_z^2 \quad (1.67)$$

Every integer (n) represents an energy state. For $n_x=1, n_y=1$ and $n_z=1$, there is only one energy state. In other words, a unit cube has one energy state. The number of energy states in any volume is proportional to that volume.

On the surface of sphere of radius n has equal values of energies. All states laying on the surface of the sphere of radius n have equal energies given by E_n . All the points within that sphere of radius n represent quantum states with energies less than E_n . The principle quantum number n can take integer values only, so the energy states are defined only in positive octant of the sphere made by the radius vector n.

So, the number of energy states within the sphere of radius n and having energies less than E_n is given by

$$N = \frac{1}{8} \frac{4\pi n^3}{3} \quad (1.68)$$

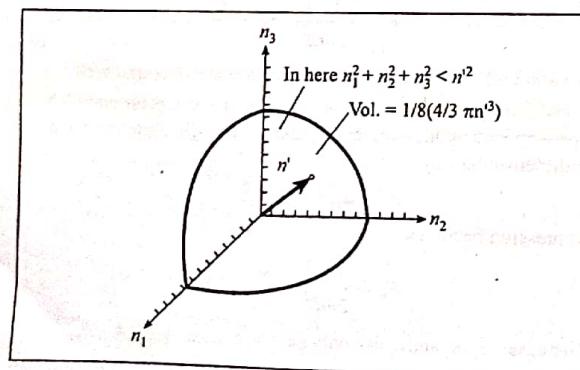


Fig. 1.14 Sphere created by radius vector n

But we have, from equation (1.57)

$$\begin{aligned} n^2 &= \frac{2mL^2}{\hbar^2} E = \frac{8mL^2}{\hbar^2} E \\ n &= \left[\frac{8mL^2}{\hbar^2} E \right]^{1/2} \end{aligned} \quad (1.69)$$

Substituting for n in equation (1.58) yields

$$\begin{aligned} N &= \frac{1}{8} \frac{4\pi}{3} \left[\frac{8mL^2}{\hbar^2} E \right]^{3/2} \\ N &= \frac{\pi}{6} K^{3/2} E^{3/2} \end{aligned} \quad (1.70)$$

$$\text{where } K = \frac{8mL^2}{\hbar^2} \quad (1.71)$$

The expression (1.70) gives us the number of energy states lying within the positive octant of the sphere of radius n. We have taken only 1/8th of the volume of sphere, which is its volume of positive octant. The number of states represents the number of energy levels in quantum space.

Differentiating equation (1.70) with respect to energy E yields

$$\frac{dN}{dE} = \frac{\pi}{4} K^{3/2} E^{1/2} \quad (1.72)$$

In the above expression, $\frac{dN}{dE} = Z(E) = \text{Density of states}$

For an electron placed in three-dimensional potential box with all sides equal to L, then the volume of the box is

$$V = L^3$$

Then the density of states function becomes

$$\begin{aligned} Z(E) &= \frac{dN}{dE} = \frac{\pi}{4} \left[\frac{2^2 \times 2mL^2}{\hbar^2} \right]^{3/2} E^{1/2} \\ &= \frac{\pi}{4} \frac{8L^3}{\hbar^3} (2m)^{3/2} E^{1/2} \\ &= 2\pi V \frac{(2m)^{3/2}}{\hbar^3} E^{1/2} \\ &= CE^{1/2} \end{aligned} \quad (1.73)$$

where

$$C = 2\pi V \frac{(2m)^{3/2}}{\hbar^3} \quad (1.74)$$

$$Z(E) = CE^{1/2}$$

Equations (1.72) and (1.74) represent the density of states function. The density of states function can be defined as "number of energy states per unit energy in an energy interval of dE ".

In the above figure (1.15) the curve representing $Z(E)$ is hyperbola where all energy levels less than E_F are taken into account. The shaded area represents the number of energy states in an elementary energy interval dE .

$$dN = Z(E)dE \quad (1.75)$$

From figure (1.15) and equation (1.75) it is clear that higher the energy, the more are the number of states available and lower the energy, fewer are the energy states available. In quantum mechanics we are concerned not only about the number of states and density of states, but also about how much of these energy states are actually occupied by electrons. We never can say precisely how many of these states are or can be occupied by electrons but can with fair accuracy predict this. To predict the number of energy states occupied by electrons, we will use suitable statistical tools that are applicable in quantum mechanics.

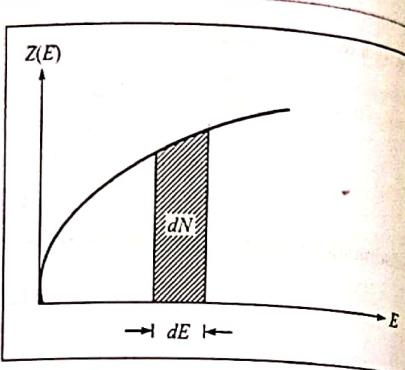


Fig. 1.15 Density of states vs. energy functions

1.5 Fermi-Dirac Distribution Function

To describe the classical physics Maxwell-Boltzmann statistics is used. But this is not applicable for systems in quantum mechanical domain. In quantum mechanics the distribution functions are governed by the fact that similar indistinguishable particle can be differentiated according to their spatial location and orientation. To describe the energy distribution in quantum mechanical system, we use what is called Fermi-Dirac distribution function. The particles, which obey the Fermi-Dirac distribution function, are called fermions. Fermions obey the Pauli exclusion principle and only one fermion can occupy a given quantum state at once.

Fermi-Dirac distribution function is written as

$$F(E) = \frac{1}{\left(1 + e^{\frac{E-E_F}{kT}}\right)} \quad (1.76)$$

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

E = Energy of the electron

E_F = Fermi energy level

T = absolute temperature

$k = 1.38 \times 10^{-23}$ J/K, called Boltzmann's universal constant.

Figure (1.16) shows the Fermi-Dirac distribution function for three different temperatures. From expression (1.76), when $E < E_F$ at $T=0K$

$$F(E) = \frac{1}{1 + \exp\left(-\frac{\Delta E}{kT}\right)} = \frac{1}{1 + e^{-\infty}} = 1$$

$$\Delta E = E_F - E$$

where

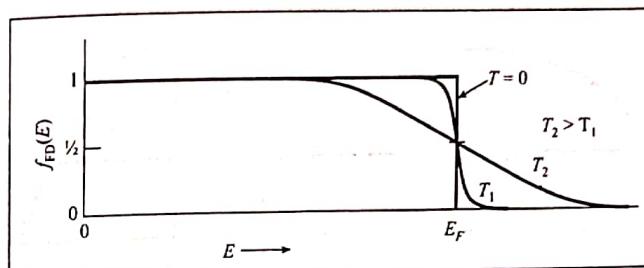


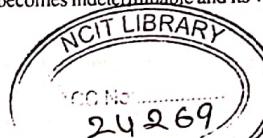
Fig. 1.16 Fermi-Dirac distribution

When at $T=0K$, $E=E_F$, the Fermi-Dirac distribution function becomes indeterminate and its value changes from 1 to 0 for the same condition.

For

$$T = 0K \text{ and } E > E_F$$

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



i.e. the probability of occupation of energy state with energy greater than Fermi energy at absolute zero is zero. Simply saying, electron cannot occupy a state higher than Fermi level at 0K.

The higher the temperature, the higher is the probability of higher energy states being occupied by the electron. One interesting property of the Fermi energy is that for any temperature the occupation index is 0.5 if the energy of the electron is equal to Fermi energy. This can be simply understood as the higher temperature imparts energy to the electron in the metal, then the electrons can be excited to higher energy levels, so the probability of finding them in these regions increases.

At higher temperatures, the Fermi-Dirac distribution function approximates to Boltzmann's classical distribution function. The occupation index rapidly decreases from 1 to 0 within the energy interval $2\Delta E$. When $E >> E_F$,

$$F(E) \approx \exp\left[-\frac{E - E_F}{kT}\right] \quad (1.77)$$

By using the Fermi function or the occupation index we can calculate the number of energy states actually occupied by the electrons. Number of energy states per unit energy in an energy interval dE is simply found by multiplying the density of states function $Z(E)$ by probability of occupation function $F(E)$. But to account for Pauli exclusion principle, which states that each state is occupied by two electrons with opposite spins, we should multiply again by 2. So, mathematically, we can write

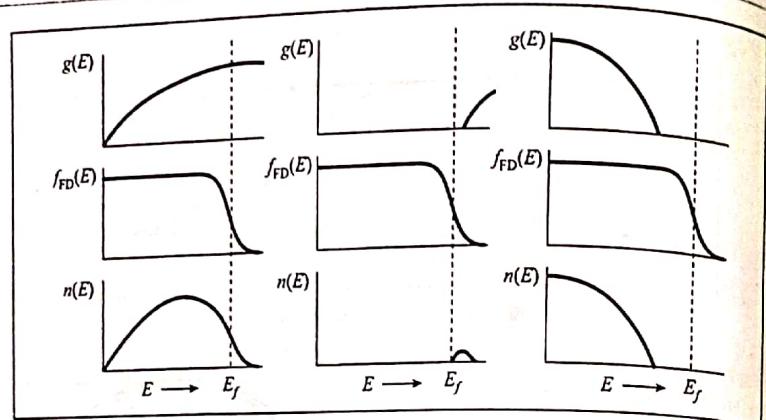
$$N(E) = 2Z(E)F(E) \quad (1.78)$$

or,

$$N(E) = 2CE^{1/2} \frac{1}{1 + \exp\left[\frac{E - E_F}{kT}\right]} \quad (1.79)$$

In above expression (1.79), $N(E)$ is called "Population density" of electrons and gives account for number of electrons per unit energy in the given energy interval.

The three functions density of states function: $Z(E)$, probability of occupation function $F(E)$ and population density function $N(E)$ are plotted below in figure 1.17.

Fig. 1.17 Three different functions - $Z(E)$, $F(E)$ and the corresponding $N(E)$.

In the above figure 1.17 the area under the curve in $N(E)$ vs E represents the number of electrons with energy equal to or less than E_n . For an elementary energy interval of dE the number of electrons can be found as

$$dN = N(E)dE \quad (1.80)$$

Integrating equation (1.80) from $E=0$ to $E=E_F$, we can get

$$\begin{aligned} N' &= \int_0^{E_F} N(E)d(E) \\ &= \int_0^{E_F} 2CE^{1/2}dE \\ &= \frac{4}{3}CE_F^{3/2} \\ &= \frac{4}{3}\frac{2\pi V}{h^3}(2m)^{3/2}E_F^{3/2} \\ &= \frac{8\pi V}{3h^3}(2m)^{3/2}E_F^{3/2} \end{aligned}$$

Now, let n be the number of electrons per unit volume, then

$$n = \frac{N'}{V} = \frac{8\pi}{3h^3}(2m)^{3/2}E_F^{3/2} \quad (1.81)$$

Solving equation (1.81) for E_F yields

$$E_F = \frac{\hbar^2}{2m} \left(\frac{3n}{8\pi} \right)^{\frac{2}{3}} \quad (1.82)$$

By using expression (1.82), Fermi Level for any metal can be calculated if number of electrons per unit volume for that metal is known. And, conversely, if Fermi level is given we can calculate the electron concentration, i.e., number of electrons per unit volume.

Putting

$$h = 6.624 \times 10^{-34} \text{ J.s}$$

$m = 9.1 \times 10^{-31} \text{ kg}$ in the expression (1.82), we obtain

$$E_F = 3.65 \times 10^{-19} \times N^{2/3} \text{ eV}$$

(1.83)

where

$$1 \text{ eV} = 1.609 \times 10^{-19} \text{ J}$$

1.6 Thermionic Emission, Work Function

When metal is heated scores of electrons within it become more energetic and at some point they can even leave the surface of the metal. The process of ejection of electrons from the surface of the metal at rather high temperature is called **thermionic emission**. Not all the electrons, which are excited by heating, are able to leave the metal surface. There is a threshold (minimum) value of energy, which the electron must possess if it is to leave the metal surface. This threshold value of energy is called **work function** of the metal. Work function is denoted by Greek alphabet Φ .

At $T=0\text{K}$, all the states up to Fermi level are filled and above are empty. An electron needs at least an energy equal to $E_F + \Phi$ to escape from the metal. We assume that the potential energy of the electron is zero and it only possesses kinetic energy. Then, we can express its energy in terms of momentum in three-dimensional geometry as

$$E = \frac{1}{2m}(P_x^2 + P_y^2 + P_z^2) \quad (1.84)$$

For the electron to be able to escape the metal it must have in addition to right value of energy, right direction as well. For example if x is the coordinate perpendicular to metal surface, the electron momentum must satisfy the following condition

$$\frac{P_x^2}{2m} > \frac{P_{x_0}^2}{2m} = E_F + \Phi \quad (1.85)$$

where P_{x_0} is the threshold momentum.

But by satisfying the above condition does not mean that the electron can escape the metal. In quantum mechanics, there is still probability that the electron will be reflected from the barrier. So, we must introduce a new parameter known as reflection coefficient $r(P_x)$.

$$\text{Probability of escape} = 1 - r(P_x)$$

The number of electrons per unit volume having momentum between P_x and $P_x + dP_x$ is given by $N(P_x)dP_x$ in analogy with the number of electrons in energy interval between E and $E + dE$ which was given by $N(E)dE$.

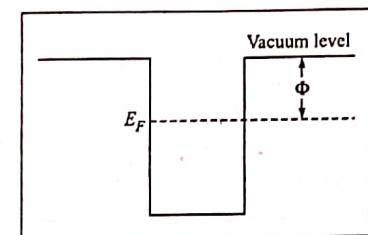


Fig. 1.18 Fermi level and work function in metal

Multiplying $N(P_x) dP_x$ by velocity of electrons associated with the momentum P_x (thus the kinetic energy $\frac{P_x^2}{2m}$), we will get the number of electrons arriving at the surface of metal per unit second per unit time given by $\frac{P_x}{m} N(P_x) dP_x$.

$$\left[\because \frac{d(p_x^2/2m)}{dP_x} = \frac{P_x}{m} \right]$$

Similarly, number of escaping electrons is given by

$$(1 - r(P_x)) \frac{P_x}{m} N(P_x) dP_x$$

Adding contribution by the entire electrons, which have momenta greater than P_{x0} , the emission current density can be written as

$$J = \frac{e}{m} \int_{P_{x0}}^{\infty} [1 - r(P_x)] P_x N(P_x) dP_x, \text{ A/m}^2 \quad (1.86)$$

In the above expression (1.86), current density

$$J = \frac{I}{A}, \quad \text{and} \quad I = \frac{dQ}{dt} = \frac{de}{dt}$$

where
I = current in A,
A = surface area, m^2
Q = charge
 e = electron charge
t = time interval

The number of electrons in an incremental momentum range can be obtained in the manner similar to the number of electrons in incremental energy range.

Comparing equations (1.65) and (1.84), we obtain

$$P_x = \frac{h}{2} n_x, \quad P_y = \frac{h}{2} n_y \quad \text{and} \quad P_z = \frac{h}{2} n_z \quad (1.87)$$

We know that the number of states in a cube of side 1 is equal to 1. Similarly, the number of states in volume of sides dn_x, dn_y, dn_z is given by

$$\left[\frac{2}{h} \right]^3 dP_x dP_y dP_z \quad (1.88)$$

As in the case of number of states with momentum not exceeding the given P_{x0}, P_{y0} and P_{z0} is found by multiplying equation (1.88) by 1/8.

$$\begin{aligned} & \frac{1}{8} \left[\frac{2}{h} \right]^3 dP_x dP_y dP_z \\ &= \frac{dP_x dP_y dP_z}{h^3} \end{aligned} \quad (1.89)$$

Now, as we found density of states function in an energy interval, we can find the same in respective momentum interval and then by multiplying equation (1.89) by 2 to account for counter spinning electrons

$$Z(P_x, P_y, P_z) = 2 \frac{dP_x dP_y dP_z}{h^3} \frac{1}{dP_x dP_y dP_z} \quad (1.90)$$

$$Z(P_x, P_y, P_z) = \frac{2}{h^3}$$

The number of electrons in momentum range $P_x + dP_x, P_y + dP_y$ and $P_z + dP_z$ is given by

$$N(P_x, P_y, P_z) dP_x dP_y dP_z = \frac{2}{h^3} \frac{dP_x dP_y dP_z}{1 + e^{\frac{E - E_F}{kT}}} \quad (1.91)$$

$$\text{where } E = \frac{1}{2m} (P_x^2 + P_y^2 + P_z^2)$$

To determine the number of electrons in the momentum range P_x to $P_x + dP_x$, the expression (1.91) should be integrated for all values of P_y and P_z .

$$N(P_x) dP_x = \frac{2}{h^3} \int \int \frac{dP_y dP_z}{\exp \left[\left\{ \frac{1}{2m} (P_x^2 + P_y^2 + P_z^2) - E_F \right\} / kT \right] + 1} \quad (1.92)$$

When the work function $\Phi \gg kT$, the unity term from the denominator of expression (1.92) can be neglected. And, by using integral table, we get

$$N(P_x) dP_x = \frac{4\pi n k T}{h^3} \exp(E_F/kT) \exp(-P_x^2/2mkT) dP_x \quad (1.93)$$

By comparing equations (1.83) and (1.93) and taking $r(P_x) = r$, we get

$$J = A_0 (1 - r) T^2 e^{-\frac{E_F}{kT}} \text{ - Richardson's equation} \quad (1.94)$$

$$\text{where } A_0 = \frac{4\pi n k^2}{h^3} = 1.2 \times 10^6 \text{ Am}^{-2} \text{ K}^{-2} \quad (1.95)$$

In expression (1.94), the emission current density is heavily dependent upon both the work function of the material and its temperature. Since both work function and temperature figure up in exponential function, a small change in either of these two parameters will cause the emission current density to change by very large amount. The increase in temperature and decrease in work function both will cause the emission current density to increase exponentially.

The stages in measuring the thermionic emission current are discussed below.

1.6.1 Schottky Effect

As a new approach for measuring thermionic emission we will use first a method known as image charge method in electrostatics. Based upon image charge method, any charge placed at a distance x from a conducting surface can be substituted by the original charge at the initial position and an image charge with opposite polarity that is situated at a distance similar to that of original charge but in just opposite direction.

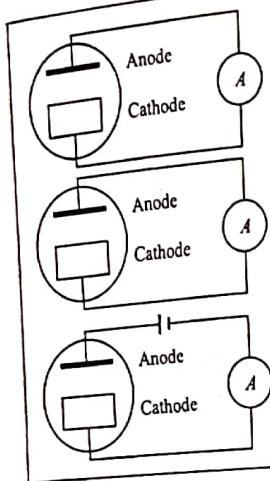


Fig. 1.19 Measurement of emission current (a) in open air, (b) in vacuum tube (c) in vacuum tube with the application of external emf.

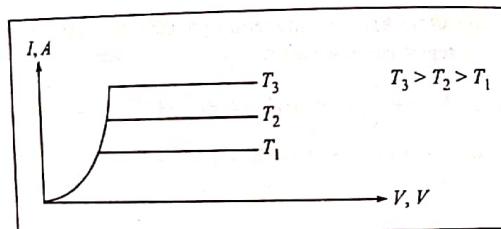


Fig. 1.20 Emission current as a function of applied voltage for different temperatures.

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

$$F = \frac{e^2}{4\pi\epsilon_0(2x)^2} = \frac{e^2}{16\pi\epsilon_0 x^2} \quad (1.96)$$

where e = charge of an electron = 1.6×10^{-19} C

ϵ_0 = absolute permittivity of the air = 8.854×10^{-12} F/m

The potential energy can be found be as an integral of force F given by equation (1.96) from x to ∞ .

$$V(x) = \int_x^{\infty} F(x) dx = \frac{e^2}{16\pi\epsilon_0 x^2} \quad (1.97)$$

Now, if we include this image field, then the potential barrier at metal-vacuum interface becomes shown in figure (1.22).

When the cathode is heated, electrons are emitted from its surface and initially current starts flowing but the flow is impeded by air molecules. So, this arrangement cannot measure the emission current

When the cathode is heated, electrons are emitted from its surface and current starts flowing through the vacuum till the build up of charge cloud that will oppose further flow. Current measured will be less than actual current

Current flow will be maintained continuously by the applied external emf. This arrangement will measure the total emission current.

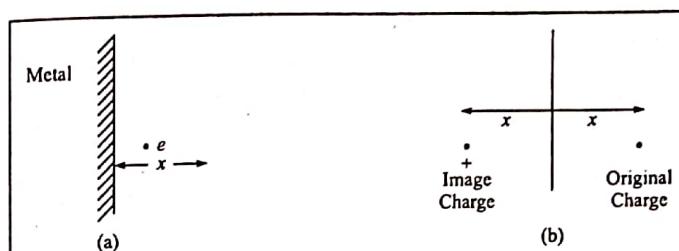


Fig. 1.21 Charge metal interface (a), with image charge (b)

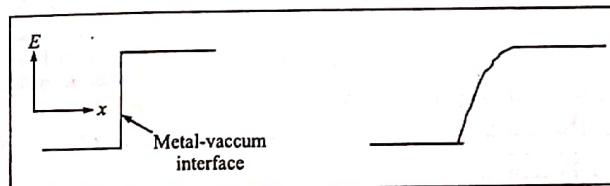


Fig. 1.22 (a) without image charge, (b) with image charge

The application of image field does not itself make any difference in the work function and potential energy barrier for electron at metal-vacuum interface. But if apply external electric field, and then there will be clear difference.

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

$$V(x) = -eEx \quad (1.98)$$

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

$$PE(x) = E_F + \Phi - \frac{e^2}{16\pi\epsilon_0 x} - eEx \quad (1.99)$$

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

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

$$V_{\max}(x) = -\left(\frac{e^3 E}{16\pi\epsilon_0} \right)^{1/2} \quad (1.100)$$

$V_{\max}(x)$ is the maximum reduction in potential energy barrier after taking into account at the effect of image field and applied external field.

The effective work function can now be written as

$$\Phi_{\text{eff}} = \Phi - \left(\frac{e^3 E}{16\pi\epsilon_0} \right)^{1/2} \quad (1.101)$$

The reduction in work function is shown in figure 1.23.

The reduced work function means the increase in emission current density as will be seen from the expression given below.

$$J = A_0(1-r)T^2 e^{-\frac{\Phi_{eff}}{kT}} \quad (1.102)$$

Equation (1.102) is called Richardson's equation for Schottky effect. For simplicity we can omit the reflection coefficient taking its value equal to zero and the equation (1.102) can be written as

$$J = A_0 T^2 e^{-\frac{\Phi_{eff}}{kT}} \quad (1.103)$$

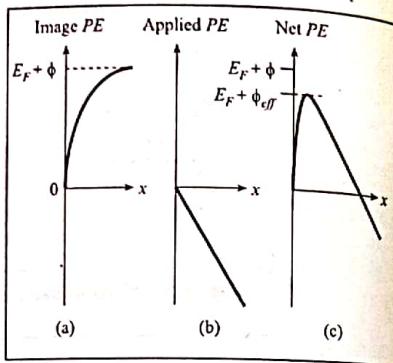


Fig. 1.23 Change in work function as the result of application of external field and use of image field.

1.7 Fermi Level at Equilibrium, Contact Potential

1.7.1 Contact Potential

As we already know each metal has different work function. For each metal different values of energy are required so that electron can be emitted. Two metals with different work functions are brought together.

Each metal has different work function signifying that their Fermi levels are different. But when these two metal with different Fermi level (work function as well) are brought into contact, electrons from metal 1 with higher Fermi level will start crossing over to metal 2 with lower Fermi level by tunneling to occupy the lower energy states that are vacant. This electron transfer from metal 1 to metal 2 reduces the total energy of the electrons in metal1-metal2 system. Metal 1 having lost electrons becomes positively charged whereas metal2 having received electrons becomes negatively charged. Consequently a potential difference is developed at the junction called **contact potential**. This process continues till the contact potential is large enough to prevent the further transfer of electrons from metal 1 to 2. So the system reaches equilibrium. At equilibrium, the Fermi level of both the metal will be same. The **contact potential** due to difference in work functions of the metals brought into contact can be calculated as

$$\begin{aligned} e\Delta V &= \Phi_2 - \Phi_1 \\ \Delta V &= \frac{\Phi_2 - \Phi_1}{e} \end{aligned} \quad (1.104)$$

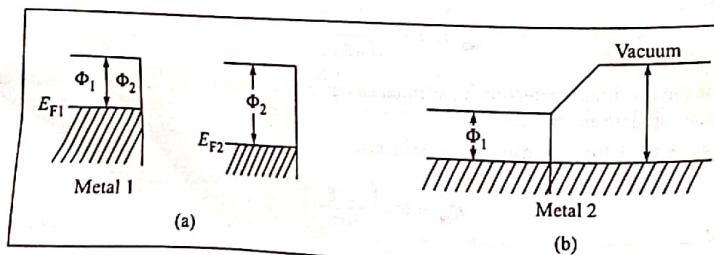


Fig. 1.24 (a) when metals are separate, (b) when metals are brought together.

1.7.2 Seebeck Effect

When two metals, one hot and the other cold are brought together, more energetic electrons in the hot metal will diffuse to the cold metal where electrons are less energetic. The electrons diffusing to cold side from the hot leave behind exposed positive ions whereas in the hot region there is excess of negative charge. So, there is net potential difference between the hot metal and cold metal due to the difference in temperature. This is called **Seebeck effect**, which states that "thermo-emf in a thermocouple can be set maintaining temperature gradient without using any cell or generator".

$$S = \frac{\Delta V}{\Delta T} \quad (1.105)$$

where S = Seebeck coefficient or thermo-electric power

ΔV = induced potential difference or thermo-emf

ΔT = temperature difference

If V_{HC} is the thermo-emf of the thermocouple arrangement, then we can write

$$V_{HC} \propto \Delta T \text{ i.e. } V_{HC} = S \Delta T \quad (1.106)$$

The values of Seebeck coefficient for different metals are different. S represents potential of cold junction with respect to the hot junction. Mostly S is negative but Cu has S positive. According to Mott_Jones, the Seebeck coefficient is given by

$$S = -\frac{\pi^2 k^2 T}{3eE_{F0}} \quad (1.107)$$

where E_{F0} is the Fermi energy at 0K.

Seebeck effect can be utilized to measure temperature in thermocouple arrangement where one junction (normally cold junction) is maintained at a constant reference temperature and the temperature of the hot junction is measured. The potential at each junction will depend upon their respective Seebeck coefficients. And if we connect these two junctions by wire and put a voltmeter across them, we can measure the thermoelectric potential difference. If ΔV_H and ΔV_C are the potentials of hot and cold junctions and S_H and S_C are their respective Seebeck coefficients, the potential difference can be found as

$$V_{HC} = \Delta V_H - \Delta V_C = \int_{T_0}^T (S_H - S_C) dT \quad (1.108)$$

where T_0 and T are the temperatures of cold junction (reference junction) and hot junction respectively.

For any thermo-couple, we can relate the potential difference and temperature difference as

$$V_{HC} = a\Delta T + b(\Delta T)^2 \quad (1.109)$$

Equation (1.109) is called thermocouple equation in which a and b are constants. The plot of V_{HC} and ΔT is shown in figure 1.25, where T_N is called neutral temperature at which thermo-emf is maximum. The temperature T_i at which the thermo-emf again falls to zero is called inversion temperature. For Fe-Cu thermo-couple, $T_N = 270^\circ\text{C}$ and $T_i = 540^\circ\text{C}$.

1.8 Solved Numerical Examples

- Calculate the wavelength of a 50 gram golf ball traveling at a velocity of 20ms^{-1} .

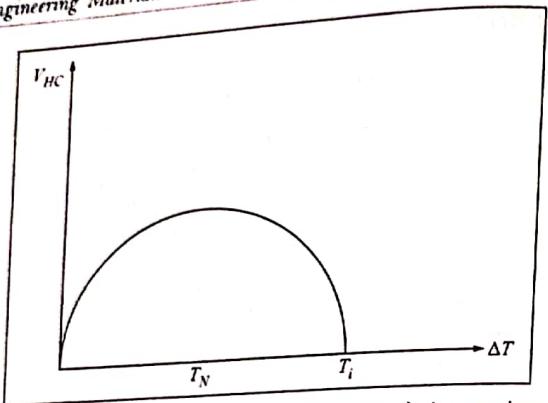


Fig. 1.25 Variation of thermo-emf with change in temperature

Solution:

We have, according to de Broglie's equation, wavelength of the golf ball

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.624 \times 10^{-34} \text{ Js}}{(50 \times 10^{-3} \text{ kg})(20 \text{ ms}^{-1})} = 6.63 \times 10^{-34} \text{ m}$$

The wavelength is so small that the golf ball will not exhibit any wave effect.

2. Calculate the wavelength of a proton traveling at 2200 ms^{-1} **Solution:**Mass of the proton = $1.67 \times 10^{-27} \text{ kg}$

So, the wavelength can be found from

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.624 \times 10^{-34} \text{ Js}}{(1.67 \times 10^{-27} \text{ kg})(2200 \text{ ms}^{-1})} = 1.8 \times 10^{-10} \text{ m} = 0.18 \text{ nm}$$

3. Find the wavelength of an electron accelerated by 100V.**Solution:**The whole potential energy ($=eV$) will be converted into kinetic.

$$KE = PE$$

$$\frac{p^2}{2m} = eV$$

$$p = (2meV)^{\frac{1}{2}}$$

Now the wavelength of the electron will be

$$\lambda = \frac{h}{p} = \frac{h}{(2meV)^{\frac{1}{2}}} = \frac{6.624 \times 10^{-34} \text{ Js}}{[(9.11 \times 10^{-31} \text{ kg})(1.6 \times 10^{-19} \text{ C})(100 \text{ V})]^{1/2}} \\ = 1.23 \times 10^{-10} \text{ m} = 0.123 \text{ nm}$$

$$\begin{aligned} N^{\omega} &\rightarrow h \\ \frac{h}{mv^2} &= \frac{eV}{m} \\ \frac{1}{v^2} &= \frac{eV}{mv^2} \end{aligned}$$

4. What is the energy of blue photon with a wavelength of 450nm?**Solution:**

The energy of the photon is given by

$$E = hf \quad \text{and} \quad f = \frac{c}{\lambda} \quad \text{where } c = 3 \times 10^8 \text{ m/s}$$

$$E = \frac{(6.624 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{450 \times 10^{-9} \text{ m}} = 4.4 \times 10^{-19} \text{ J}$$

which is very small and is generally expressed in electron-volt.

So, the electron energy $E = 2.75 \text{ eV}$.**5. In the photoelectric experiment, green light, with a wavelength of 522 nm is the longest wavelength radiation that can cause photoemission of electron from a clean sodium surface. Calculate the work function of sodium. If ultraviolet radiation with a wavelength 250 nm is incident to the sodium surface, what will be the kinetic energy of the photo-emitted electrons?****Solution:**At threshold, the photon energy just causes the photoemission, that is, the electrons just overcome the potential barrier Φ . Thus the work function of sodium

$$hf = \Phi$$

$$\Phi = \frac{hc}{\lambda} = \frac{(6.624 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{522 \times 10^{-9} \text{ m}} = 2.38 \text{ eV}$$

The energy of the incoming photon is

$$E_1 = \frac{hc}{\lambda_1} = \frac{(6.624 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{250 \times 10^{-9} \text{ m}} = 4.96 \text{ eV}$$

Only 2.38eV is required to eject electrons from the surface of sodium. So, the excess energy ($4.96 \text{ eV} - 2.38 \text{ eV} = 2.58 \text{ eV}$) will go to the electron in the form of kinetic energy.**6. An electron is confined to an infinite potential well of size 0.1nm. Calculate the ground energy of the electron and radian frequency. How this electron can be put to the third energy level?****Solution:**

The energy of electron confined to an infinite potential well is given by

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

 $n = 1$ for ground state and $L = 0.1 \text{ nm}$. So,

$$E_1 = \frac{1 \times (6.624 \times 10^{-34} \text{ Js})^2}{8 \times (9.11 \times 10^{-31} \text{ kg})(0.1 \times 10^{-9})^2} = 37.6 \text{ eV}$$

Radian frequency of electron associated with this energy is

$$\omega = \frac{E}{\hbar} = \frac{37.6 \times 1.6 \times 10^{-19} \text{ J}}{1.055 \times 10^{-34} \text{ Js}} = 5.71 \times 10^{16} \text{ rad.s}^{-1}$$

Energy of electron in third energy level is

$$E_3 = n^2 E_1 = 3^2 \times 37.6 \text{ eV} = 338.4 \text{ eV}$$

The short fall in energy required to put the electron in to the third level is

$$E_3 - E_1 = 338.4 \text{ eV} - 37.6 \text{ eV} = 300.8 \text{ eV}$$

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

$$\lambda = \frac{hc}{E} = \frac{(6.624 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ ms}^{-1})}{300.8 \times 1.6 \times 10^{-19} \text{ J}} = 4.12 \text{ nm}$$

Photon with a wavelength of 4.12 nm is a x-ray photon.

7. An apple of 100g is confined to move within a rigid crate of 1m size. What is the minimum speed of the object? What should be the quantum number n if the object is moving with a speed of 1m/s?

Solution:

Since the object is within rigid walls, we can PE outside the walls as an infinite and calculate energy as

$$E_n = \frac{n^2 h^2}{8mL^2} \text{ This energy will be minimum for } n=1. \text{ So,}$$

$$E_1 = \frac{1^2 (6.624 \times 10^{-34} \text{ Js})^2}{8 \times (0.1 \text{ kg}) (1 \text{ m})^2} = 5.45 \times 10^{-67} \text{ J} = 3.4 \times 10^{-48} \text{ eV}$$

So, the minimum velocity can be calculated using the above kinetic energy

$$E_1 = \frac{mv^2}{2}$$

$$v = (2E_1/m)^{1/2} = (2 \times 5.45 \times 10^{-67} \text{ J}/0.1 \text{ kg})^{1/2} = 3.3 \times 10^{-33} \text{ ms}^{-1}$$

This speed can not be measured by any instrument and thus for all practical purposes the apple within the crate is at rest.

8. 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

$$\Delta p_x \Delta x \geq \hbar$$

$$\Delta p_x = \frac{\hbar}{\Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{0.1 \times 10^{-9} \text{ m}} = 1.054 \times 10^{-24} \text{ kg.m.s}^{-1}$$

Now, the uncertainty in kinetic energy associated with this uncertainty in momentum

$$\Delta E(KE) = \frac{\Delta p_x^2}{2m} = \frac{(1.054 \times 10^{-24} \text{ kg.m.s}^{-1})^2}{2 \times 9.11 \times 10^{-31} \text{ kg}} = 6.1 \times 10^{-19} \text{ J} = 3.81 \text{ eV}$$

9. Estimate the minimum velocity of an apple of 100g confined to a crate of 1m size.

Solution:

Uncertainty in momentum of apple is

$$\Delta p_x = \frac{\hbar}{m \Delta x}$$

$$\Delta v_x = \frac{\Delta p_x}{m} = \frac{\hbar}{m \Delta x} = \frac{1.054 \times 10^{-34} \text{ Js}}{(0.1 \text{ kg}) (1 \text{ m})} = 1.054 \times 10^{-33} \text{ ms}^{-1}$$

Quantum nature of the universe implies that the apple in the crate is moving with a velocity of the order of 10^{-33} ms^{-1} and will take the apple to cover an atomic distance of 0.1 nm around 10^{19} years.

10. Prove the uncertainty principle $\Delta p_x \Delta x \geq \hbar$ from an analogy with the classical wave frequency f , having an uncertainty of frequency Δf when measured over a finite period of Δt .

Solution:

Let f_1 and f_2 be two frequencies which differ by Δf when measured over Δt . Time to observe one beat is $1/\Delta f$ second. One beat may certainly be observed if $\Delta t/1/\Delta f$ which will lead to $\Delta t \Delta f \geq 1$

The distance traveled by wave in time Δt will be $\Delta x = v \Delta t$

$$\Delta x \geq v \Delta t$$

But

$$f = v/\lambda \text{ or, } \frac{\Delta f}{\Delta \lambda} = -\frac{v}{\lambda^2}$$

or

$$\frac{v}{\Delta f} = -\frac{\lambda^2}{\Delta \lambda}$$

$\therefore \Delta x \Delta \lambda \geq \lambda^2$ If λ is measured over distance Δx , the wavelength is uncertain by $\Delta \lambda$. We also have

$$\lambda = \frac{h}{p}$$

$$\left| \frac{\Delta \lambda}{\Delta p} \right| = \frac{h}{p^2}$$

$$\Delta \lambda = \frac{h}{p^2} \Delta p$$

$$\Delta x \frac{h}{p^2} \Delta p \geq \lambda^2$$

So,

$$\Delta x \frac{h}{p^2} \Delta p \geq \frac{h}{p^2}$$

$$\Delta x \Delta p \geq h$$

We can come to another interesting and important conclusion. Since energy is associated with frequency, the frequency uncertainty will lead to energy uncertainty.

$$\Delta E = \hbar \Delta f$$

But,

$$\Delta f \Delta t \geq 1$$

$$\Delta f \geq \frac{1}{\Delta t}$$

So,

$$\Delta E \geq \frac{h}{\Delta t}$$

$$\Delta E \Delta t \geq h$$

A particle having an energy E for an interval Δt will have its energy uncertain by ΔE .

11. Calculate the number of photons emitted by a radio station broadcasting at 792 kHz operating at 50 W.

Solution:

$$\text{Photon energy} = hf = (6.624 \times 10^{-34} \text{ Js})(792 \times 10^3 \text{ s}^{-1}) = 5.246 \times 10^{-25} \text{ J}$$

$$\text{Number of photon/sec} = 5.246 \times 10^{-25} \text{ J}/(5 \times 1000 \text{ Js}^{-1}) = 9.53 \times 10^{27} \text{ s}^{-1}$$

12. Evaluate the probability that an energy state kT above the Fermi level will be occupied by an electron.

Solution:

Here

$$E = E_F + kT$$

$$F(E) = \frac{1}{1 + \exp[(E - E_F)/kT]} = \frac{1}{1 + \exp[(E_F + kT - E_F)/kT]}$$

$$= \frac{1}{1 + e} \approx 0.27$$

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

Solution:

$$\text{Temperature, } T = 1600 + 273 \text{ K} = 1873 \text{ K}$$

Richardson's equation is

$$J = A_0 T^2 \exp\left[-\frac{\phi}{kT}\right] = (3 \times 10^4 \text{ Am}^{-2} \text{ K}^{-2})(1873 \text{ K})^2 \exp\left[-\frac{2.6 \times 1.6 \times 10^{-19}}{(1.38 \times 10^{-23} \text{ JK}^{-1})(1873 \text{ K})}\right]$$

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

The emission surface area is

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

The saturation current or the maximum current obtainable is

$$I = JA = (1.08 \times 10^4 \text{ Am}^{-2})(2.5 \times 10^{-4} \text{ m}^2) = 2.7 \text{ A}$$

14. Calculate the saturation emission current for the example 8, if the cathode is separated from anode by 1mm and the anode voltage is 4kV.

Solution:

The field at the cathode is

$$E = V/d = 4 \times 1000 \text{ V}/(1 \times 10^{-3} \text{ m}) = 4 \times 10^6 \text{ V/m}$$

The effective work function is

$$\Phi_{\text{eff}} = \Phi - e(eE/16\Phi\epsilon_0)^{1/2}$$

$$\Phi_{\text{eff}} = 2.6 - (1.6 \times 10^{-19} \text{ C}) \times \frac{1}{2} \times \left(\frac{(1.6 \times 10^{-19} \text{ C})(4 \times 10^6 \text{ V/m})}{4\pi \times 8.854 \times 10^{-12} \text{ F/m}} \right) = 2.52 \text{ eV}$$

The new saturation current is

$$I_{\text{new}} = A_0 T^2 \exp(-\Phi_{\text{eff}}/kT) = (3 \times 10^4 \text{ Am}^{-2} \text{ K}^{-2})(1873 \text{ K})^2 \exp\left[-\frac{2.52 \times 1.6 \times 10^{-19} \text{ J}}{1.38 \times 10^{-23} \text{ JK}^{-1} \times 1873 \text{ K}}\right]$$

$$= 4.3 \text{ A}$$

Exercise

- Calculate the De Broglie wave-length associated with a proton moving with a velocity equal to $\frac{1}{20}$ th of the velocity of light. [2.6 $\times 10^{-14}$ m]
- Calculate the smallest possible uncertainty in the position of an electron moving with velocity $3 \times 10^7 \text{ ms}^{-1}$. [3.8 $\times 10^{-12}$ m]
- 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. [0.033 eV]
- Calculate the kinetic energy of a neutron having de Broglie wave-length 1 Å. [0.082 eV]
- If an electron is confined a box of length 10^{12} Å , calculate the minimum uncertainty in its velocity. [1.1 $\times 10^4 \text{ ms}^{-1}$]
- Find the energy of an electron moving in one dimension in an infinitely high potential box of width 1.5 Å. [16.735 eV]
- Prove that the density of states of free electrons (N) and energy E is $Z(E) = \frac{3N}{2E}$.
- Show that the average kinetic energy per electron for 3D free electron gas at 0K is $\frac{3}{5} E_{FO}$. [2.02 eV]
- The density of potassium is 860 kg m^{-3} . Calculate the Fermi energy at 0K.
- X-rays of wavelength 0.91 Å fall on a metal plate having work function 2eV. Find the wavelength associated with emitted photoelectrons.
- Calculate the density of states for 1m³ of Na at Fermi level for T=0K and for 1g-mole of Na.
- Discuss the significance of wave-particle duality in quantum mechanics.
- What is the reason behind some materials being heavier than others? Discuss.
- Explain why silver is a better conductor compared to iron.