$T = E - V$; E is the total energy of the particle

also, the K.E., $T = \frac{1}{2} m v^2$; $m \rightarrow$ mass of particle
$v \rightarrow$ velocity of the particle

$$\therefore \quad T = E - V = \frac{1}{2} m v^2 \qquad \text{--- 13)}$$

$\because$ Momentum, $p = mv$ or $p^2 = m^2 v^2$

$$\text{or,} \quad \frac{p^2}{2m} = \frac{m^{\cancel{2}} v^2}{2 \cancel{m}} = \frac{1}{2} m v^2$$

Equation 13) becomes

$$T = E - V = \frac{p^2}{2m} \qquad \text{--- 14)}$$

$$\text{or,} \quad p^2 = 2m (E - V)$$

Putting the value of p^2 from eq^n 14) into eq^n 12),

we have,
$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = - \frac{4\pi^2 . 2m (E-V)}{h^2} \psi$$

$$\text{or,} \quad \boxed{\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2} (E-V) \psi = 0} \longleftarrow 15)$$

$\Rightarrow$ Schrödinger wave equation (1926)

The equation is represented as:

$$\boxed{\nabla^2 \psi + \frac{8\pi^2 m (E-V)}{h^2} \psi = 0} \qquad \text{--- 16)}$$

where $\nabla^2 \rightarrow$ del square $\rightarrow$ Laplacian operator

$$\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$$

Eq^n 11) becomes, $\nabla^2 \psi = - \frac{4\pi^2}{\lambda^2} \psi$ --- 17)

Eq^n 15) may be rearranged,

$$- \frac{h^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi$$

$$\text{or,} \quad - \frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V\psi = E\psi$$

$$\left[\hbar = \frac{h}{2\pi} \right.$$

or, $[-\frac{\hbar^2}{2m}(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}) + V]\psi = E\psi$ ——— 18)

or, $[-\frac{\hbar^2}{2m}\nabla^2 + V]\psi = E\psi$

——— 19)

or, $\boxed{\hat{H}\psi = E\psi}$

where $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V$

$\hat{H} \rightarrow$ Hamiltonian operator i.e.. the total energy of the system

Equations 15) and 19) are different forms of Schrödinger equations and have been applied to solve a number of problems related with atomic and molecular structures.

The Schrödinger equation can have several solutions, not all of which correspond to any physical or chemical reality. Such solution or wave functions, are!. not acceptable.

Physical Significance of Psi (Ψ)

The symbol Ψ is used to denote the wavefunction of an electron or particle. The square of wavefunction of an electron i.e; Ψ^2 is proportional to the probability of finding the electron in the given volume element.

Very often Ψ contains the imaginary quantity i, and $\boxed{i = \sqrt{-1}}$

Thus the value of Ψ^2 may be real or imaginary depending upon the nature of expression.

Since the probability of finding the material particle at a given point in space must always be a real quantity.

The product $\Psi\Psi^*$ sometime written as $|\Psi^2|$ and it is always real irrespective of fact that Ψ is real or imaginary.

We write $|\Psi^2|$ instead of Ψ^2

Ex. If Ψ is a complex quantity and $\Psi = a \pm ib$ and

$\therefore$ complex conjugate of this

$$\Psi^* = a \mp ib$$

$$\therefore \Psi\Psi^* = a^2 + b^2 \quad \because i^2 = -1 \quad ; i = \sqrt{-1}$$

$(a - ib)(a + ib)$

$a^2 + \cancel{a}ib - \cancel{a}ib - i^2b^2$

$a^2 - i^2b^2$

$a^2 - (-1)b^2$

$= a^2 + b^2$

If a particular eigen function is a real function and it contains no imaginary terms then the function and its complex conjugate will be identical

$$\psi \psi^{*} = \psi^{2}$$

Thus, (In view of the above fact) the $\psi(x, y, z) * \psi^{*}(x, y, z)\, dx.dy.dz$ is proportional to the probability of finding the particle in the small volume element $dx.dy.dz$, situated at a point in the space represented by the coordinate x, y, z. The above expression may be written as

$$\psi \psi^{*} d\tau$$

where $d\tau = dx.dy.dz. \Rightarrow$ small volume element

Thus $\psi \psi^{*} d\tau$ is referred as probability distribution function of the given system. Greater the amplitude greater is the probability of finding the particles at that point at a given instant.

The integral of $-\infty$ to $+\infty$

$\int_{-\infty}^{+\infty} \psi \psi^* d\tau$ is proportional to total probability of finding the particle somewhere in space. And for a well-behaved or acceptable wave function, this quantity must be finite, single valued and continuous throughout whole of the configuration space.

For many purposes, the function $\psi \psi^*$ be taken as equal to rather than proportional to the probability of finding the particle at a given point in space. Hence under this condition, the integral over the whole configuration space is equal to unity.

$$\int_{-\infty}^{+\infty} \psi \psi^* d\tau = 1 \qquad \text{— 1)}$$

Eigen function of wave function satisfying this relationship is known as Normalized wave function and if an electron is in volume element $d\tau$ ($d\tau = dx.dy.dz$) then

$$\int \psi \psi^* d\tau = 1$$

will be equal to the probability that is present in their volume element $d\tau$.

Some times ψ is not a normalized wave function and if it be made normalized by multiplying a constant A then the new wave function will be $A\psi$ and this also a solution to the wave function. [which will make the new ψ a normalized ψ then the problem becomes one of the choosing value of A] for the wave function $\underline{A\psi}$ to be normalized, it must satisfy the condition

$$\int_{-\infty}^{+\infty} A\psi \times A\psi^{*} \, d\tau = 1 \quad \text{———} \quad 2)$$

A ⇒ Normalized constant and can be determined by solving eq. 3)

or

$$\int_{-\infty}^{+\infty} \psi\psi^{*} \, d\tau = \frac{1}{A^2} \quad \text{———} \quad 3)$$

If we represent 2 different acceptable wavefunctions ψ_i and ψ_j, then the wave function will be normalized if they meet the requirement

$$\int \psi_i \times \psi_i^{*} \, d\tau = 1$$

← Complex conjugate of same wave function

or $\int \psi_j \times \psi_j^{*} \, d\tau = 1$

On the other hand if they behave such that

$$\int \psi_i \psi_j^{*} \, d\tau = 0$$

← Complex conjugate of different wave function

For $i \neq j$ or $\int \psi_i^{*} \psi_j \, d\tau = 0$

then they are said to be mutually orthogonal.

Orthonormal Set

wave function forms a orthonormal set if the relationship

$$\boxed{\begin{aligned} &\int_{-\infty}^{+\infty} \psi_j \psi_i^{*} \, d\tau = 1 \quad \text{for } i = j \quad \text{normalized} \\ \text{and} \quad &\int_{-\infty}^{+\infty} \psi_j \psi_i^{*} \, d\tau = 0 \quad \text{for } i \neq j \quad \text{orthogonal} \end{aligned}}$$

Conditions for acceptable wave function or well behaved

For a wave function to be acceptable over a specified interval, it must satisfy the following conditions;

(i) The function must be single valued

(ii) It must have a finite value (it is to be normalised)

(iii) It must be continuous in the given interval

~ The wave function ψ is single valued, i.e. for each value of the variables x, y, z, there is only one value of ψ.

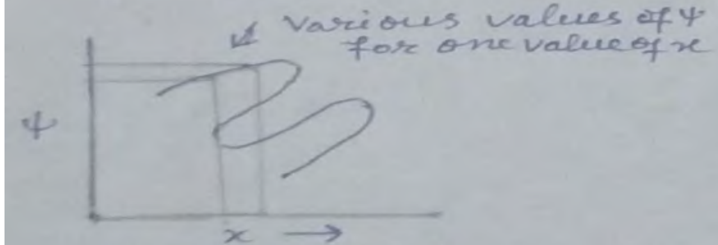
~ The wave function ψ and its first derivative w.r.t. its variables must be continuous i.e. there must not be any sudden change in ψ when its variables are changed

~ For bound states, ψ must vanish at infinity. If ψ is a complex function, then $\psi^*\psi$ must vanish at infinity (ψ^* is the complex conjugate of ψ)

Node $\rightarrow$ point where wave function is zero.

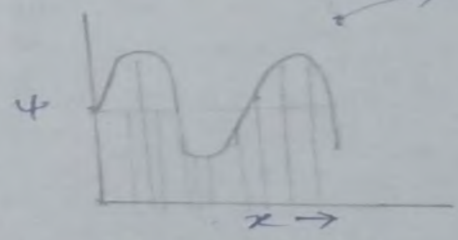
$\int_{-\infty}^{\infty} \psi \, d\tau$ this must be finite where the integration is carried out over the whole space of which $d\tau$ is small volume element. $d\tau = dx\,dy\,dz$

Examples:

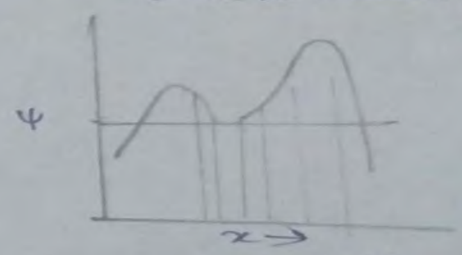


Not acceptable

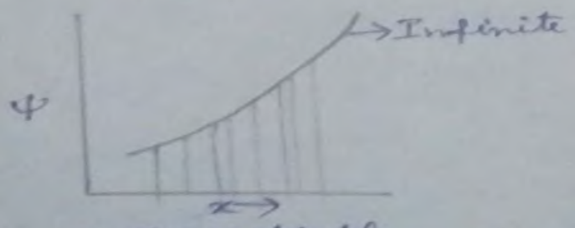
For one Ψ, there is only one x value



Acceptable



Acceptable



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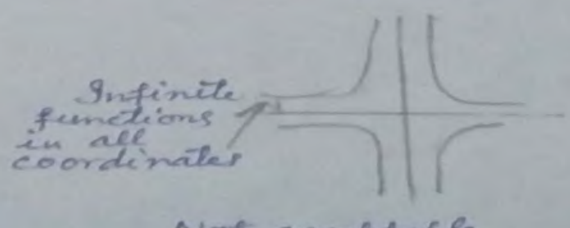
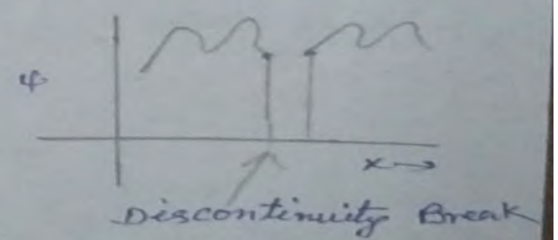


Not acceptable



Not acceptable

Q. Indicate, which of the following functions are acceptable wavefunctions?

(i) $\psi = x$
Not acceptable ; as $x \to \infty$, $\psi \to \infty$
$x \to -\infty$, $\psi \to -\infty$

ii) $\psi = x^2$ Not acceptable ; as $x \to \pm\infty$, $\psi \to \infty$
$\to$ not finite

(iii) $\psi = \sin x \to$ Acceptable :
single valued, continuous, finite

iv) $\psi = e^{x} \longrightarrow$ Not acceptable
single valued, continuous, not finite (infinite)
as $x \to \infty$, $\psi \to \infty$

v) $\psi = \tan x \to$ Not acceptable $\longrightarrow$ single valued, not continuous
$\psi \to \infty$ as $x = \pi/2$

vi) e^{-x} , $-\infty < x < \infty$
$\Rightarrow$ unacceptable, because e^{-x} diverges as $x \to -\infty$

vi) $\frac{1}{x}$, $1 < x < \infty$ $\to$ acceptable
Away from $x = 0$, $1/x$ is continuous, differentiable
and normalizable
$f(x) = \frac{1}{x}$ is normalized
$\int_{1}^{\infty} x^{-2}\, dx = 1$