Postulates

Postulate 1: The wavefunction attempts to describe a quantum mechanical entity (photon, electron, x-ray, etc.) through its spatial location and time dependence, i.e. the wavefunction is in the most general sense dependent on time and space:

$$\Psi = \Psi(x, t)$$

The ***state*** of a quantum mechanical system is completely specified by the wavefunction $\Psi(x, t)$.

The Probability that a particle will be found at time t_0 in a spatial interval of width dx centered about x_0 is determined by the wavefunction as:

$$P(x_0, t_0)\, dx = \Psi^*(x_0, t_0)\Psi(x_0, t_0)dx = |\Psi(x_0, t_0)|^2\, dx$$

Note: Unlike for a classical wave, with a well-defined amplitude (as discussed earlier), the $\Psi(x, t)$ amplitude is not ascribed a meaning.

Note: Since the postulate of the probability is defined through the use of a ***complex conjugate***, Ψ^*, it is accepted that the wavefunction is a complex-valued entity.

Note: Since the wavefunction is squared to obtain the probability, the wavefunction itself can be complex and/or negative. This still leaves a probability of zero to one.

Note: Ψ^* is the complex conjugate of Ψ. For instance:

$$\Psi(x) = A\, e^{i k x}$$

$$\Psi^*(x) = (A^*)\, e^{-i k x}$$

Since the probability of a particle being somewhere in space is unity, the integration of the wavefunction over all space leads to a probability of 1. That is, the wavefunction is normalized:

$$\int_{-\infty}^{\infty} \Psi^*(x, t)\Psi(x, t)dx = 1$$

In order for $\Psi(x, t)$ to represent a viable physical state, certain conditions are required:

1. The wavefunction must be a single-valued function of the spatial coordinates. (single probability for being in a given spatial interval)

2. The first derivative of the wavefunction must be continuous so that the second derivative exists in order to satisfiy the Schrödinger equation.

3. The wavefunction cannot have an infinite amplitude over a finite in- terval. This would preclude normalization over the interval.

Postulate 2: For every measurable property of the system in classical mechanics such as position, momentum, and energy, there exists a corre- sponding operator in quantum mechanics. An experiment in the lab to measure a value for such an observable is simulated in theory by operating on the wavefunction of the system with the corresponding operator.

Postulate 3: For a single measurement of an observable corresponding to a quantum mechanical operator, only values that are eigenvalues of the operator will be measured.

If measuring energy: one obtains eigenvalues of the time-independent Schrödinger equation:

$$\hat{H}\Psi_n(x,t) = E_n\Psi_n(x,t)$$

Postulate 4: The average, or expectation, value of an observable cor-responding to a quantum mechanical operator is given by

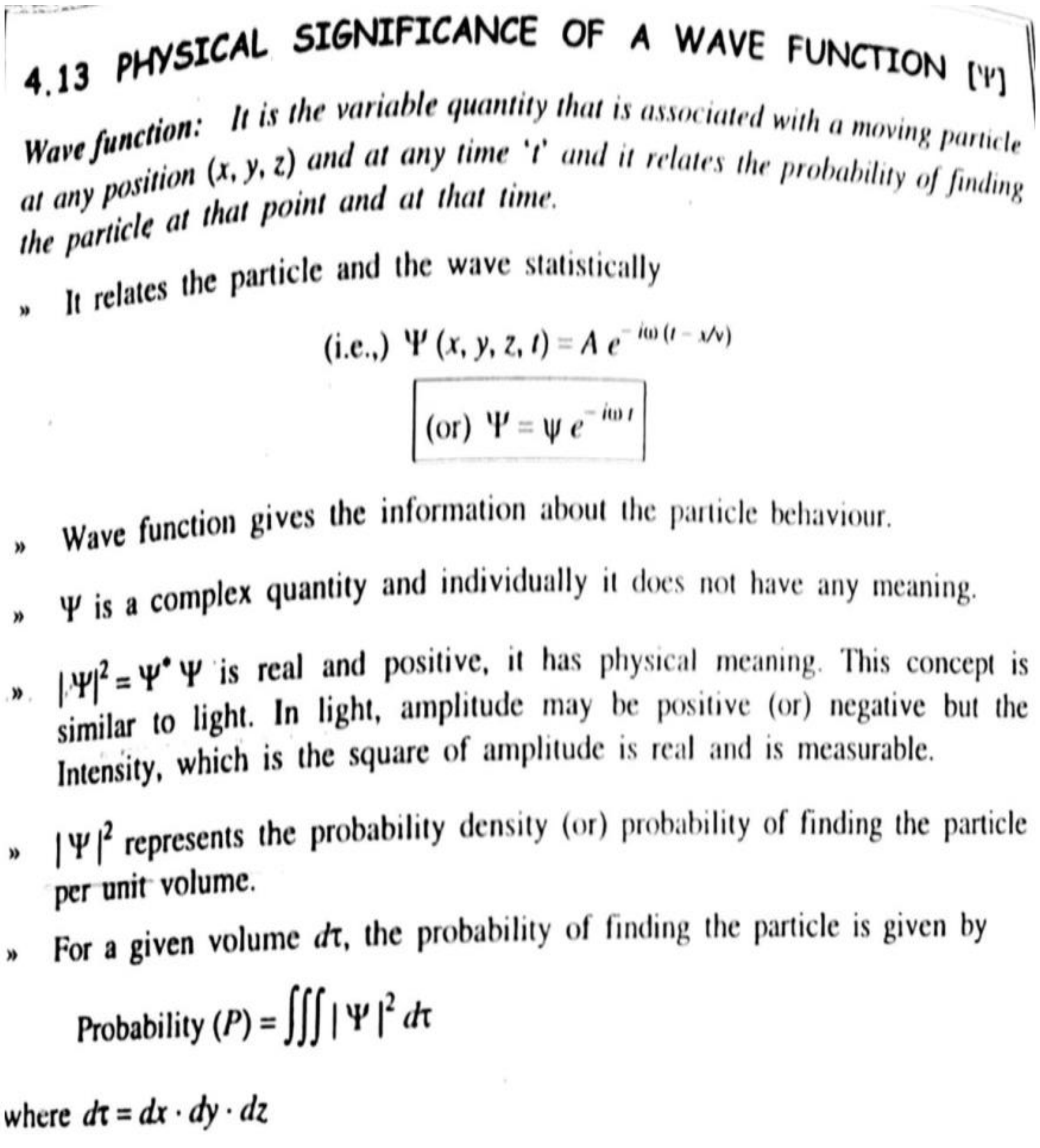
$$< a >= \frac{\int_{-\infty}^{\infty} \Psi^*(x, t)A\Psi(x, t)dx}{\int_{-\infty}^{\infty} \Psi^*(x, t)\Psi(x, t)dx}$$

Postulate 4: The time-dependent Schrödinger equation governs the time evolution of a quantum mechanical system:

$$\hat{H}\Psi(x,t) = i\hbar\frac{\partial\Psi(x,t)}{\partial t}$$

Schrödinger Wave Equation

The Schrödinger equation has two ‘forms’ , one in which time explicitly appears, and so describes how the wave function of a particle will evolve in time. In general, the wave function behaves like a wave, and so the equation is often referred to as the time dependent Schrödinger wave equation. The other is the equation in which the time dependence has been ‘removed’ and hence is known as the time independent Schrӧdinger equation and is found to describe, amongst other things, what the allowed energies are of the particle. These are not two separate, independent equations – the time independent equation can be derived readily from the time dependent equation (except if the potential is time dependent, a development we will not be discussing here). In the following we will describe how the first, time dependent equation can be ‘derived’, and in then how the second follows from the first.



4.13 PHYSICAL SIGNIFICANCE OF A WAVE FUNCTION [Ψ]

Wave function: *It is the variable quantity that is associated with a moving particle at any position (x, y, z) and at any time 't' and it relates the probability of finding the particle at that point and at that time.*

» It relates the particle and the wave statistically

$$\text{(i.e.,)}\ \Psi(x, y, z, t) = A\, e^{-i\omega(t - x/v)}$$

$$\boxed{\text{(or)}\ \Psi = \psi\, e^{-i\omega t}}$$

» Wave function gives the information about the particle behaviour.

» Ψ is a complex quantity and individually it does not have any meaning.

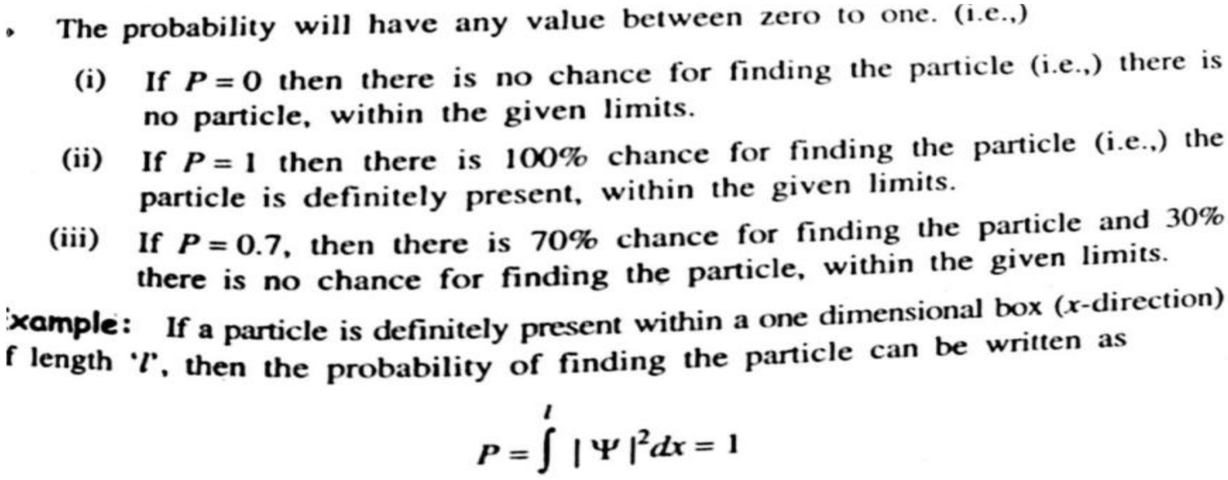
» $|\Psi|^2 = \Psi^* \Psi$ is real and positive, it has physical meaning. This concept is similar to light. In light, amplitude may be positive (or) negative but the Intensity, which is the square of amplitude is real and is measurable.

» $|\Psi|^2$ represents the probability density (or) probability of finding the particle per unit volume.

» For a given volume $d\tau$, the probability of finding the particle is given by

$$\text{Probability}\ (P) = \iiint |\Psi|^2\, d\tau$$

where $d\tau = dx \cdot dy \cdot dz$

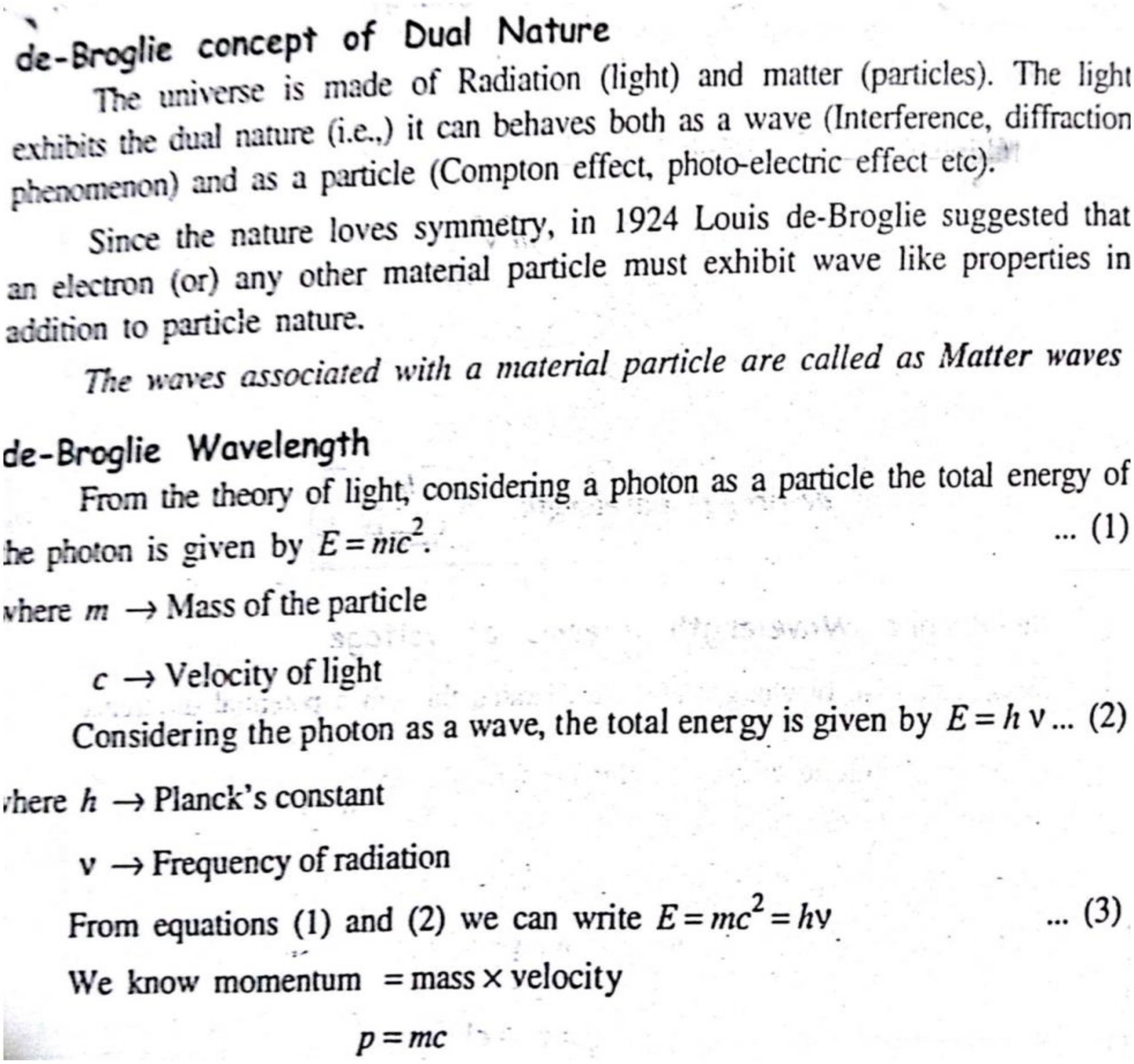


- The probability will have any value between zero to one. (i.e.,)
  - (i) If $P = 0$ then there is no chance for finding the particle (i.e.,) there is no particle, within the given limits.
  - (ii) If $P = 1$ then there is 100% chance for finding the particle (i.e.,) the particle is definitely present, within the given limits.
  - (iii) If $P = 0.7$, then there is 70% chance for finding the particle and 30% there is no chance for finding the particle, within the given limits.

xample: If a particle is definitely present within a one dimensional box (x-direction) f length 'l', then the probability of finding the particle can be written as

$$P = \int^{l} | \Psi |^2 dx = 1$$

DUAL NATURE OF RADIATION (LIGHT) AND MATTER (PARTICLES) – MATTER WAVES



de-Broglie concept of Dual Nature

The universe is made of Radiation (light) and matter (particles). The light exhibits the dual nature (i.e.,) it can behaves both as a wave (Interference, diffraction phenomenon) and as a particle (Compton effect, photo-electric effect etc).

Since the nature loves symmetry, in 1924 Louis de-Broglie suggested that an electron (or) any other material particle must exhibit wave like properties in addition to particle nature.

The waves associated with a material particle are called as Matter waves

de-Broglie Wavelength

From the theory of light, considering a photon as a particle the total energy of he photon is given by $E = mc^2$. ... (1)

vhere $m \rightarrow$ Mass of the particle

$c \rightarrow$ Velocity of light

Considering the photon as a wave, the total energy is given by $E = h\nu$ ... (2)

here $h \rightarrow$ Planck's constant

$\nu \rightarrow$ Frequency of radiation

From equations (1) and (2) we can write $E = mc^2 = h\nu$ ... (3)

We know momentum $=$ mass $\times$ velocity

$$p = mc$$

$$p = \frac{h\nu}{c}$$

Since $\frac{c}{\nu} = \lambda$ we can write $p = \frac{h}{\lambda}$

(or) The wavelength of a photon $\lambda = \frac{h}{p}$ ... (

de-Broglie suggested that equation (4) can be applied both for photons a material particles. If m is the mass of the particle and v is the velocity of t particle, then

Momentum $p = m\text{v}$.

$$\boxed{\therefore \text{ de-Broglie wavelength } \lambda = \frac{h}{m\text{v}}} \quad \text{... (5)}$$

Other forms of de-Broglie Wavelength

(i) de-Broglie wavelength interms of Energy

We know kinetic energy $E = \frac{1}{2} m\text{v}^2$

Multiplying by 'm' on both sides we get

$$Em = \frac{1}{2} m^2\text{v}^2$$

$$\text{(or)} \quad m^2\text{v}^2 = 2Em$$

$$m\text{v} = \sqrt{2Em}$$

$$\boxed{\therefore \text{ de-Broglie wavelength } \lambda = \frac{h}{\sqrt{2mE}}} \quad \text{... (6)}$$

(ii) de-Broglie Wavelength interms of voltage

If a charged particle of charge 'e' is accelerated through a potential difference 'V'

Then the kinetic energy of the particle $= \frac{1}{2} m\text{v}^2$ ... (7

Also we know energy $= eV$ ... (

Equating equations (7) and (8) we get

$$\frac{1}{2} m\text{v}^2 = eV$$

Multiplying by 'm' on both sides we get

$$m^2v^2 = 2meV$$

$$\text{(or)} \quad mv = \sqrt{2meV} \qquad \text{...(9)}$$

Substituting equation (9) in (5), we get

$$\boxed{\text{de-Broglie wavelength } \lambda = \frac{h}{\sqrt{2meV}}} \qquad \text{... (10)}$$

(iii) de-Broglie wavelength interms of Temperature

When a particle like neutron is in thermal equilibrum at temperature T, then they possess Maxwell distribution of velocities.

$\therefore$ Their kinetic energy $E_k = \frac{1}{2} mv_{rms}^2$ ... (11)

where v_{rms} is the Root mean square velocity of the particle.

Also, we know Energy $= \frac{3}{2} K_B T$ ... (12)

where K_B is the Boltzmann constant.

$\therefore$ Equating equations (11) and (12) we get

$$\frac{1}{2}mv^2 = \frac{3}{2} K_B T$$

$$\text{(or)} \quad m^2v^2 = 3m\, K_B T$$

$$mv = \sqrt{3mK_BT}$$

$$\boxed{\therefore \quad \text{de-Broglie wavelength } \lambda = \frac{h}{mv} = \frac{h}{\sqrt{3mK_BT}}} \qquad \text{... (13)}$$