

Dual Character of Electron—

de-Broglie equation—Einstein had suggested, in 1905, that light has dual character; as wave and also as particle. Louis de-Broglie proposed that electron (or matter) also has a dual character, as wave, and as particle and he derived an equation to prove his view—

$$E = mc^2 \quad (\text{Einstein equation})$$

We know that

(Planck) $E = h\nu$ (Max - Planck)

So $h\nu = mc^2$

Since $\nu = c/\lambda$

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

Hence $\lambda = \frac{h}{mc}$

Replacing c by the velocity of electron v , we have

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

(de Broglie equation)

where $p =$ momentum of electron.

de Broglie's equation is applicable only for small particles like electrons, neutrons etc. and has no significance for large particles. Davission and Germer's experimentally verify the wave nature of moving electrons.

Why quantization of momentum ? According to Bohr, electrons move around the nucleus in circular path. Since electron has a wave character, the electron waves can be assumed to move in a circle. The wave motion is said to be in phase if the two ends of the wave meet to give a regular series of crests and troughs [Fig. 1.13(a)]. In such a situation, the circumference ($2\pi r$) of the orbit must be equal to integral multiple of its wavelength (λ). Thus, $2\pi r = n\lambda$.

or $\lambda = \frac{2\pi r}{n}$..(i)

where $r =$ radius of orbit and $\lambda =$ wavelength of electron.

According to de-Broglie equation $\lambda = \frac{h}{mv}$..(ii)

From equation (i) and (ii), we get $\frac{2\pi r}{n} = \frac{h}{mv}$ or $2\pi r = \frac{nh}{mv}$ or $mvr = \frac{nh}{2\pi}$

where $mvr =$ angular momentum of electron, and $n = 1, 2, 3, \dots$ and not a fraction.

Thus dual nature of electron (wave as well as particle) has confirmed the nature of motion of electron in an orbit.

If ' mvr ' is not an integral multiple of $\frac{h}{2\pi}$, the wave motion of the electron will not move in a circular orbit. It will thus, come out of it and lose energy. But it is not possible. **Hence angular momentum of the electron is quantised.**

Significance of de-Broglie equation

Significance of de-Broglie equation

(i) The wave character of large objects (in motion) has no practical significance. It is, because their wavelength is too small to be observed. It has no significance in every day life.

(ii) The wave character of microscopic particles (in motion) has practical significance. It is because their wavelength is easily observed in electromagnetic spectrum.

Applications of Wave-nature of Electrons

1. The wave-nature of electrons is utilised in making electron microscope which is a very powerful tool in scientific research. The electron microscope uses electron waves to see very small objects.

2. Wave-nature of electrons has also been used for studying the surface structure of solids.

Limitations. It is not valid for macroscopic objects but only applicable for microscopic moving objects.

For example, the wavelength of an electron having mass, 9.11×10^{-31} kg and moving with the velocity of 10^6 ms⁻¹ is 7.27×10^{-10} m and is calculated as follows :

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2}}{9.11 \times 10^{-31} \text{ kg} \times 10^6 \text{ ms}^{-1}} = 7.27 \times 10^{-10} \text{ m}$$

This wave length associated with the moving electron is of the same order of magnitude as of X-rays which can be easily measured.

On the other hand, material objects having fairly large mass possess extremely small wave length.

For example, the wavelength associated with a ball weighing 10^{-2} kg and moving with the same velocity as that of electron i.e., 10^6 ms⁻¹ is only 6.625×10^{-38} m as calculated below :

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-2}}{10^{-2} \text{ kg} \times 10^6 \text{ m s}^{-1}} = 6.625 \times 10^{-38} \text{ m}.$$

Example 4. What is the mass of a photon of sodium light ?

$$(\lambda = 5894 \text{ \AA}, v = 3 \times 10^8 \text{ ms}^{-1}, h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}).$$

Solution. Wavelength (λ) = $5894 \text{ \AA} = 5894 \times 10^{-10} \text{ m}$

$$\text{Velocity } (v) = 3 \times 10^8 \text{ ms}^{-1}; \lambda = \frac{h}{mv} \therefore m = \frac{h}{\lambda v} = \frac{6.625 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{5894 \times 10^{-10} \text{ m} \times 3 \times 10^8 \text{ ms}^{-1}};$$

$$\therefore m = 3.75 \times 10^{-36} \text{ kg}.$$

Example 5. An electron diffraction experiment was performed with a beam of electrons accelerated by a potential difference of 10 kV. What was the wavelength of the electron beam?

Solution. Kinetic energy of the electron,

$$\frac{1}{2} mv^2 = 10^4 \text{ eV} = 10^4 \times 1.602 \times 10^{-19} \text{ J} = 1.602 \times 10^{-15} \text{ J} = 1.602 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2} \\ (1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

Mass of electron, $m = 9.11 \times 10^{-31}$ kg

$$\text{Velocity of electron, } v = \left(\frac{2 \times 1.602 \times 10^{-15} \text{ kg m}^2 \text{ s}^{-2}}{9.11 \times 10^{-31} \text{ kg}} \right)^{1/2} \\ = (35.17 \times 10^{14})^{1/2} \text{ ms}^{-1} = 5.93 \times 10^7 \text{ ms}^{-1}$$

According to de Broglie's equation,

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34} \text{ Js}}{(9.11 \times 10^{-31} \text{ kg})(5.93 \times 10^7 \text{ ms}^{-1})} = \frac{6.625 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{(9.11 \times 10^{-31} \text{ kg})(5.93 \times 10^7 \text{ ms}^{-1})} \\ = 1.23 \times 10^{-11} \text{ m} = 0.123 \text{ \AA}.$$

Example 6. Find the de-Broglie wave length of an electron (mass = $9.11 \times 10^{-31} \text{ kg}$) moving at 1% speed of light. ($h = 6.625 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}$).

Solution. Given that ; $m = 9.11 \times 10^{-31} \text{ kg}$

$$v = 1\% \text{ of speed of light} = \frac{1}{100} \times 3.0 \times 10^8 \text{ m s}^{-1} = 1 \times 3.0 \times 10^6 \text{ m s}^{-1}$$

[\therefore speed of light = $3.0 \times 10^8 \text{ m s}^{-1}$]

$$\text{We know that : } \lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{9.11 \times 10^{-31} \text{ kg} \times 1 \times 3.0 \times 10^6 \text{ m s}^{-1}} = 2.42 \times 10^{-10} \text{ m}$$

Example 7. Calculate de-Broglie wavelength of helium atom at 27°C moving with velocity of $2.40 \times 10^2 \text{ m s}^{-1}$.

Solution. Velocity of He atom = $2.40 \times 10^2 \text{ m s}^{-1}$

$$\begin{aligned} \text{Mass of He atom, } m &= \frac{\text{Gram atomic mass of He}}{\text{Avogadro's number}} = \frac{4}{6.02 \times 10^{23}} \\ &= 6.64 \times 10^{-24} \text{ g} = 6.64 \times 10^{-27} \text{ kg} \end{aligned}$$

According to de-Broglie equation, $\lambda = \frac{h}{mv}$

$$= \frac{6.625 \times 10^{-34} \text{ J s}}{6.64 \times 10^{-27} \text{ kg} \times 2.4 \times 10^2 \text{ m s}^{-1}} = 4.15 \times 10^{-10} \text{ m}$$

Heisenberg uncertainty principle—It is not possible to determine precisely both the position and the momentum (velocity) of a small moving particle like electron. In view of this principle the Bohr model in which electrons are considered as particles revolving in definite orbits, cannot hold good. It is more correct to say that an electron is associated with definite energy and it belongs to definite energy level.

Mathematical expression of Heisenberg uncertainty principle is—

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

where Δx and Δp are uncertainty with regards to position and momentum respectively.

It is important to note that the uncertainty is not due to lack of better techniques for measurement of position and momentum. It is due to the fact that we cannot observe microscopic objects without disturbing them.

Physical concept of uncertainty principle. In order to understand the physical concept of uncertainty, we have to study the effect of light on material objects. Exact position of an object can be determined only if it is visible. An object will be visible only if the light reflected by it falls in the visible region.

When a beam of ordinary light (Fig. 1.15) falls on an object of reasonable size (**Macro or semi-micro**), it will be visible with the naked eye. Its position or velocity will not be altered by the impact of light radiations (photons). Thus, it is possible to know both the position and velocity of the object

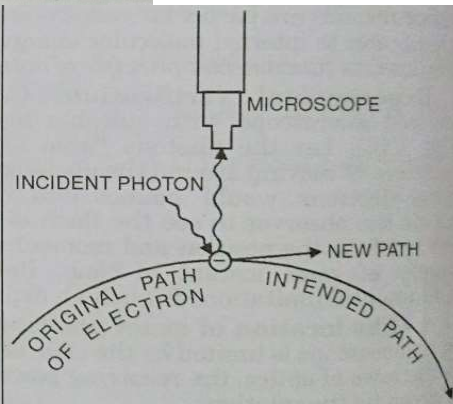


Fig. 1.15 Change in path and momentum of an electron by the impact of photon of light.

exactly. However, the situation is different in the case of **microscopic objects** such as electrons. These objects are not visible if ordinary light is used. Therefore, light radiations of short wavelength (high energy) are to be used. When such a photon of radiation strikes an electron, it transfers some of its energy to the electron. Therefore, velocity and hence momentum of the electron changes. On the other hand, if we use photons of radiations having longer wavelength (low energy), the velocity and the momentum will not change appreciably but its position cannot be determined because object will not be visible. Thus, we cannot simultaneously determine the position and momentum of a small moving particle like electron.

- NOTE.**
1. Uncertainty principle applies to location and momentum along the same axis. i.e., if Δx is the uncertainty in position along x-axis, then Δp must also be the uncertainty in momentum along the x-axis.
 2. The uncertainty is not due to lack of better techniques for measurement of position and momentum. It is due to the fact that we cannot observe microscopic objects without disturbing them.

Example 9. Calculate the uncertainty in position of a dust particle with mass equal to 1 mg if the uncertainty in its velocity is $5.5 \times 10^{-20} \text{ ms}^{-1}$. ($h = 6.626 \times 10^{-34} \text{ Js}$).

Solution. Mass of dust particle = 1 mg = $10^{-3} \text{ g} = 10^{-6} \text{ kg}$

Uncertainty in velocity, $\Delta v = 5.5 \times 10^{-20} \text{ ms}^{-1}$; $\Delta x = ?$; $\pi = \frac{22}{7} = 3.14$

According to uncertainty principle, $\Delta x \cdot \Delta p = \frac{h}{4\pi}$ or $\Delta x \times m\Delta v = \frac{h}{4\pi}$

$$\therefore \Delta x = \frac{h}{4\pi \times m\Delta v} = \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 10^{-6} \text{ kg} \times 5.5 \times 10^{-20} \text{ ms}^{-1}} = 9.59 \times 10^{-10} \text{ m} \quad [\text{J} = \text{kg m}^2 \text{ s}^{-2}]$$

Example 10. Calculate the product of uncertainties of displacement and velocity of a moving electron having a mass of $9.1 \times 10^{-28} \text{ g}$ ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$).

Solution. Mass (m) of electron = $9.1 \times 10^{-28} \text{ g} = 9.1 \times 10^{-31} \text{ kg}$

According to Heisenberg's uncertainty principle, $\Delta x \times m\Delta v = \frac{h}{4\pi}$

\therefore Product of uncertainties of displacement and velocity, $\Delta x \times \Delta v = \frac{h}{4\pi m}$

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 9.1 \times 10^{-31} \text{ kg}} = 5.77 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

Example 11. A proton is accelerated to one tenth the velocity of light. Suppose its velocity can be measured with a precision of $\pm 1\%$. What must be its uncertainty in position?

Solution. We have $\Delta v = \left(\frac{1}{100}\right) \left(\frac{1}{10} c\right) = \frac{3 \times 10^8 \text{ ms}^{-1}}{1000} = 3 \times 10^5 \text{ ms}^{-1}$

Mass of proton = $1.672 \times 10^{-27} \text{ kg}$

According to Heisenberg's uncertainty principle,

$$\Delta x \cdot m\Delta v \geq \frac{h}{4\pi} \therefore \Delta x \geq \frac{1}{m\Delta v} \cdot \left(\frac{h}{4\pi}\right) \geq \frac{1}{(1.672 \times 10^{-27} \text{ kg})(3 \times 10^5 \text{ ms}^{-1})} \times \left(\frac{6.625 \times 10^{-34} \text{ Js}}{4 \times 3.142}\right)$$

$$\geq 1.05 \times 10^{-13} \text{ m.}$$

Example 12. On the basis of Heisenberg's uncertainty principle, show that an electron cannot exist in the nucleus. (Radius of nucleus = 10^{-15} m ; ($h = 6.6 \times 10^{-34} \text{ Js}$; $m = 9.1 \times 10^{-31} \text{ kg}$)

Solution. Radius of nucleus = 10^{-15} m .

Therefore, uncertainty in position of electron will be 10^{-15} m i.e. $\Delta x = 10^{-15} \text{ m}$.
According to uncertainty principle,

$$\Delta x \times \Delta p = \frac{h}{4\pi} \text{ or } \Delta x \times (m \cdot \Delta v) = \frac{h}{4\pi}$$

$$\therefore \Delta v = \frac{h}{4\pi \cdot m \cdot \Delta x} = \frac{6.6 \times 10^{-34} \text{ Js (or kg m}^2 \text{ s}^{-1})}{4 \times 3.142 \times 9.1 \times 10^{-31} \text{ kg} \times 10^{-15} \text{ m}} = 5.77 \times 10^{10} \text{ ms}^{-1}$$

which is about 200 times the velocity of light. Such a velocity for electron can never be possible as it cannot have velocity greater than the velocity of light. Hence electron does not exist in the nucleus of an atom.

1.7. SCHRODINGER WAVE EQUATION (WAVE MECHANICAL MODEL OF ATOM)

Schrodinger (1926) made use of the ideas of de Broglie, Heisenberg's uncertainty principle and Bohr's fixed orbits and developed a mathematical differential equation called Schrodinger wave equation*. The solution of this wave equation yields the electron distribution in space as well as the allowed energy levels of a particle (electron) moving in a given field. Keeping in view the particle nature of an electron, following classical wave equation describing the wave motion of a particle along the x-axis can be applied to it.

$$\Psi = A \sin 2\pi \frac{x}{\lambda} \text{ (classical wave equation) } \dots(1)$$

where Ψ = wave function

A = maximum value of Ψ

λ = wavelength of standing wave

(such as vibrating string fixed at its ends fig. 1.16)
travelling along x-axis and

x = Distance of particle from the nucleus.

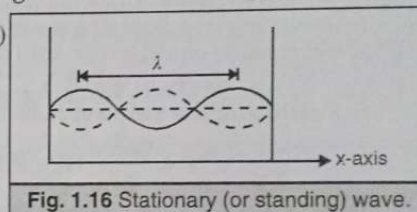


Fig. 1.16 Stationary (or standing) wave.

Differentiating Ψ with respect to x , we get $\frac{d\Psi}{dx} = A \cos 2\pi \frac{x}{\lambda} \left(\frac{2\pi}{\lambda} \right) = 2\pi \frac{A}{\lambda} \cdot \cos 2\pi \frac{x}{\lambda}$

Differentiating again, we get

$$\begin{aligned} \frac{d^2\Psi}{dx^2} &= 2\pi \frac{A}{\lambda} \left(-\sin \frac{2\pi x}{\lambda} \right) \frac{2\pi}{\lambda} = \frac{-4\pi^2 A}{\lambda^2} \sin \frac{2\pi x}{\lambda} = \frac{-4\pi^2}{\lambda^2} \left(A \sin \frac{2\pi x}{\lambda} \right) \\ &= \frac{-4\pi^2}{\lambda^2} \Psi \quad \left[\because \Psi = A \sin \frac{2\pi x}{\lambda} \text{ (classical wave equation) } \right] \end{aligned}$$

$$\therefore \frac{d^2\Psi}{dx^2} + \frac{4\pi^2}{\lambda^2} \Psi = 0 \dots(2)$$

This equation (2) represents wave motion of any particle along x-axis.

Since electron has a wave as well as particle character, the equation (2) also represents the wave motion of *electron wave* along x-axis.

If the electron is considered to move along x, y and z-axis, then

$$\frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} + \frac{4\pi^2\Psi}{\lambda^2} = 0 \quad \text{or} \quad \nabla^2\Psi + \frac{4\pi^2\Psi}{\lambda^2} = 0 \dots(i)$$

where $\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} = \nabla^2$ (The Laplacian operator)

∇^2 (read as del squared) is a mathematical operator called **Laplacian operator**

$$\frac{4\pi^2\Psi}{\lambda^2} = -\nabla^2\Psi \text{ (From equation (i)) } \quad \therefore \quad \frac{1}{\lambda^2} = -\nabla^2\Psi \frac{1}{4\pi^2\Psi} \dots(ii)$$

According to de Broglie $\lambda = \frac{h}{mv}$.

Squaring both sides, we get $\lambda^2 = \frac{h^2}{m^2v^2}$; $\frac{1}{\lambda^2} = \frac{m^2v^2}{h^2}$... (iii)

From equations (ii) and (iii), we get

$$\frac{m^2v^2}{h^2} = -\nabla^2\Psi \cdot \frac{1}{4\pi^2\Psi} \quad \text{or} \quad mv^2 = -\nabla^2\Psi \cdot \frac{h^2}{4\pi^2\Psi m}$$

$$\frac{1}{2}mv^2 = -\nabla^2\Psi \cdot \frac{h^2}{8\pi^2\Psi m} \quad \text{or} \quad \text{K.E.} = -\nabla^2\Psi \cdot \frac{h^2}{8\pi^2\Psi m}$$

$$\therefore \nabla^2\Psi = -\frac{8\pi^2\Psi m}{h^2} \cdot \text{K.E.} \quad \text{Thus} \quad \nabla^2\Psi + \frac{8\pi^2m}{h^2} \cdot \text{K.E.} \cdot \Psi = 0 \quad \dots(iv)$$

So far we have assumed that the electron is present in a field free space. Thus its potential energy (P.E.) is considered constant. But for most of the systems, such as an electron moving in a field of a positive nucleus, the P.E. can also vary. Thus, the total energy (E) of a system is equal to the sum total of potential energy (P.E.) and kinetic energy (K.E.)

$$\therefore \quad E = \text{K.E.} + \text{P.E.} \quad \text{or} \quad \text{K.E.} = E - \text{P.E.} \quad \dots(v)$$

Substituting the value of K.E. from (v) in (iv), we get

$$\nabla^2\Psi + \frac{8\pi^2m}{h^2} (E - \text{P.E.}) \Psi = 0 \quad \dots(vi)$$

This is known as the **Schrodinger wave equation**.

Schrodinger wave equation for hydrogen atom

Consider that hydrogen atom has nuclear charge $+Ze$ ($Z =$ atomic number) and charge on the electron is $-e$.

Potential energy of the electron $V = -kZe^2/r$ where $k = 9 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$. Thus, the Schrodinger wave equation takes the following form.

$$\nabla^2\Psi + \frac{8\pi^2m}{h^2} \left(E - \frac{-kZe^2}{r} \right) \Psi = 0 \quad \dots(vi)$$

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2m}{h^2} \left(E + \frac{e^2}{r} \right) \Psi = 0 \quad [\text{For H-atom, } k \text{ is constant ; } Z = 1]. \quad \dots(vii)$$

It is the Schrodinger wave equation for hydrogen atom.

Time Independent Schrodinger Equation

Ervin Schrodinger proposed an equation for finding the wave function of any system. The time independent Schrodinger equation for a particle of mass m moving in one dimension with energy E is :

$$\nabla^2\Psi + \frac{8\pi^2m}{h^2} [(E - V) \Psi(x)] = 0 \quad [V = \text{potential energy}]$$

Significance of Schrodinger wave equation (Eigen function, Eigen Values etc.)

1. Eigen values and eigen functions. Schrodinger wave equation is a second order differential equation. So, it has many solutions for Ψ . Many of them are imaginary and have no significance.

* An electron in an atom is in a more complex environment. It is confined in three dimensions by a potential derived from its attraction to the oppositely charged nucleus and modified by the repulsion between it and any other electron present. **The equation that summarises this principle is known as Schrodinger wave equation.**

Only those values of Ψ will be significant which satisfy the following conditions :

(i) The wave function must be finite and continuous.
(ii) The solution must be single valued *i.e.*, at a given point, there can never be more than one value for the amplitude, Ψ .

(iii) $\frac{d\Psi}{dx}$, $\frac{d\Psi}{dy}$ and $\frac{d\Psi}{dz}$ must be continuous function of x , y and z respectively.

(iv) The probability of finding an electron (around nucleus) over all the space from plus infinity to minus infinity must be equal to one. Thus,

$$\int_{-\infty}^{+\infty} d\Psi^2 dx dy dz = 1$$

where Ψ^2 represents the probability of finding an electron at a point x , y and z . Several wave functions, Ψ_1, Ψ_2, \dots which satisfy the above conditions have significant values and are called *eigen functions*. These significant values (called *eigen values*) are obtained by substituting proper values of total energy E in the wave equation. Each of the above wave functions has corresponding energy E_1, E_2, \dots and is called an **orbital**.

For an atom, these Eigen values correspond to discrete sets of energy values postulated by Bohr. Thus, we find that the **concept of wave mechanics leads to the presence of definite energy levels in an atom**.

5. 'Wave' is associated with the electron 'particle' and there are no specified discrete orbits for the movement of the electron. The frequency of wave describing the electron is related to its energy, given by $E = h\nu$

Limitation of Schrodinger wave equation. This equation can be solved **exactly** for one electron systems like hydrogen atom, hydrogen like atoms ($\text{He}^+, \text{Li}^{2+}$, etc.) **only**.

Significance of ψ . (i) It is a wave function which is solution to the Schrodinger wave equation.

(ii) It represents amplitude of wave and describes how this amplitude varies with distance and direction.

(iii) The Schrodinger wave equation may have different values of Ψ . All values may not be significant. The significant values of wave functions, Ψ are known as **EIGEN functions**. These functions give significant values of total energy (E) of the electron. These values are called **Eigen values**.

Significance of Ψ^2 i.e., square of amplitude. (i) For light waves, it represents intensity of light.

(ii) For electron waves, it represents intensity of electrons at any point, *i.e.*, it represents the probability of finding electron (of specific energy) at different regions in space.

(iii) It leads to the idea of orbital.

Ψ^2 is more significant than Ψ . Wave function Ψ represents an orbital. It depends on the coordinates of the particle. In certain cases, Ψ may turn out to be a complex function of the form, $\Psi = a + ib$ where $i = (-1)^{1/2}$ and a and b are the real functions of coordinates. In such a situation, complex conjugate of Ψ is Ψ^* where $\Psi^* = a - ib$ and $\Psi\Psi^* = (a + b)(a - ib) = a^2 - i^2 b^2 = a^2 - [(-1)^{1/2}]^2 b^2 = a^2 + b^2$.

Neither Ψ nor Ψ^* has any physical significance but $\Psi\Psi^*$ (written also as $|\Psi^2|$) has physical significance and is identical with Ψ^2 when Ψ is real. Thus to deal with all waves (like light, sound, matter or electrical etc.), the square of amplitude (Ψ^2) at any point is interpreted as intensities of that wave or effect at that point.

Since exact position of a wave or particle can not be known accurately (Heisenberg's uncertainty principle) at a point, we say that there is **probability** of finding that wave or particle at that point.

It should be remembered that Ψ^2 (but not Ψ) must be associated with probability density. It is because when wave equation is solved, there are some regions in which Ψ is positive and in some other regions Ψ is negative. But probability can never be negative. It must be positive or zero. Hence Ψ^2 is more significant than Ψ .