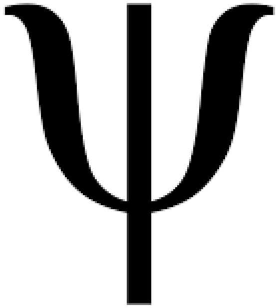
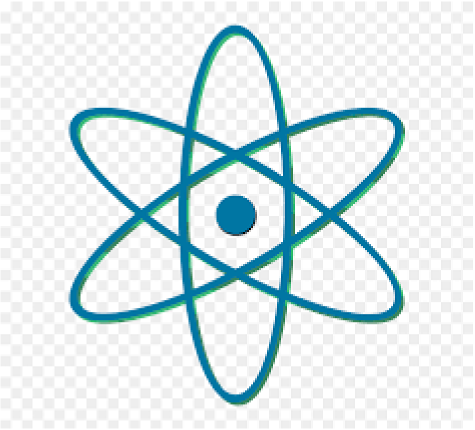
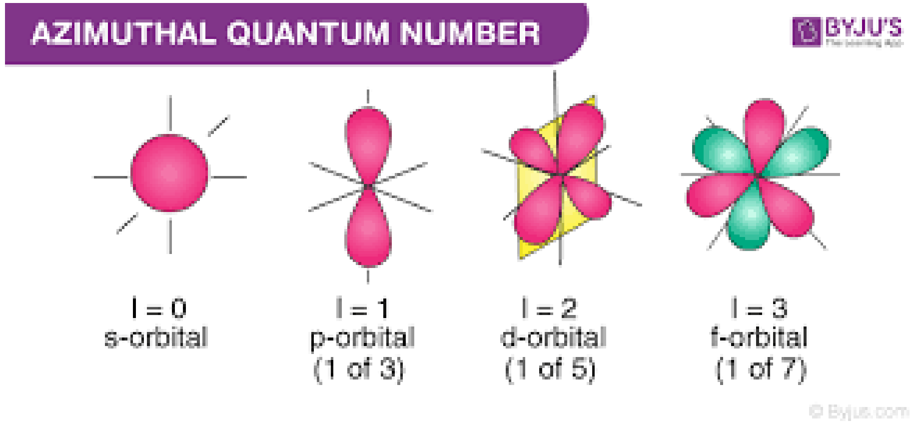
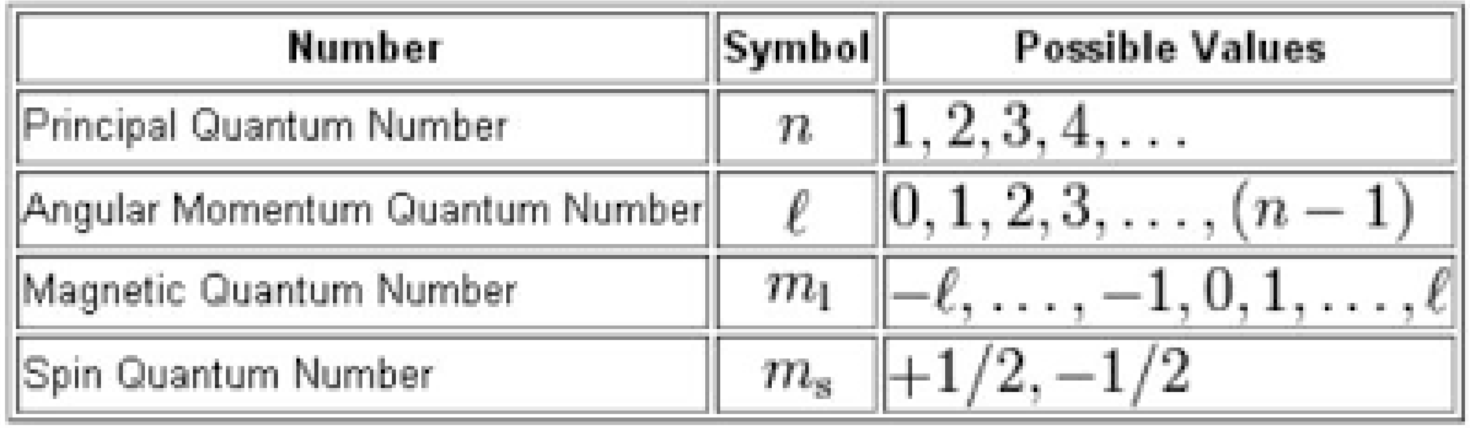




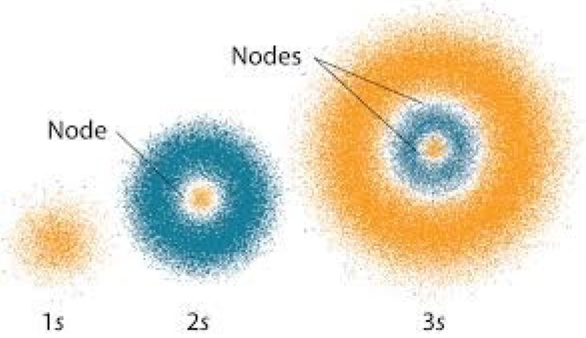


QUANTUM MECHANICS

Dr. Sangeeta Kumar, Dept of Chemistry



Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$
Magnetic Quantum Number	m_l	$-\ell, \ldots, -1, 0, 1, \ldots, \ell$
Spin Quantum Number	m_s	$+1/2, -1/2$



BLACK BODY &BLACK BODY RADIATION

When radiant energy falls on the surface of any body, the radiation is

a) Reflected
b) Absorbed
c) Transmitted

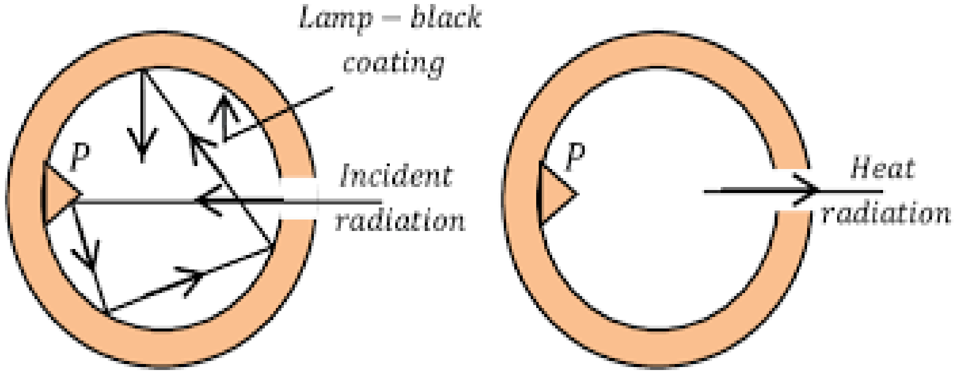
We find that:

- Whole energy is not absorbed
- If radiation is allowed to fall on a blackened material surface or carbon black, it is found that energy is completely absorbed
- A body which completely absorbs the radiant energy falling on it is called a **perfectly black body**.

- The absorption is found to be more perfect if we take a hollow sphere

  blackened on the inside and having a small hole for the entry of

  radiation.

- 

  The inside of this double walled metallic sphere is coated with

  lamp black.

  A black body is a perfect absorber and a perfect radiator.

- The radiation thus emitted is called **Black Body Radiation**.

- It was found that radiation emitted by **Black Body** is not continuous. Max Planck put forward the theory that Black Body cannot have any amount of energy.

He proposed that:

'Energy is emitted or absorbed NOT continuously but discontinuously in the form of packets of energy called **quanta'.**

The energy of each quanta is given by the relation **$E=h\nu$**

where **ν** is the frequency of radiation and '**h**' is the **Planck's constant.**

The value of Planck's constant is 6.6×10^{-34}J sec

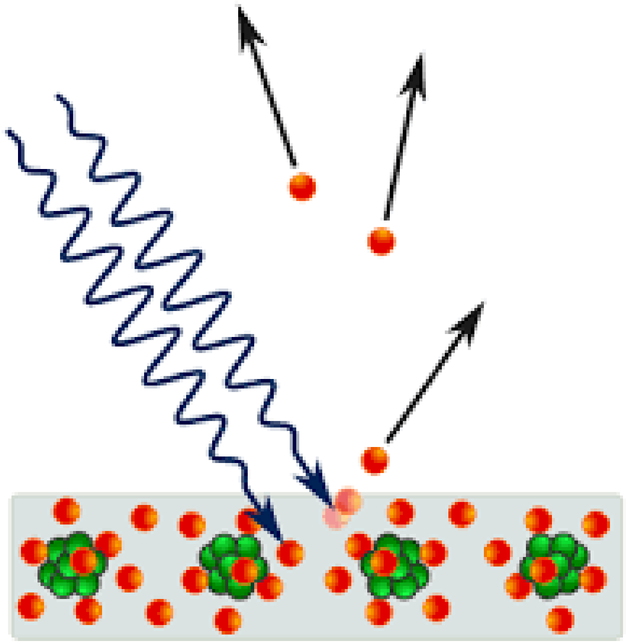
- Total energy emitted or absorbed is either 1 **hν** or 2**hν … …nhν.**

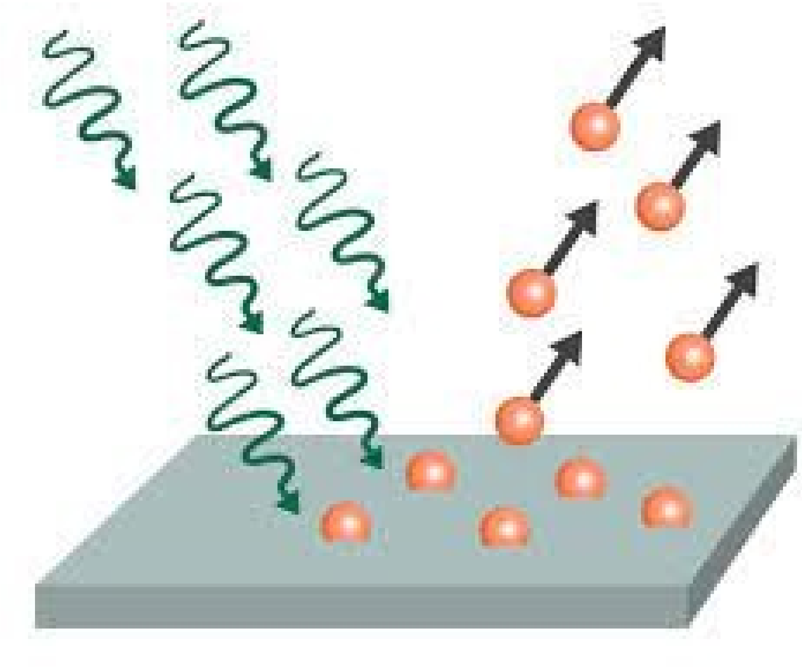
THUS FROM BLACK BODY RADIATION WE CAN CONCLUDE THAT RADIATION HAS PARTICLE LIKE NATURE.

QUANTA IS THE PARTICLE

PHOTOELECTRIC EFFECT

When a beam of light with frequency greater than or equal to a particular value is allowed to strike the surface of a metal, electrons are ejected from the surface of the metal. This is called the **Photoelectric Effect.**





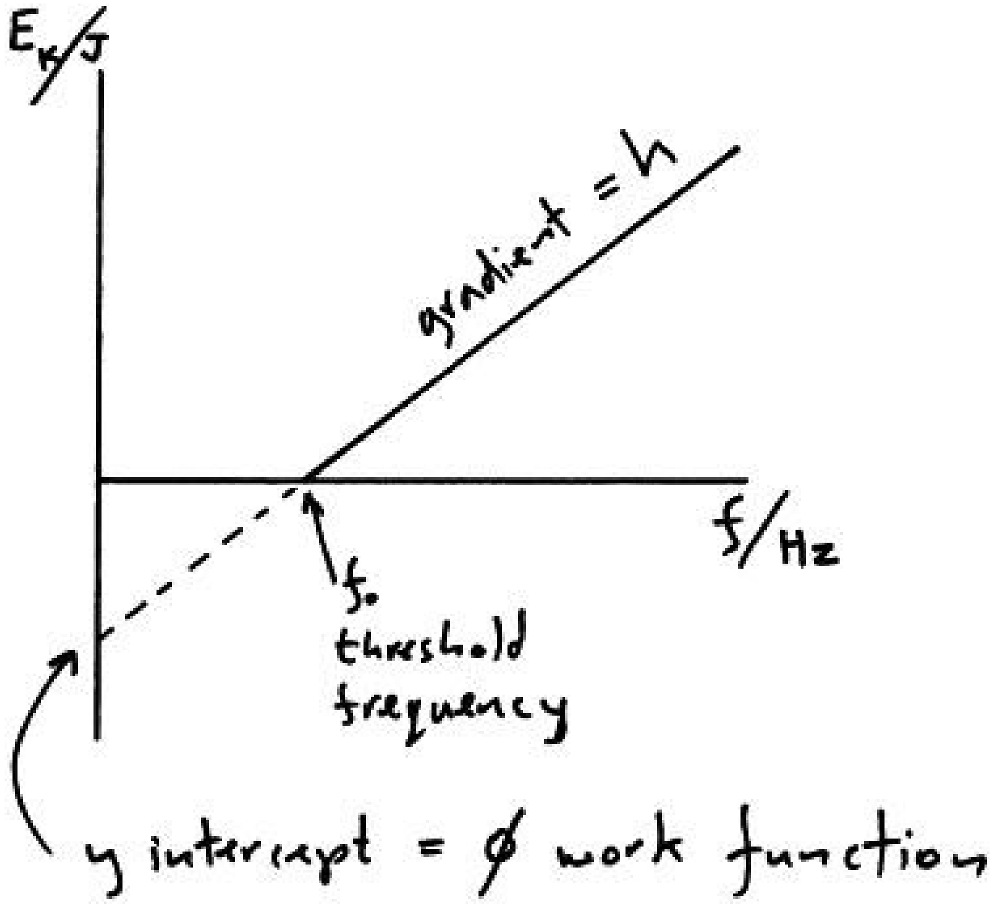
1. The electrons are ejected only if the frequency of the incident light is equal to or greater than a minimum value, called the **Threshold frequency (v_0)$_t$** . Energy associated with threshold frequency is called the **Work Function.**
2. The electrons are emitted instantaneously i.e., there is no time interval between hitting of the metal surface by the light and emission of electrons.
3. The kinetic energy of the emitted electrons depends upon the frequency of the incident light.
4. The number of electrons emitted is proportional to the intensity of incident light.

- Einstein applied Planck’s quantum theory to photoelectric effect.
- According to this theory, each quantum of light called ‘photon’ has energy equal to hν.
- When the photon hits the metal atom, it transfers energy to the electron.
- Energy equal to the threshold value is used for ionizing (release of electron) and remaining energy is converted to kinetic energy of electron.
- The quantity **$h\nu_0$** is called the **Work Function** and is equal to the ionization energy of the metal atom.

Thus,

$$h\nu = h\nu_0 + \tfrac{1}{2}mv^2$$

The x-axis shows the frequency of radiation while the y-axis shows the kinetic energy of electrons.
The y-intercept denotes the work Function.
Photoelectric effect showed a **"Particle like nature"** of light or radiation.



COMPTON EFFECT

A.H Compton observed that if monochromatic X-rays are incident on a material, like graphite, the scattered radiation contained not only the wavelengths of the incident X-rays but also contained radiations of higher wavelength.

This effect is called **Compton Effect**.

The classical theory failed to explain this effect.

The quantum theory could, however, explain this effect.

As the scattering is produced by electrons, it was suggested that it must be due to collision between the X-ray photon and the individual electron that must have resulted in the increase of the wavelength of the scattered X-Rays.

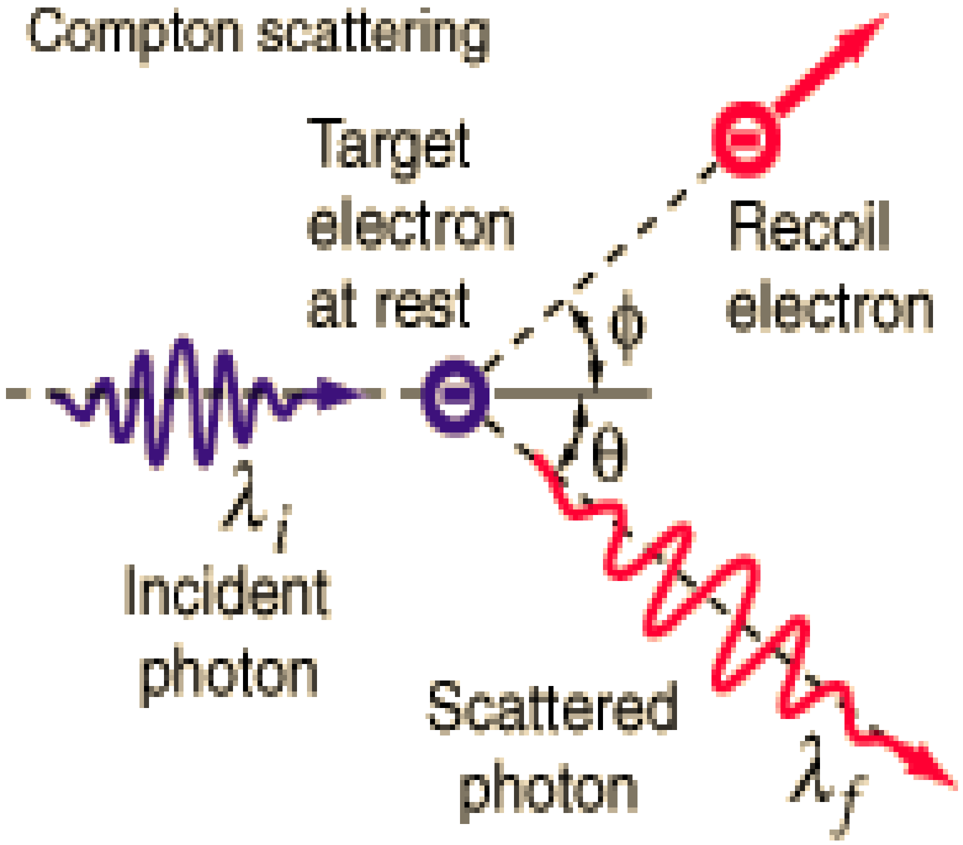
COMPTON EFFECT

If λ is the wavelength of the incident X-ray photon, and λ' the wavelength of the scattered X-ray, then the difference

$\Delta\lambda = \lambda' - \lambda = 2h/mc \times (\sin^2\theta/2)$

where θ is the angle between the incident and scattered X-rays.

$\Delta\lambda$ is called the **Compton shift**.



COMPTON EFFECT

The scattered radiation experiences a wavelength shift that cannot be explained in terms of classical wave theory.

The effect is important because it demonstrates that light cannot be explained purely as a wave phenomenon.

Light must behave as if it consists of particles in order to explain the low-intensity Compton scattering.

Compton's experiment convinced physicists that light can behave as a stream of particles whose energy is proportional to the frequency.

LIGHT HAS WAVE LIKE NATURE AS WELL AS PARTICLE LIKE NATURE.

DUAL NATURE OF LIGHT

It was clearly known that radiation had wave like nature.

The three observations, Black body radiation, Photoelectric effect and Compton effect gave a new insight to the particle like nature of radiation.

Properties like diffraction, interference could be explained by the wave like nature of radiation but it could not explain black body radiation, photoelectric effect and Compton effect.

These effects could be explained only by particle like nature of radiation. That is, radiation was in packets of energy, called the Photon.

DUAL NATURE OF MATTER

Discovery of dual nature of radiation had interesting consequences for a similar concept for matter.

Louis de Broglie , a French aristocrat, connected the mass energy equivalence of Einstein and Planck’s theory of quanta.

$$E=mc^2$$

and $$E=h\nu$$

Equating the two, we get

$$mc^2 = h\nu$$

Putting $\nu=c/\lambda$, $mc^2 = h\,c/\lambda$

$$mc=h/\lambda$$

$$\boxed{p=h/\lambda}$$ ………… de Broglie Equation

DUAL NATURE OF MATTER: DE BROGLIE EQUATION

Through the work of Max Planck, Albert Einstein, Louis de Broglie, Arthur Compton, Niels Bohr, and many others, current scientific theory holds that all particles exhibit a wave nature and vice versa.

This phenomenon has been verified not only for elementary particles, but also for compound particles like atoms and even molecules. For macroscopic particles, because of their extremely short wavelengths, wave properties usually cannot be detected.

De Broglie was awarded the Nobel Prize for Physics in 1929 for his hypothesis

HEISENBERG'S UNCERTAINTY PRINCIPLE

According to classical mechanics, we can determine simultaneously and precisely both position and momentum of a particle at any point in space.

However, with particle like and wave like nature being equally important, the properties of microscopic bodies are different from macroscopic bodies.

As a result, it is not possible to determine accurately the position and momentum of a microparticle simultaneously.

HEISENBERG'S UNCERTAINTY PRINCIPLE

Introduced first in 1927 by the German physicist Werner Heisenberg, the uncertainty principle states that the more precisely the position of some particle is determined, the less precisely its momentum can be predicted from initial conditions, and vice versa.

This gives rise to an uncertainty in either the position or momentum, which is, however due to interaction of the system and the measuring technique.(That is, light)

This uncertainty is, therefore, a fundamental limit of nature and holds for a pair of conjugate variables like position and momentum, Energy and time, and angular momentum and its angular position.

HEISENBERG'S UNCERTAINTY PRINCIPLE

Heisenberg showed that the product of uncertainty in position (Δx) and the uncertainty in momentum (Δp) is equal to or greater than $h/4\pi$

$$(\Delta x).\,(\Delta p) \geq h/4\pi \qquad (1)$$

This is known as **Heisenberg's Uncertainty Principle**

Heisenberg showed that a similar relationship existed between Energy and time.

$$(\Delta E).\,(\Delta t) \geq h/4\pi \qquad (2)$$

ΔE is the uncertainty in the energy and Δt is the uncertainty in lifetime.

If a state has an infinite lifetime, $\Delta t=\infty$ and the precise value of energy of the system, we say that the system is in a stationary state.

But if the lifetime is finite, the precision with which the energy may be determined is limited.

HEISENBERG'S UNCERTAINTY PRINCIPLE

Because of the small value of 'h', the uncertainties are not detectable for macroscopic objects but for electrons, atoms and molecules, the Heisenberg's relations are significant.

These relations indicate that it is meaningless to ask about the exact position and exact velocity of an electron in an atom or even to ask about the exact energy of an atom in an experiment in which lifetime of that atomic energy state is finite.

The uncertainty Principle is a direct consequence of *dual nature of matter.*

HEISENBERG'S UNCERTAINTY PRINCIPLE

Since the dual nature is evident only in subatomic particles, these particles show an uncertainty which is not shown by macro bodies.

The microparticle itself cannot have a definite position and definite momentum simultaneously.

Therefore we cannot draw a trajectory of a microparticle in contrast to macroparticle.

Hence , the Bohr concept of 'orbit' of an electron becomes unacceptable.

The Uncertainty Principle does not hold for variables which are not conjugate.

NUMERICALS

Q 1. What is the product in uncertainty in position and velocity for an electron of mass 9.11×10^{-31} kg according to Heisenberg Uncertainty Principle? Compare with a ball of mass 100 gm.

A. For the electron $(\Delta x).(\Delta p) \geq h/4\pi$

$$(\Delta x).(m\Delta v) \geq h/4\pi$$

$$(\Delta x).(\Delta v) \geq h/4\pi m$$

$$= \frac{6.627 \times 10^{-34}\ \mathrm{Js}}{4 \times 3.14 \times 9.11 \times 10^{-31}\mathrm{kg}}$$

$$= 5.78 \times 10^{-5}\ \mathrm{m^2 s^{-1}}$$

For the ball, $(\Delta x).(\Delta v) = \frac{6.627 \times 10^{-34}\ \mathrm{Js}}{4 \times 3.14 \times 0.1\mathrm{kg}} = 5.27 \times 10^{-34}\ \mathrm{m^2 s^{-1}}$

From a comparison of uncertainties of the two particles it is evident that the uncertainty of the macroparticle is so small so as to be negligible. However, for the microparticle, the uncertainty is higher considering the mass of the particle.

Q 2. Calculate the minimum uncertainty in the position or velocity for the following cases. Comment

a) The position of an electron of mass $9.1X10^{-31}$ kg is known within 1mm

b) An automobile of mass 500 kg moving with speed 50±0.001 km/hr

Ans. (a) The uncertainty in velocity can be written as

$$(\Delta v) = h/4\pi m(\Delta x)$$

$$= \frac{6.627X10^{-34}\ Js}{4X3.14X\ 9.1X10^{-31}kg\ X10^{-3}\ m}$$

$$=5.795X\ 10^{-2}\ ms^{-1}$$

This uncertainty in velocity is significant for the electron

(b) The uncertainty in velocity of the automobile is

$$(\Delta v)=0.001\ \text{km/hr}=2.778\text{X}10^{-4}\ \text{ms}^{-1}$$

$$(\Delta x) = h/4\pi m(\Delta v)$$

$$=\frac{6.627\text{X}10^{-34}\ \text{Js}}{4\text{X}3.14\text{X}\ 500\text{kg X}\ 2.778\text{X}10^{-4}\ \text{ms}^{-1}}$$

$$=3.796\text{X}10^{-34}\ \text{m}$$

This value is negligible as compared to mass and velocity of the automobile.

THE SCHRÖDINGER WAVE EQUATION

Recognition of de Broglie relationship and the Uncertainty Principle should prepare our minds to accept that Newton’s mechanics is not suitable for predicting the position and momenta of microscopic particles like electrons, atoms and molecules.

A new approach was needed to understand the behaviour of atomic, subatomic or molecular species.

We may think about the probability of finding a particle in a region of space rather than assign it to a given position.

We may also think in terms a particle possessing an ‘expectation’ value of energy instead of a precise value of energy as was done by Bohr.

THE SCHRÖDINGER WAVE EQUATION

Schrodinger reasoned that a bound electron behaves like a 'standing wave' . The wave equation for a standing wave was known Already. By analogy he wrote down the famous equation from mathematical intuition.

SCHRODINGER EQUATION

If electrons have wave properties then there must be a wave equation And a wave function to describe the electron waves just as the waves of light, sound and strings are described.

Let us consider the motion of a string which is held fixed at two ends.

THE SCHRÖDINGER WAVE EQUATION

It is possible to excite with care certain kinds of vibrations in which all points of the string are at their maximum displacement at the same time and have maximum velocity at the same time.

If the displacement occurs in the y-direction, these functions can be described by functions of the form:

$$y(x,t) = f(x).\emptyset(t) \qquad (1)$$

where f(x) is independent of t and $\emptyset(t)$ is independent of x.

Such vibrations are called normal modes of vibration.

The wave equation has the form:

$$\frac{d^2y}{dx^2}=\frac{1}{c^2}.\frac{d^2y}{dt^2} \qquad (2)$$

Where **c** is the velocity of the wave. Differentiating y wrt x and t twice, we get

$$\frac{dy}{dx} = \emptyset(t).\frac{df(x)}{dx}$$

$$\frac{d^2y}{dx^2} = \emptyset(t).\frac{d^2f(x)}{dx^2} \qquad (3)$$

Differentiating with respect to t, we get

$$\frac{dy}{dt} = f(x).\frac{d\emptyset(t)}{dt}$$

$$\frac{d^2y}{dt^2} = f(x).\frac{d^2\emptyset(t)}{dt^2} \qquad (4)$$

If the wave is assumed to be travelling along the x-direction with a frequency v then since the wave must start and terminate at the ends and therefore, it has to be a sine wave.

Let it be expressed as:

$$\emptyset(t)=D\sin 2\pi\nu t$$

$$\frac{d\emptyset(t)}{dt}=2\pi\nu D.\cos 2\pi\nu t$$

and $$\frac{d^2\emptyset(t)}{dt^2}=-(2\pi\nu)^2 D.\sin 2\pi\nu t$$

$$\frac{d^2\emptyset(t)}{dt^2}=-(2\pi\nu)^2.\ \emptyset(t) \qquad (5)$$

Substituting (5) in equation (4), we get

$$\frac{d^2y}{dt^2}=-f(x).(2\pi\nu)^2.\ \emptyset(t) \qquad (6)$$

Substituting (6) in (2), we get

$$\frac{d^2y}{dx^2}=\frac{-1}{c^2}.f(x).(2\pi\nu)^2.\ \emptyset(t)$$

$$\frac{d^2y}{dx^2} = \frac{-\,4\pi^2\nu^2.f(x)\ \phi(t)}{c^2}$$

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2\nu^2.y}{c^2} \qquad (7)$$

Now, using the relationship $\nu = c/\lambda$ (8)

and $\lambda = h/p = h/mc$ (9)

and substituting in (7), we get:

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2}{c^2}.\frac{c^2}{\lambda^2}.y$$

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2}{\lambda^2}.y$$

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2}{\lambda^2}.y$$

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2}{}.\frac{(mv)2}{h^2}.y$$

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2}{}.\frac{m\ mv^2}{h^2}.y$$

$$\frac{d^2y}{dx^2} = \frac{-4\pi^2}{}.\frac{2m.mv^2}{2h^2}.y$$

$$\frac{d^2y}{dx^2} = \frac{-8m\pi^2}{h^2}.\frac{mv^2}{2}.y \qquad (10)$$

Since in a string, the total energy is the sum total of kinetic and potential energies, the total energy E can be expressed as a sum of Potential energy U and KE=1/2 mv^2

$$E=U+ 1/2\ mv^2 \qquad (11)$$

Substituting (11) in (10), we get

$$\frac{d^2y}{dx^2} = \frac{-8\pi^2 m}{h^2}(E\text{-}U).y$$

Rearranging, we get

$$\frac{h^2}{-8\pi^2 m}\frac{d^2y}{dx^2} = (E\text{-}U).y$$

$$\frac{h^2}{-8\pi^2 m}\frac{d^2y}{dx^2} = E.y - U.y$$

$$\frac{h^2}{-8\pi^2 m}\frac{d^2y}{dx^2} + U.y = E.y \qquad (12)$$

We had assumed the wave to be travelling along x-direction.
Let us now consider a wave travelling in any direction.
Therefore, instead of y let us denote the wave by Ψ where Ψ is a Function of x,y,z and t or Ψ(x,y,z,t).

Therefore for a general wave we can write equation (12) as

$$\frac{-h^2}{8\pi^2 m}\left[\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right]+U\Psi=E\Psi \qquad (13)$$

where $\frac{\partial^2\Psi}{\partial x^2}, \frac{\partial^2\Psi}{\partial y^2}, \frac{\partial^2\Psi}{\partial z^2}$ are partial derivatives of Ψ as Ψ is a function of x,y,z and t.

Equation (13) can be rewritten as

$$\frac{-h^2}{8\pi^2 m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\Psi+U\Psi=E\Psi \qquad (14)$$

$$\frac{-h^2}{8\pi^2 m}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]\Psi+U\Psi=E\Psi \qquad (14)$$

$$\frac{-h^2}{8\pi^2 m}.\nabla^2\Psi+U\Psi=E\Psi \qquad (15)$$

Equation (14) is the expanded form of Schrodinger's equation while Equation (15) is the condensed form of this equation.

The term ∇^2 is called the Laplacian operator and is denoted by

$$\nabla^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

$$\left[\frac{-h^2}{8\pi^2 m}.\nabla^2+U\right]\Psi=E\Psi \qquad (16)$$

$$\left[\frac{-h^2}{8\pi^2 m}.\nabla^2 + U\right]\Psi = E\Psi \qquad (16)$$

The above equation can be condensed as

$$\hat{H}\Psi = E\Psi \qquad (17)$$

where $\hat{H}$ is called the Hamiltonian operator, expressed as a sum of two operators, the Laplacian operator ∇^2 and the potential energy operator U.

where $\hat{H} = \frac{-h^2}{8\pi^2 m}(\nabla^2) + U$

INTERPRETATION OF THE WAVE FUNCTION

The wave function is a kind of amplitude function. In classical mechanics the square of the wave amplitude , associated with an electromagnetic radiation is proportional to the intensity of radiation.

$$A^2 \alpha I$$

By analogy, the square of the absolute value of Ψ is a measure of the intensity or particle density.

However, our present idea of Ψ in quantum mechanics is based on The uncertainty principle. According to this principle, it is not possible to simultaneously measure the position and momentum of a microparticle such as an electron precisely.

INTERPRETATION OF THE WAVE FUNCTION

According to Max Born, $|\Psi|^2$ should be treated as proportional to the probability of finding a particle at a given point at any given time.

$$|\Psi|^2 \propto \text{probability}$$

Since the probability of finding a particle at a given point must be real, generally $\Psi^*\Psi$ is taken as the measure of finding a particle at any point , if Ψ is a complex function.

The function Ψ^* is the complex conjugate of Ψ and their product $\Psi^*\Psi$ will always be a real non negative quantity.

INTERPRETATION OF THE WAVE FUNCTION

- Generally, the probability of finding particle in a certain volume element dxdydz is expressed as $\Psi^*\Psi$dxdydz or $|\Psi|^2$dxdydz and the probability of finding a particle per unit volume is represented by $\Psi^*\Psi$ and is known as probability density. Very often dxdydz is abbreviated as dτ.
- The interpretation of Ψ^2 may be made more clear by considering a hypothetical experiment. Suppose we have an electron bound to the nucleus of an atom. The position of this electron can be specified exactly by taking a 3-dimensional photograph. Since the electron is in a state of continuous motion, a photograph taken a fraction of second later would show the electron in a new position.

If we take thousands of such pictures and we draw a diagram we shall find innumerable dots corresponding to different positions of the electron. This figure would look like a projection of the electron cloud around the nucleus in the plane of paper.

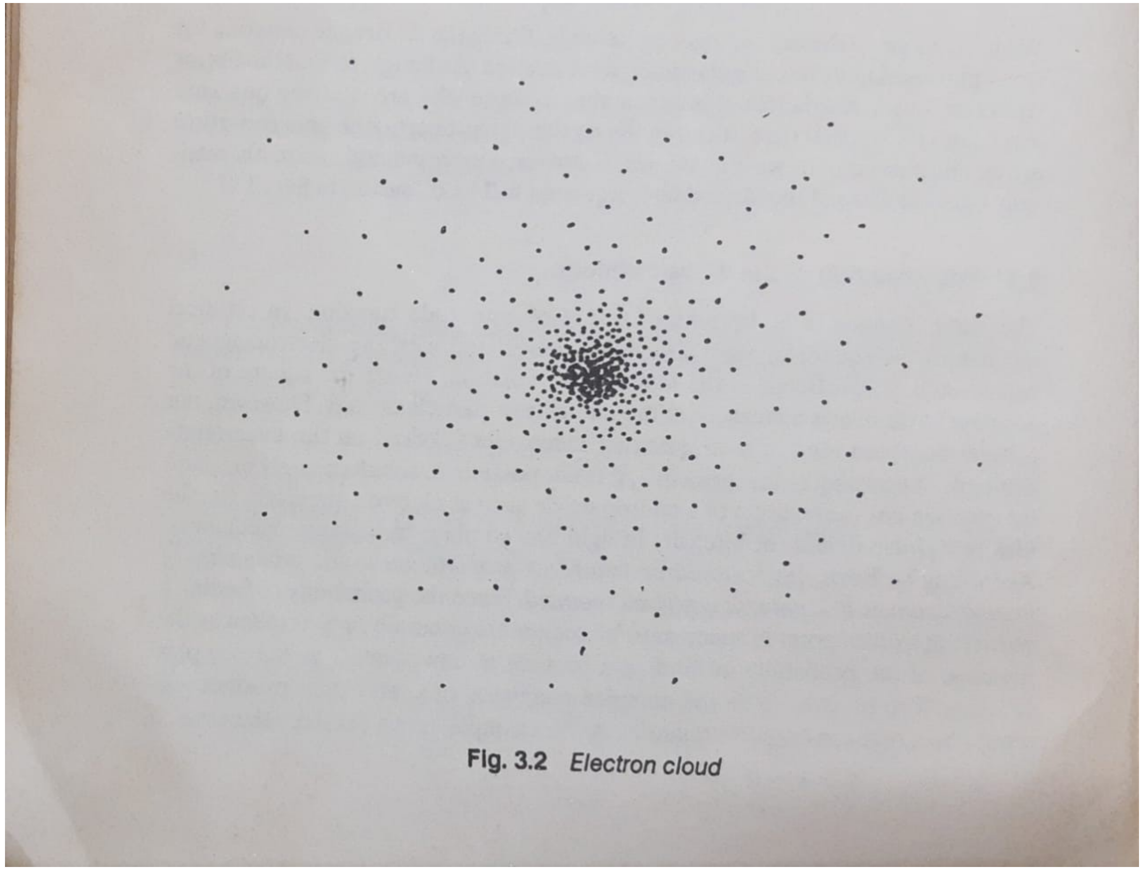


Fig. 3.2 *Electron cloud*

It is obvious that the electron cloud would appear more dense in the regions where the number of dots are more. In other words, the probability of finding the electron is maximum in that particular region.

The density of this charge cloud at any point corresponds to the probability density and is given by the square of the wave function, that is Ψ^2

PROPERTIES OF THE WAVE FUNCTION

- The Schrodinger wave equation is a second order differential equation and has an infinite number of solutions.

- However, only a few solutions have any physical or chemical significance.

- The physical interpretation of $|\Psi|^2 d\tau$ as a measure of probability of finding the particle in the volume element $d\tau$ implies that Ψ must obey certain mathematical conditions.

PROPERTIES OF THE WAVE FUNCTION

These conditions are:

(1) Ψ must be single valued.
(2) Ψ and its first derivative must be continuous.
(3) Ψ must be finite for all physically possible values of x, y, z.

- Ψ must be single valued since the probability density of a particle at a point (x,y,z) must be unique.
- Ψ cannot be infinite at any point , otherwise probability density will be infinite.
- The requirement of continuity implies that there must not be any sudden changes in Ψ when the variables are changed.

Such a wave function is said to be a well behaved wave function.

EXAMPLES OF WAVE FUNCTIONS

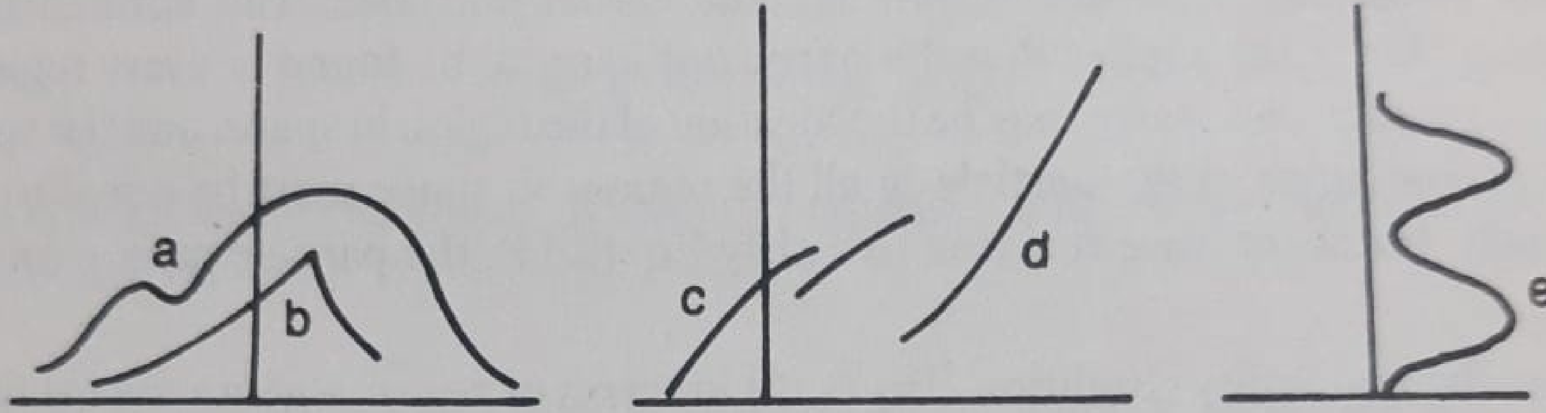


Fig. 3.3 *Function (a) is continuous and its first derivative is also continuous . Function (b) is continuous but its first derivative has a discontinuity. Function (c) is discontinuous. Function (d) approaches infinity and function (e) is multivalued*

NORMALIZED WAVE FUNCTION

If Ψ*Ψdxdydz is the probability of finding the particle in the volume element dxdydz, then the sum of such probabilities over the whole space must be unity. This can be expressed mathematically as :

$$\int_{-\infty}^{+\infty} \Psi * \Psi dxdydz = 1 \qquad (18)$$

Thus, for the electron, we can say that the total probability Integrated over all space accessible to it is 1.

Such wave functions are said to be ‘normalized wave functions’.

Very often Ψ is not a normalized wave function. But if Ψ is multiplied by A constant and its value chosen in such a way so as to satisfy equation (18), Then the wave function becomes ‘normalized’.

PARTICLE IN 1-D BOX

Let us write the Schrodinger wave equation in one dimension.

$$-h^2/8\pi^2 m.\ d^2\Psi\ /dx^2\ +U\Psi=E\ \Psi\ldots\ldots(1)$$

If we consider an electron of mass m in a box of 1-dimension whose length is a.

The particle can exist anywhere between $x=0$ to $x=a$.

Let the potential energy of the particle be zero inside this potential energy well and let the potential energy at $x=0$ and $x=a$ as well as outside the box be ∞.

Thus the particle is unable to cross this energy barrier and go outside the box.

We can write the Schrodinger wave equation outside the box:

$$-h^2/8\pi^2 m.\ d^2\Psi\ /dx^2 + \infty\Psi = E\ \Psi \ldots\ldots(2)$$

Multiplying this equation (2) by $-8\pi^2 m/h^2$, we get

$$d^2\Psi\ /dx^2 - 8\pi^2 m/h^2\ \infty\Psi = -8\pi^2 m/h^2\ E\ \Psi$$

This equation can be rearranged as

$$d^2\Psi\ /dx^2 = 8\pi^2 m/h^2\ \infty\Psi\ - 8\pi^2 m/h^2\ E\ \Psi$$

$$= 8\pi^2 m/h^2\ (\infty - E)\ \Psi \ldots\ldots\ldots(3)$$

For finite values of energy, equation (3) can be written as $d^2\Psi / dx^2 = \infty \Psi$……(4)

The left hand side of this equation has to be finite (Ψ is a well behaved wave function), so the right hand side has to be finite which is possible only if $\Psi=0$.

Thus $\Psi=0$ for all points outside the box and the particle cannot exist outside the box at all.

When the particle is inside the box, the potential energy is 0. Therefore the Schrodinger wave equation inside the box is :

$$-h^2/8\pi^2m.\ d^2\Psi/dx^2 = E\ \Psi \text{........}(5)$$

Or $$d^2\Psi/dx^2 + 8\pi^2 mE\ \Psi/h^2 = 0 \text{.........}(6)$$

Let $$k^2 = 8\pi^2 mE/h^2 \text{ ....}(7)$$

Thus, rewriting we have

$$d^2\Psi/dx^2 + k^2\Psi = 0 \text{ ....}(8)$$

-

Thus, rewriting we have

$$d^2\Psi /dx^2 + k^2\Psi = 0 \;\ldots\ldots\ldots\ldots(8)$$

This is a second order differential equation whose solution is of the form

$$\Psi = A.\sin kx + B.\cos kx \;\ldots(9)$$

where A and B are arbitrary constants.

The values of these constants can be calculated using the boundary conditions.

Since the wave function is 0 outside the box,

It must also be 0 at the walls of the box as there must be a continuity in the values of Ψ at the walls of the box.

Thus Ψ must be 0 at $x=0$ and $x=a$.

Thus at $x=0$ the equation (9) becomes:

$0= A\sin k.0+B\cos k.0$

$0=B\cos k.0$

Since $\cos k.0=1$, therefore $B=0$

Thus equation (9) is reduced to

$\Psi=A\sin kx$ ……….(10)

At the point $x=a$, equation (9) becomes:

$$0=A\sin ka$$

For this to be true, either $A=0$ or $\sin ka=0$

If $A=0$, the wave function will become 0 everywhere inside the box which is not acceptable, so $\sin ka=0$

Since $\sin ka$ can be zero for all values of $\sin n\pi$
Therefore $\sin ka= \sin n\pi$

$$\text{Or } ka= n\pi$$

$$\textbf{Or } \boldsymbol{k= n\pi/a} \textbf{ ……..(11)}$$

Where n is an integer having values 0,1,2,3…

Finally, the wave function for the particle inside the box becomes

$$\boldsymbol{\Psi = A \sin n\pi x/a \;\ldots\ldots\ldots(12)}$$

Using equation (7) and (11), we get

$$(n\pi/a)^2 = 8\pi^2 mE/h^2$$

$$\text{or } n^2\pi^2/a^2 = 8\pi^2 mE/h^2$$

$$\text{or } \boldsymbol{E_n = n^2 h^2/8ma^2 \;\ldots\ldots\ldots.(13)}$$

For a particle moving between two points , the energy is quantized.

For a particle moving between two points, the energy is quantized.

n	**$E_n = n^2h^2/8ma^2$**
1	$h^2/8ma^2$
2	$4h^2/8ma^2$
3	$9h^2/8ma^2$
4	$16h^2/8ma^2$

No such discrete levels are expected from classical mechanics.

Although n=0 is permitted but it is not acceptable as it would make the wave function 0 everywhere inside the box.

Thus, lowest energy is obtained by substituting n=1 in equation (13).

This energy is known as the Zero point energy.

$$\mathbf{E_{\text{zero point}} = h^2/8ma^2}$$

The salient features of the particle in a box problem are summarized below.

1) The particle is not at rest even at 0 Kelvin.

Therefore, the position of the particle cannot be precisely known.

In such a situation, only the mean value of the kinetic energy can be known. Therefore, the momentum of the particle is also not known precisely.

The occurrence of zero point energy is in accordance with Heisenberg’s Uncertainty Principle.

2) The allowed integral values of n come naturally as a consequence of the solution and not as an arbitrary postulate as given by Bohr.

‘n’ is called a quantum number.

3) The energies of the electron are quantized. The only permitted values are as given in the table.

4) Plots of Ψ and Ψ^2 for different values of n are as shown.

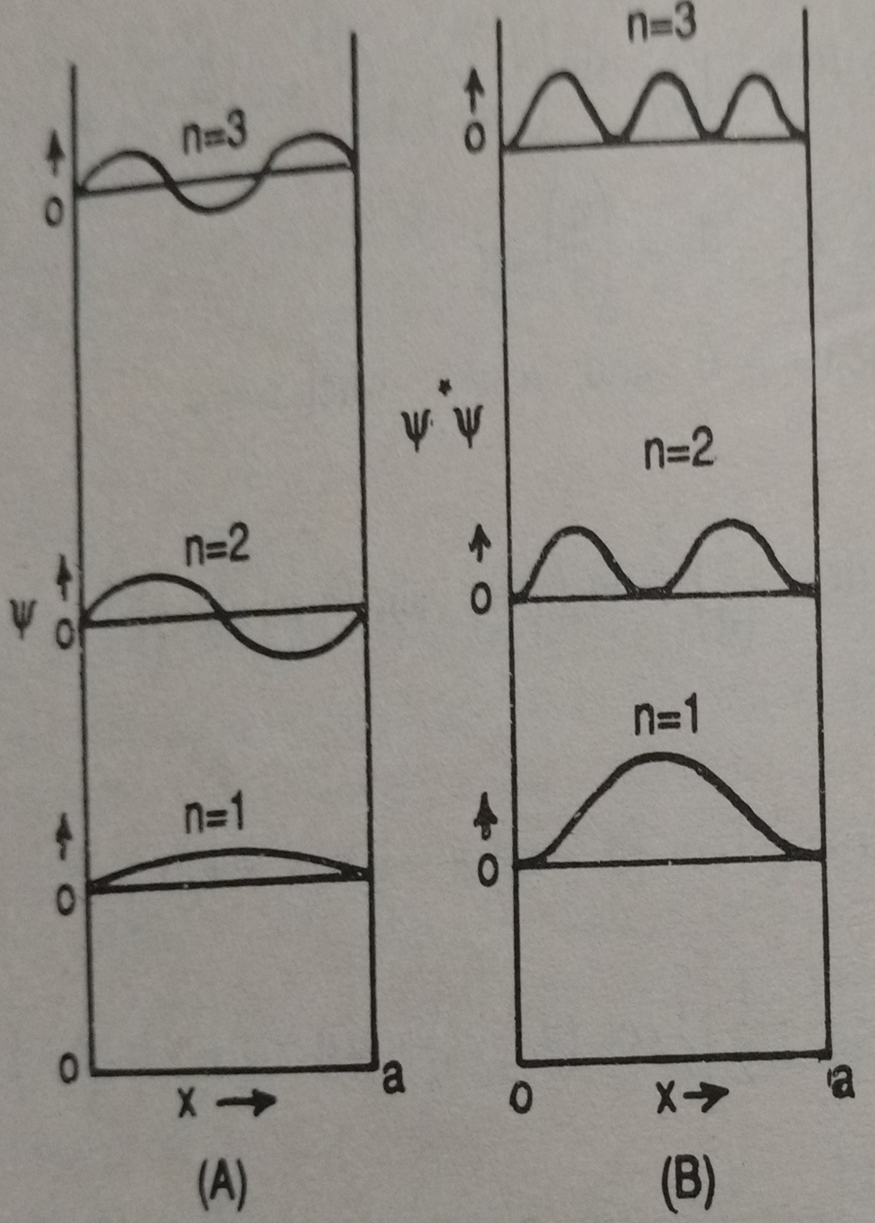


Fig. 3.5 (A) Wave function ψ and (B) probability density function ψ*ψ for the lowest three energy levels for a particle in a box

The plots of Ψ and $Ψ^2$ for different values of n are as shown. The appearance of nodes and antinodes in the wave function is another striking feature of this problem.

The plots of Ψ versus x show that there are n-1 nodes (regions of zero amplitude and zero probability) in each wave function. The antinodes are regions of high probability e.g. at x=a/2, in case of $Ψ_1$ and at x=a/4 and 3a/4 in case of $Ψ_2$.

There are nodal points in between positions other than x=0 and x=a

5) The probability density Ψ^2 has the same number of maxima as the quantum number 'n'.

For n=2, the probability of finding the particle at the centre of the box is zero, which is quite different from the classical result.

6) As we go to higher energy levels with more nodes, the maxima and minima of probability curves come closer together and the variations in probability along the 1-d box become undetectable.

For higher quantum numbers, we approach the results of uniform probability density.

This is in agreement with ‘Bohr Correspondence Principle’. According to this principle, the quantum mechanical result must go over to classical mechanics when the quantum number describing the system becomes very large.

7) The energy expression $E_n = n^2 h^2/8ma^2$ shows that energy is inversely proportional to a^2 i.e., square of the length of the box.

Longer the box, lower will be its energy.

More localized the electron, higher will be its energy.

In chemical systems , larger the extent of delocalization, more stable is the system energetically. (For example, benzene and other conjugated systems.)

8) At a first glance, the energy expression is inversely proportional to the mass of the particle. It seems to contradict the fact that kinetic energy is proportional to mass of the particle.

However, if we understand that submicroscopic particles travel close to the speeds of light, we can understand this contradiction.

- The energy expression suggests that the lighter particles will have velocities close to the velocity of light and heavier particles will have lower velocities.
- This would suggest that β-rays would have higher velocities than α- rays.

NORMALIZATION OF THE WAVE FUNCTION

We have not yet determined the value of arbitrary constant A of the wave function $\Psi = A \sin n\pi x/a$.

This is calculated by normalizing the wave function.

Applying the normalizing condition, we get

$$\int \Psi^{*}\Psi dx = 1 \qquad (14)$$

Substituting the wave function in the above equation we get

$$\int_0^a A^2 \sin^2 \frac{n\pi x}{a} dx = 1$$

$$A^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = 1$$

SIMPLE TRIGONOMETRIC EXPRESSIONS

$\cos(A+B)=\cos A\cos B-\sin A\sin B$

Therefore, $\cos 2A=\cos^2 A-\sin^2 A$

$\cos 2A=(1-\sin^2 A)-\sin^2 A$ as $\sin^2 A+\cos^2 A=1$

$\cos 2A=1-2\sin^2 A$

$2\sin^2 A=1-\cos 2A$

$\sin^2 A=1/2(1-\cos 2A)$

$$\frac{A^2}{2}\int_0^a \left(1-\cos\frac{2n\pi x}{a}\right)dx=1 \qquad \text{........ } \sin^2\Theta=1/2(1-\cos2\Theta)$$

$$\frac{A^2}{2}\left[x-\frac{a}{2n\pi}\sin\frac{2n\pi x}{a}\right]_0^a=1$$

$$\frac{A^2}{2}\left[(a-0)-\frac{a}{2n\pi}(\sin 2n\pi-\sin 0)\right]=1$$

$$\frac{aA^2}{2}=1$$

$$A^2=\frac{2}{a}$$

$$A=\sqrt{2/a} \qquad \text{........(15)}$$

Putting the value of A in equation (12),

Thus wave function becomes $\Psi=\sqrt{2/a}\,\sin\frac{n\pi x}{a}$

MACROPARTICLE VS MICROPARTICLE

You may make an interesting comparison between the results of particle-in- a –box problem and a circus girl walking on a tightly stretched wire, which is an example of classical mechanics, and realize the striking difference between the behaviour of a microscopic particle and a macroscopic body.

After all, the electron is also dancing its way out on a very thin wire but very differently.

FREE PARTICLE

By free particle we mean a particle of mass m, not under the influence of any force. For simplicity we also assume the particle to have 0 potential energy. If the particle moves along the x direction, then the Wave equation of such a particle can be given by the equation

$$d^2\Psi / dx^2 + 8\pi^2 mE\, \Psi / h^2 = 0 \text{.........}(6)$$

If $\frac{8\pi^2 mE}{h^2} = k^2$

then $E = \frac{k^2 h^2}{8\pi^2 m}$

Where k is any arbitrary constant. Thus, we can see that

1. The energy of the free particle is not quantized.
2. The energy of the free particle does not depend upon the length or size of the box.
3. Since the energy is inversely proportional to mass m of the particle, larger the particle, lower is its kinetic energy.
4. The energy spectrum of such a particle will be continuous. The dissociation of an electron from an atom and the emission of α or β rays are examples of free particles, provided they do not interact with other particles.

OPERATORS

An operator can be defined as '*a symbol for a certain mathematical procedure which transforms one function into another*'.

Any mathematical operation such as integration, differentiation, division, multiplication, addition, subtraction, square root etc can be represented by certain symbols known as operators.

For example, the operator of evaluating the derivative with respect to x Is represented by the symbol $\frac{\mathrm{d}}{\mathrm{dx}}$. When this operator is applied to the function x^n , we obtain a new function as

$$\frac{d(xn)}{dx} = nx^{n-1} \qquad (1)$$

Therefore, in general, we can write the operator as Â, then Â operates on a function f(x) and transforms it to a new function g(x).

$$\hat{A}.f(x)=g(x) \qquad (2)$$

Mathematical operations operating on x^4

S. No	Operation	Operator	Result of operation on x^4
1	Taking square	$(\quad)^2$	x^8
2	Taking the square root	√	x^2
3	Multiplication by a constant k	X k	kx^4
4	Differentiation with respect to x	$\frac{d}{dx}$	$4x^3$
5	Integration with respect to x	$\int (\ )dx$	$\frac{x^5}{5} + c$

The function on which an operation is carried out is often called an ‘*operand*’.

In fact equation (2) does not mean that the function is multiplied by the operator. The operator does not have any meaning when it stands alone.

If $\hat{A}\Psi = a\Psi$, **then** $\hat{A} \neq a$

An operator is generally denoted by a capital letter with a superscript symbol (^) overhead. For example, Â and Ĥ.

OPERATOR ALGEBRA

Addition and subtraction of operators.

New operators can be created by addition and subtraction of operators.

If Â and Ê are two different operators , then new operators are

$$(\hat{A}+\hat{E})f=\hat{A}f+\hat{E}f$$

and $$(\hat{A}-\hat{E})f=\hat{A}f-\hat{E}f$$

Multiplication of operators

The consecutive operations with two or more operators on a function may be called multiplication of operators.

If Â and Ê represent two different operators and f the operand

Then the expression $\hat{A}.\hat{E}f$ means the function f is first operated upon by Ê to obtain a new function f’ as:

$$\hat{E}f=f'$$

Then f' is operated upon by $\hat{A}$ to obtain the final function f'' as

$$\hat{A}f'= f'' \qquad (3)$$

The order of operation is always from right to left as they are written.

If the same operator is applied several times in succession, it is written with a power. Thus,

$$\hat{A}\,\hat{A}f= \hat{A}^2 f \qquad (4)$$

and $$\hat{A}\,\hat{A}\,\hat{A}\,\hat{A}\ldots\ldots\text{n times}\ldots f= \hat{A}^n f$$

IS MULTIPLICATION OF OPERATORS COMMUTATIVE

Let us see whether multiplication of operators is commutative or not?

Is $\hat{A} \times \hat{C} = \hat{C} \times \hat{A}$?

Let us choose an operator Â as taking the derivative wrt x and operator Ĉ for multiplication by x. Then,

$$\hat{A}.\,\hat{C}f(x) = \hat{A}[\hat{C}f(x)] = \hat{A}[x.\,f(x)]$$

$$= x\frac{df(x)}{dx} + f(x) \qquad (5)$$

$$\hat{C}.\,\hat{A}f(x) = \hat{C}\,[\hat{A}f(x)] = \hat{C}[\frac{df(x)}{dx}]$$

$$= x\,\frac{df(x)}{dx} \qquad (6)$$

We can see from equations (5) and (6) that

$$\hat{A}\,\hat{C}f(x) \neq \hat{C}\,\hat{A}f(x)$$

This shows that the result of a series of operations is often different depending upon the sequence in the operations are performed.

If the outcome of the two operations is same, regardless of the sequence in which the operations are performed, the operators are said to *commute.*

The above two operators do not commute. This distinguishes an operator algebra from the ordinary algebra where for any two numbers a and b,

$$a \times b = b \times a$$

THE COMMUTATOR

Using two operators, Â and Ĉ it is possible to construct a new operator Â Ĉ - Ĉ Â, called the commutator of the two operators Â and Ĉ, usually written as [Â, Ĉ].

If these two operators commute then

$$[\hat{A}, \hat{C}] = \hat{A}\hat{C} - \hat{C}\hat{A} = 0$$

Since an operator by itself does not have any meaning, the commutator Will operate on a function.

Thus, $$[\hat{A}, \hat{C}]\Psi = (\hat{A}\hat{C} - \hat{C}\hat{A})\Psi = 0$$

Therefore this commutator means multiplication by 0.

We have seen in equations (5) and (6) that the two operators do not commute. This has implications in measurement of certain variables.

COMMUTATOR AND THE UNCERTAINTY PRINCIPLE

When the commutator is zero, or when the operators do not commute Those are the operators whose simultaneous measurement with accuracy is not possible.

These pair of operators will not commute which are the pair of variables in the uncertainty principle.

This essentially means that the multiplication of the following pair of operators will not be commutative:

- Position and momentum i.e., $[x, p_x] \neq 0$
- Energy and time period i.e., $[E, t] \neq 0$
- Angular momentum and theta i.e., $[L,\Theta] \neq 0$

LINEAR OPERATOR

If an operation on sum of two functions gives the same result as the sum of operations on the two functions separately, then the operator is said to be linear.

Thus, the operator Â is said to be linear if

$$\hat{A}(f+g)=\hat{A}f+\hat{A}g$$

And $\hat{A}cf=c\,\hat{A}f$ where c is a constant

For example, taking derivative is a linear operator as

$$\frac{d}{dx}(f+g)=\frac{d}{dx}f+\frac{d}{dx}g$$

While taking square root is not a linear operator:

$$\sqrt{(f+g)} \neq \sqrt{f}+\sqrt{g}$$

LAPLACIAN OPERATOR

The Laplacian operator is of particular interest in quantum chemistry.

The operator is defined as

$$\nabla^2 = \frac{\partial^2}{\partial x2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Since the function Ψ depends upon the variables x,y,z the partial derivatives are written as ‘del’(∂).

The double derivative of wave function is taken wrt x,y,z and the values added to give the value of Kinetic energy.

The Laplacian operator and the potential energy operator is added to get the Hamiltonian operator.

$$\frac{-h^2}{8\pi^2 m} . \nabla^2 + U = \hat{H}$$

$$\left[\frac{-h^2}{8\pi^2 m} . \nabla^2 + U \right] \Psi = E\Psi$$

$$\hat{H}\,\Psi = E\,\Psi$$