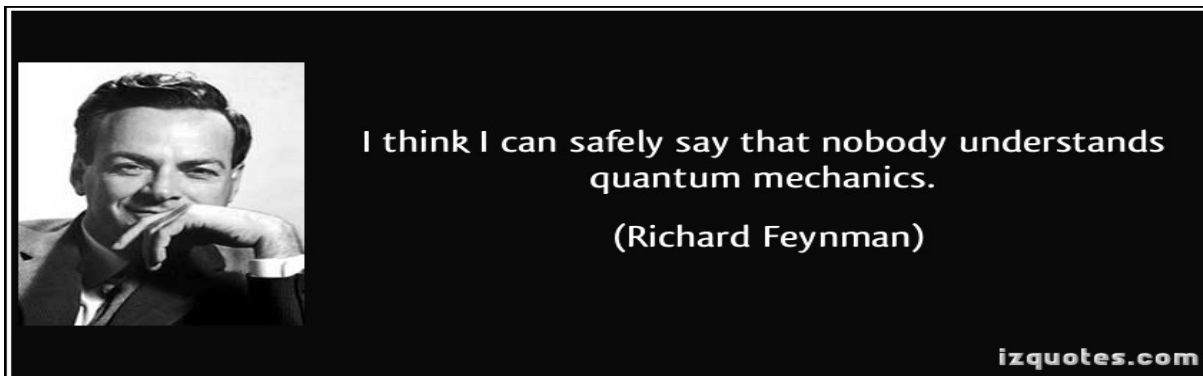


Quantum Mechanics

Unit : II



Dr. Somnath Biswas

Wave function associated with an electron

A microscopic particle is guided by a wave function Ψ , which is assumed to be a function of position vector \vec{r} and time t .

Such that

$$\Psi = \Psi(\vec{r}, t) \quad (5.18)$$

In general, Ψ is a complex number and the Probability of finding the particle is given by

$$\Psi^*(\vec{r}, t) \Psi(\vec{r}, t) = P(\vec{r}, t) \quad (5.19)$$

where $P(\vec{r}, t)$ is called the Probability density.

Therefore, the net probability of finding the particle in a particular volume

$dv = dx dy dz$ is given by

$$P(\vec{r}, t) dx dy dz = \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) dx dy dz \quad (5.20)$$

The wave function should be chosen in such a way that $P(\vec{r}, t)$ should be normalized. That is, Eq (5.20) should be integrated over whole space such that the particle should exist in that region. Therefore

$$\iiint_{\text{space}} P(\vec{r}, t) dx dy dz = \iiint_{\text{space}} \Psi^*(\vec{r}, t) \Psi(\vec{r}, t) dx dy dz = 1 \quad (5.21)$$

This is also called the normalization of the wave function.

for a beam of particles of identical energy ($= \frac{P^2}{2m}$) moving in one-dimension (say along x-axis) is considered to be a travelling wave

$$\Psi(x,t) = \sqrt{\frac{1}{L}} e^{i(kx - \omega t)} = \sqrt{\frac{1}{L}} [\cos(kx - \omega t) + i \sin(kx - \omega t)] \quad (5.12)$$

where $k = \frac{2\pi}{\lambda}$ is the angular wave-number and $\omega = 2\pi\nu$ is the angular frequency and $\sqrt{\frac{1}{L}}$ is the normalization factor which physically means the presence of one particle in each length L , along an infinite x-axis.

Also, according to the de Broglie relation

$$P = \frac{h}{\lambda} = \frac{hk}{2\pi} = \hbar k \quad (5.13)$$

and

$$E = h\nu = \frac{h\omega}{2\pi} = \hbar\omega \quad (5.14)$$

where \hbar is the reduced plank's constant ($= 1.0546 \times 10^{-34} \text{ J-s}$). Therefore Ψ (5.12) can be rewritten in terms of energy of the particle (E) and momentum (P) as

$$\begin{aligned} \Psi(x,t) &= \sqrt{\frac{1}{L}} e^{i(Px - Et)/\hbar} \\ &= \sqrt{\frac{1}{L}} \left[\cos \frac{1}{\hbar} (Px - Et) + i \sin \frac{1}{\hbar} (Px - Et) \right] \quad (5.15) \end{aligned}$$

Required Properties of Ψ

Vanish at endpoints (or infinity) $\Psi \rightarrow 0$ as $x \rightarrow \pm\infty$
 $y \rightarrow \pm\infty$
 $z \rightarrow \pm\infty$

Must be "Square Integrable"

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\Psi(\vec{r})|^2 dx dy dz < \infty \quad \text{or} \quad \int |\Psi(\vec{r})|^2 d\tau < \infty$$

Shorthand notation

Reason: Can "normalize" wavefunction

$$\int |\Psi(\vec{r})|^2 d\tau = 1$$

This equation is more logical for particle wave as it contains physical parameters like energy and momentum, related to matter, rather than wave number and frequency.

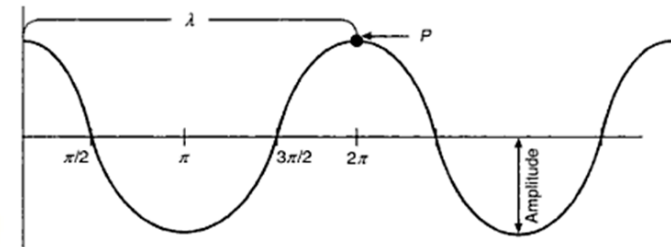
Now it is to be noted that in Eqs (5.22) and (5.25), a point of fixed phase (such as a peak in the real part of the wave, shown at point P in ~~Figure 5.2~~ the figure) moves as $x = (v_p/k)t$, so that

$$v_{ph} = \frac{\omega}{k} \quad (5.26)$$

is called phase velocity. Also $\Psi(x,t)$ has a constant absolute value at any x , describing a particle equally likely to be at any position on the infinite x -axis and there is no localization in this wave- f^u . Since the momentum is perfectly described, implying $\Delta x \rightarrow \infty$!!

Also, from relativistic formula, $E = mc^2$, we can write the phase velocity as

$$\begin{aligned} v_{ph} &= \frac{\omega}{k} = \left(\frac{E}{\hbar} \right) \left(\frac{\lambda}{2\pi} \right) \\ &= \left(\frac{mc^2}{\hbar} \right) \left(\frac{h}{p} \right) = \left(\frac{mc^2}{mv} \right) = \frac{c^2}{v} \end{aligned} \quad (5.27)$$



Representation of a cosine wave.

As particle velocity $v < c$, the velocity of light, therefore $v_{ph} > c$. That is, the de Broglie waves travel faster than light !!! To understand this unexpected result, the Heisenberg Uncertainty Principle comes into play to give the wave description of the location of a particle and introduce the term 'group velocity v_g ' to explain the matter wave.

Heisenberg Uncertainty Principle : Matter Wave and Wave Packets

Heisenberg Uncertainty principle states that the position x , and momentum p , of a particle can be measured simultaneously only to minimum levels of uncertainty, Δx and Δp respectively, such that

$$\Delta x \Delta p \geq \frac{h}{2} \quad (5.28)$$

The Uncertainty principle is basically a consequence of the wave description of the location of particle. For the wave function $\psi(x, t)$ described in Eq (5.22), as the free particle momentum $p = \hbar k$ can be measured precisely, therefore $\Delta p = 0$, which represents a case $\Delta x \rightarrow \infty$.

Description of localized particle can be done by a wavefunction which will be a linear combination of waves having a distribution of k and ω values. For example, a linear combination of two waves having can be written as

$$\begin{aligned} \psi(x, t) &= \psi_1(x, t) + \psi_2(x, t) \\ &= A \{ \cos(kx - \omega t) + \cos[(k + \Delta k)x - (\omega + \Delta \omega)t] \} \\ &= 2A \cos\left(\frac{\Delta k x - \Delta \omega t}{2}\right) \cos(kx - \bar{\omega} t) \end{aligned} \quad (5.29)$$

where $\bar{k} = k + \frac{\Delta k}{2}$ and

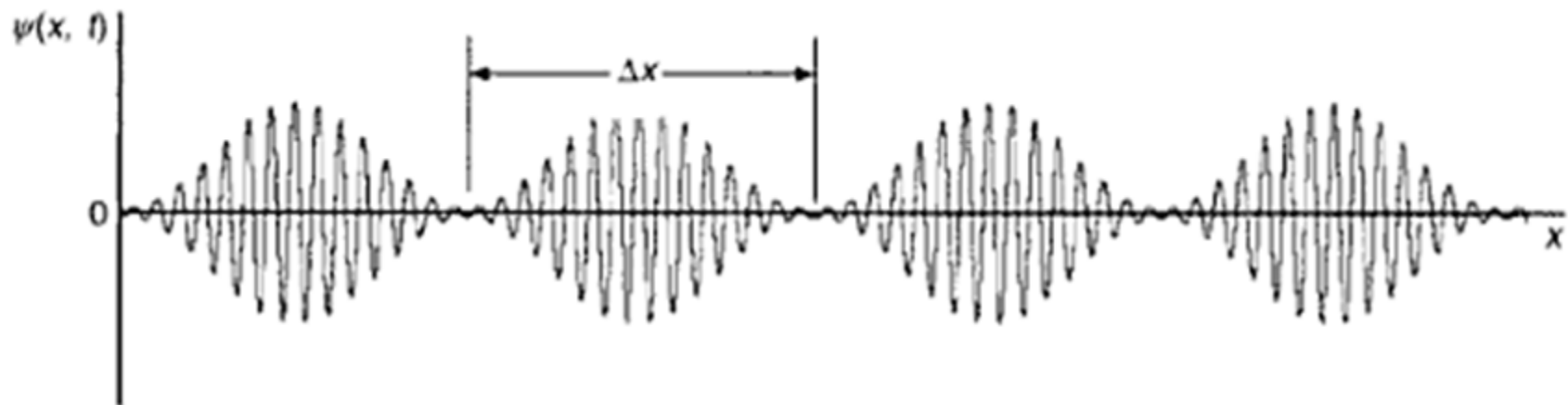
$\bar{\omega} = \omega + \frac{\Delta \omega}{2}$ now for $\Delta k \rightarrow 0$

and $\Delta \omega \rightarrow 0$, the factor

$\cos\left(\frac{\Delta k}{2}x - \left(\frac{\Delta \omega}{2}\right)t\right)$ acts like

an envelope function of long
wavelength and low frequency

which modulates the original
wave as shown in Fig.



Modulated waves showing regions of localization that move with group velocity.

At a fixed time t , the distance between two adjacent nodes, Δx , can be considered as the localization of the particle represented by the superposition of two waves and represented by

$$\Rightarrow \left. \begin{aligned} \Delta x &= \frac{2\pi}{\Delta k} \\ \Delta x \Delta k &= 2\pi \end{aligned} \right\} \quad (5.30)$$

This is a form of Uncertainty principle, which is basically a wave property. Now according to de Broglie relation, $\lambda p = h$ This gives

$$\Delta p \Delta x = h \quad (5.31)$$

This resembles with eq (5.28), but an accurate localization through Gaussian distribution of k values gives a narrower Uncertainty Value as stated in eq (5.28).

This group velocity (v_g) of the wave packet is described by the motion of the envelope function of eq (5.29) as

$$v_g = \frac{x}{t} = \frac{\Delta \omega}{\Delta k} \approx \frac{\partial \omega}{\partial k} \quad \text{at } \Delta k \rightarrow 0 \quad (5.32)$$

Now, for a localized moving particle of energy E , we have

$$\left. \begin{aligned} E = \hbar \omega &= \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \\ \omega &= \frac{\hbar k^2}{2m} \end{aligned} \right\} \quad (5.33)$$

$$\begin{aligned} p &= \hbar k \\ \Delta p &= \hbar \Delta k \end{aligned}$$

therefore, the group velocity v_g , will be given by

$$v_g = \frac{\partial \omega}{\partial k} = \frac{\hbar k}{m} = \frac{p}{m} = v \quad (5.24)$$

Thus the group velocity and the de Broglie relation reproduces the classical particle velocity v . Hence, this expression of group velocity has physical significance for particle wave, unlike phase velocity.

The EM field serves as a model for particle fields

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0} \text{ (Gauss's law)}$$

$$\nabla \cdot \mathbf{B} = 0 \text{ (Gauss's law for magnetism)}$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \text{ (Faraday's law)}$$

$$\nabla \times \mathbf{B} = \mu_0 \mathbf{J} + \mu_0 \epsilon_0 \frac{\partial \mathbf{E}}{\partial t} \text{ (Ampère-Maxwell law)}$$

ρ = charge density, \mathbf{J} = current density

Schrödinger Equation

Erwin Schrödinger first formulated the equation of the wavefunction $\Psi(x, t)$, describing the location of a particle in a given physical situation [10]. This equation is formulated on the following basis:

(i) The correct wave equation must reflect the de Broglie relation

$$\lambda = h/p \quad (\text{i.e. } E = \hbar\omega, \quad p = \hbar k).$$

(ii) The solution must be compatible with the Davison - Germer experiment of electron diffraction and must represent a travelling wave solution.

for a free particle. $\Psi(x, t) = \sqrt{1/2} e^{(i/\hbar)(px - Et)}$

To formulate the correct wave equation, the electromagnetic wave equation derived from Maxwell's equation has been taken as the guiding direction.

This wave equation is a second order partial differential equation of electric field \vec{E} and magnetic field \vec{H} as

$$\left. \begin{aligned} (\nabla^2 - \mu_0 \epsilon_0 \frac{\partial^2}{\partial t^2}) \vec{E}(\vec{r}, t) &= 0 \\ (\nabla^2 - \mu_0 \epsilon_0 \frac{\partial^2}{\partial t^2}) \vec{H}(\vec{r}, t) &= 0 \end{aligned} \right\} \quad (5.25)$$

where $\mu_0 \epsilon_0 = 1/c^2$; c is the speed of light, indicating that the origin of electromagnetic wave is similar to light.

Applying the above equation (in one-dimension) for the travelling wave solution $\psi(x,t)$

$\psi(x,t) = \int_{-\infty}^{\infty} e^{i(kx - \omega t)} dk$, we get

$$\begin{aligned} & \left(\frac{\partial^2}{\partial x^2} - \mu_0 \epsilon_0 \frac{\partial^2}{\partial t^2} \right) \psi(x,t) = 0 \\ \text{or} & \left(\frac{\partial^2}{\partial x^2} - \mu_0 \epsilon_0 \frac{\partial^2}{\partial t^2} \right) \int_{-\infty}^{\infty} e^{i(kx - \omega t)} dk = 0 \\ \text{or} & (-k^2 + \omega^2 \mu_0 \epsilon_0) \psi(x,t) = 0 \quad (5.36) \end{aligned}$$

The factors in the bracket relates to the speed of light as $\omega/k = \sqrt{1/\mu_0 \epsilon_0}$

$$\Rightarrow \omega/k = c.$$

This indicates that we need to form a matter-wave equation which should have a bracketed term as that given in Eq (5.36), which is having a physical significance as that of electromagnetic wave equation.

Looking at the bracketed term of Eq (5.36),
 a reasonable guess of the starting ^{relation} equation
 may be the expression of energy as
 Kinetic Energy ($\frac{P^2}{2m}$) + Potential Energy (U)
 = Total Energy (E), which can be
 converted into the following expression,
 when substituted with de Broglie relation:

$$\boxed{\frac{\hbar^2 k^2}{2m} + U = \hbar \omega} \quad (5.37)$$

Therefore, similar to Eq (5.36), one can be
 converted into the following
 generate an equivalent equation as

$$\boxed{\left(\frac{\hbar^2 k^2}{2m} + U - \hbar \omega \right) \Psi(x, t) = 0} \quad (5.38)$$

Now, knowing the solution of the
 wave-function to be $\Psi(x, t) \sim e^{\frac{i}{\hbar}(px - Et)} = e^{i(kx - \omega t)}$,

One can reproduce a wave-equation
 which should involve a term $\frac{\partial^2}{\partial x^2} \Psi(x, t)$

(for introduction of k^2 term)

and

$\frac{\partial}{\partial t} \Psi(x, t)$ (to introduce ω term).

Hence, the one-dimensional time
 dependent Schrodinger equation can be
 written as

$$\boxed{-\frac{\hbar^2}{2m} \times \frac{\partial^2}{\partial x^2} \Psi(x, t) + U(x, t) \Psi(x, t) = i \hbar \frac{\partial}{\partial t} \Psi(x, t)} \quad (5.39)$$

In 3D, this equation will look like

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\vec{r}, t) - i\hbar \frac{\partial}{\partial t} \right] \Psi(\vec{r}, t) = 0 \quad (5.40)$$

when the potential function is independent of time, i.e. $U = U(\vec{r})$ (in 1D), then spatial and time dependent parts of the total wave function $\Psi(x, t)$ can be separated as

$$\Psi(x, t) = \psi(x) \phi(t) \quad (5.41)$$

and when substituted in Eq (5.39), we get the dependant part as

$$\phi(t) = e^{-(i/\hbar)(Et)} \quad (5.42)$$

and the spatial part as

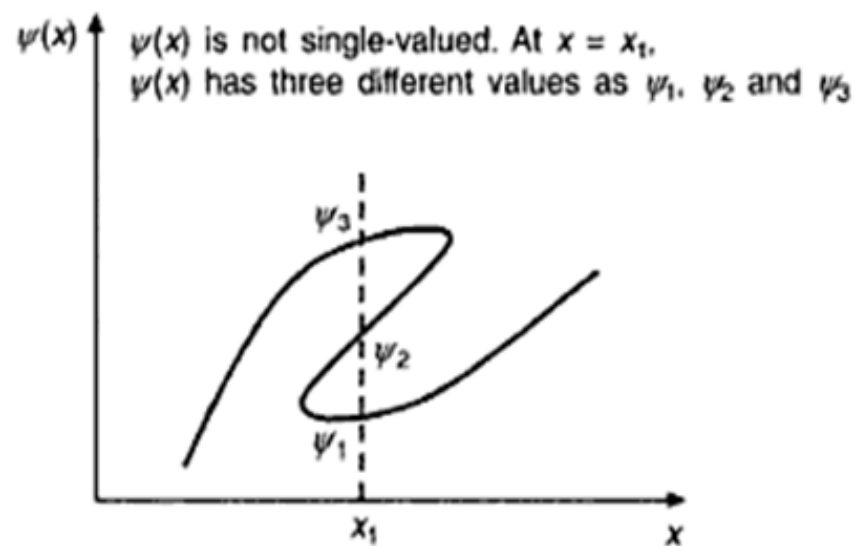
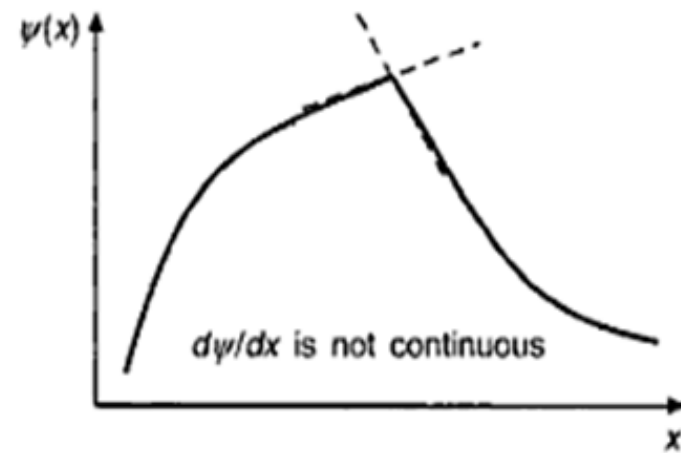
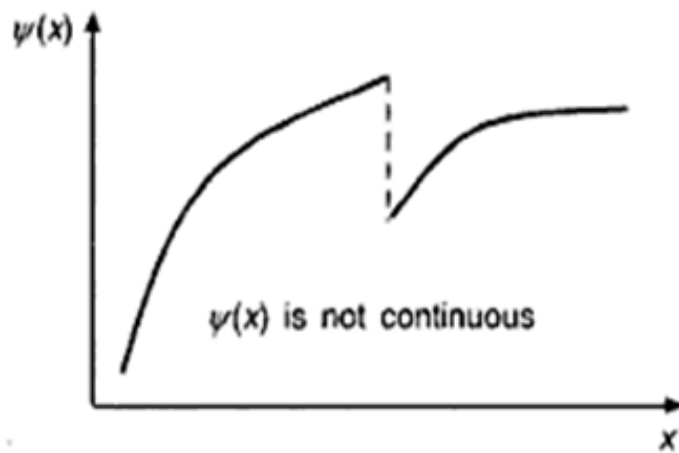
$$-\frac{\hbar^2}{2m} \times \frac{d^2}{dx^2} \psi(x) + U(x) \psi(x) = E \psi(x) \quad (5.43)$$

which is the time-independent Schrodinger equation (in 1D)

The solution $\psi(x)$ of this equation must satisfy the boundary conditions and physical requirements.

The requirements are:

1. $\psi(x)$ must be continuous.
2. $\psi(x)$ should have continuous derivative (unless the potential is infinite).
3. $\psi(x)$ should be single-valued and smooth as the probability of finding the particle is $|\psi(x)|^2$.



Unacceptable results of $\psi(x)$.

Mathematical Operators in Quantum Mechanics

$f(x)$	Any function of position, such as x , or potential $V(x)$	$f(x)$
p_x	x component of momentum (y and z same form)	$\frac{\hbar}{i} \frac{\partial}{\partial x}$
E	Hamiltonian (time independent)	$\frac{p_{op}^2}{2m} + V(x)$
E	Hamiltonian (time dependent)	$i\hbar \frac{\partial}{\partial t}$
KE	Kinetic energy	$\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
L_z	z component of angular momentum	$-i\hbar \frac{\partial}{\partial \phi}$

A quantum mechanical operator must be linear

$$\hat{A}(c\phi + d\psi) = c\hat{A}\phi + d\hat{A}\psi$$

Operator	Linear ?
$x^2 \cdot$	Yes
$\sqrt{}$	No
\log	No
\sin	No
$\frac{d}{dx}$	Yes
$\frac{d^2}{dx^2}$	Yes

Name of Observable	Symbol of Observable	Symbol of Operator	Operator
Position in 1D	x	\hat{x}	Multiply by x
Position in 3D	\mathbf{r}	\hat{r}	Multiply by r
Momentum in 1D	p	\hat{p}_x	$-i\hbar \partial / \partial x$
Momentum in 3D	\mathbf{p}	$\hat{\mathbf{p}}$	$-i\hbar \left(\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right)$
Kinetic energy	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	Multiply by $V(\mathbf{r})$
Total energy	E	\hat{H}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\mathbf{r})$
Angular momentum: x- component	l_x	\hat{l}_x	$-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
Angular momentum: y- component	l_y	\hat{l}_y	$-i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
Angular momentum: z- component	l_z	\hat{l}_z	$-i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

Operators, Eigen functions and Eigen values

Corresponding to every physical observable in Classical Mechanics, there is an operator in quantum mechanics which operates on the wavefunction(state) to produce another wavefunction. Thus we have

$$\hat{O}\psi = \psi'$$

All operators in quantum mechanics can be constructed from the basic operators for position and momentum.

$$\hat{x}\psi = x \times \psi$$
$$\hat{p}_x\psi = -i\hbar \frac{\partial}{\partial x} \psi$$

There are some generic properties of operators corresponding to observables. Firstly, they are linear operators so

$$\hat{O}(a\psi_1 + b\psi_2) = a\hat{O}\psi_1 + b\hat{O}\psi_2$$

Thus the form of operators includes multiplication by functions of position and derivatives of different orders of x , but no squares or other powers of the wavefunction or its derivatives. For a particle in 1-dimension, we have the kinetic energy operator derived as follows:

$$\hat{T} = \frac{\hat{p}_x^2}{2m} = \frac{\hat{p}_x \hat{p}_x}{2m} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

Similarly, the potential energy is a function of x and is denoted by $V(x)$. The operator for the potential energy is given by

$$\hat{V} = V(x) \times$$

In higher dimensions, we can construct operators for vector quantities and distances as follows:

$$\hat{\vec{r}} = \vec{r} \times$$
$$\hat{r} = |\hat{\vec{r}}| = r \times$$

Two operators \hat{O}_1 and \hat{O}_2 are said to commute if

$$\hat{O}_1\hat{O}_2\psi = \hat{O}_2\hat{O}_1\psi$$

for all ψ . If two operators commute, they can be simultaneously determined precisely. You should check that \hat{x} and \hat{p}_x do not commute. In fact, the form of these operators is chosen to satisfy the uncertainty principle.

Given an operator \hat{O} , it is possible to find a wavefunction $\psi(x)$ such that

$$\hat{O}\psi(x) = \lambda\psi(x)$$

where λ is a constant independent of x . The function ψ is called an eigenfunction of \hat{O} and λ is the corresponding eigenvalue of \hat{O} . Note that, if $\psi(x)$ is an eigenfunction with eigenvalue λ , then $a\psi(x)$ is also an eigenfunction with the same eigenvalue λ . Thus multiplying an eigenfunction by a constant does not change the eigenvalue.

Eigenvalues are related to observed values in experimental measurements as follows. In a single experiment, the measured value is an eigenvalue. In a large number of measurements (or measurement over a long period of time), the measured values is the expectation value or the average value defined as

$$\langle O \rangle = \int_S \psi^*(x)\hat{O}\psi(x)dx$$

where it is assumed that $\psi(x)$ is normalized, so $\int_S \psi^*(x)\psi(x)dx = 1$.

Notice that the expectation value of an eigenfunction state is simply the eigenvalue. If there are two different eigenfunctions with the same eigenvalue, then the eigenfunctions are said to be degenerate eigenfunctions.

Consider two eigenfunctions ψ_1 and ψ_2 of an operator \hat{O} with corresponding eigenvalues λ_1 and λ_2 respectively. The operator \hat{O} is called a Hermitian operator if all its eigenvalues are real and its eigenfunctions corresponding to different eigenvalues are orthogonal so that

$$\int_S \psi_1^*(x)\psi_2(x)dx = 0$$

if $\lambda_1 \neq \lambda_2$. It turns out that even if we have two degenerate eigenfunctions, we can construct orthogonal eigenfunctions.

A wavefunction that is not an eigenfunction can be expanded as a linear combination of eigenfunctions

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x)$$

Verify that if $\psi_1(x)$ and $\psi_2(x)$ are normalized, then the normalized wavefunction is

$$\psi(x) = \frac{1}{\sqrt{c_1^2 + c_2^2}}c_1\psi_1(x) + c_2\psi_2(x)$$

A generalization of the above statement is the superposition principle

Superposition Principle

Any wavefunction can be written as a linear combination of eigenfunctions of any operator.

$$\psi(x) = c_1\psi_1(x) + c_2\psi_2(x) + c_3\psi_3(x) + \dots$$

We can show that the expectation value of the observable O is given by

$$\langle \hat{O} \rangle = \frac{1}{\sqrt{c_1^2 + c_2^2}} (c_1^2\lambda_1 + c_2^2\lambda_2 + \dots)$$

The superposition principle is really the heart of the difference between QM and CM. The fact that particles are described by waves whose amplitudes can be added and combined is allows mixing of states, something that has no parallel in CM.

Before we go to the next section, we make a little point about the eigenvalue equation.

$$\hat{O}\psi = \lambda\psi$$

This single equation will yield both the allowed values of λ and the corresponding ψ . If the operator has a differential in it, then this equation becomes a differential equation. A crucial question that will be addressed in the following sections is whether the eigenvalues are countable (discrete) or continuous. It turns out that the boundary conditions for the eigenvalue equations will necessarily restrict the set of allowed eigenfunctions and eigenvalues for the system.

The equation of motion of the wave function

We now move on to an operator called the Hamiltonian operator which plays a central role in quantum mechanics. The Hamiltonian operator corresponds to the total energy of the system. For a single particle moving in 1-dimensions in a potential $V(x)$, the Hamiltonian operator is given by

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

In 3-D, we can write

$$\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(\vec{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$$

For a many particle system, we have to write the expression for the total energy which consists of the kinetic energy of the particles and the total potential energy of the system. For two particles in 3-dimensions, we can write

$$\hat{H} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V(\vec{r}_1, \vec{r}_2)$$

where

$$\nabla_1^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}$$

and so on. If the particles are interacting via a central potential and there is no external field, then

$$V(\vec{r}_1, \vec{r}_2) = V(|\vec{r}_1 - \vec{r}_2|) = V(r)$$

For example, if the particles are charged particles with charges q_1 and q_2 , then

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}$$

In general, you should be able to write the Hamiltonian operator for most simple systems.

The Hamiltonian operator plays a central role in the time dependent evolution of the wavefunction. A time-dependent wavefunction will have its equation of motion given by the **Time dependent Schrödinger equation(TDSE)**

$$i\hbar \frac{\partial \psi}{\partial t} = \hat{H} \psi$$

Thus the Hamiltonian operator is central to the time-evolution of the system. The above equation is independent of the number of particles. It is a fundamental equation that describes the motion of a quantum mechanical system.

Eigen values of the Hamiltonian Operator

If there is an eigenfunction ψ of the Hamiltonian operator with energy eigenvalue E , i.e. $\hat{H}\psi = E\psi$, then the time-evolution of the wavefunction starting from ψ at $t=0$ is given by the solution of the TDSE

$$\psi(t) = \psi e^{iEt/\hbar}$$

Note that the wavefunction does not change amplitude but only changes phase. Thus, all eigenvalues are the same. In particular, the energy does not change with time. Therefore, an energy eigenstate is called a Stationary state.

Stationary states are of fundamental importance in description of quantum systems. Therefore, the eigenvalue equation

$$\hat{H}\psi = E\psi$$

is referred to as the Time-Independent Schrödinger equation(TISE).

For a particle in 1D, we can see that the TISE is a 2nd order Differential equation, that can be solved for any value of E . However, as we shall see, the boundary conditions

of the system and the various properties of the wavefunction will impose restrictions on the allowed values that E can take for there to exist a solution of the TDSE. This will lead to quantization of energy.

For the remaining part of this course, our focus will be on solving the TISE and obtaining the allowed values of energy and their corresponding eigenfunctions for simple systems.

The methodology we adopt in all the systems is the same:

1. Decide on the variables of the system and the boundary conditions.
2. Write the Hamiltonian operator including the kinetic energy and the potential energy.
3. If necessary, simplify the TISE (Separation of variables, change of coordinates, etc.).
4. Solve the various pieces of the TISE and combine them to the final solutions
5. Analyze the solutions

We will put this methodology into action in the next few lectures.

Matter Waves & wave function

The quantity whose variations make up matter waves is called the wave function, symbol ψ .

The wave function ψ itself, however, has no direct physical significance.

There is simple reason why ψ can not be interpreted in terms of an experiment. The probability that something be in a certain place at a given time must lie between 0 (the object is definitely not there) and 1 (the object is definitely there). An intermediate probability, say 0.2, means that there is a 20% chance of finding the object.

But the amplitude of wave can be negative as well as positive and a negative probability, say -0.2, is meaningless.

Hence ψ by itself cannot be observable quantity.

This objection does not apply to $|\psi|^2$, the square of the absolute value of wave function, which is known as probability density;

The probability of experimentally finding the body described by the wave function ψ at the point x, y, z at the time t is proportional to the value of $|\psi|^2$ there at t .

A large value of $|\psi|^2$ means the strong possibility of the body's presence, while a small value of $|\psi|^2$ means the slight possibility of its presence. As long as $|\psi|^2$ is not actually 0 somewhere, however small, of detecting it there, there is a definite chance however small, of detecting it there.

This interpretation was first made by Max Born in 1926.

Probability amplitude \rightarrow amplitude that a particle from sources will arrive at x .

we will use short hand notation for probability amplitude invented by Dirac and generally used in Q.M.

Dirac Notation

In early days of quantum theory, P. A. M. (Paul Adrian Maurice) Dirac created a powerful and concise formalism for it which is now referred to Dirac notation or bra-ket. (bracket $\langle | \rangle$). Two major mathematical traditions emerged in quantum mechanics

1. Heisenberg's Matrix mechanics
2. Schrodinger's Wave mechanics.

Let us talk about Dirac Notation

In Dirac's notation what is put in ket, $| \rangle$.
Known

So for example

- ① $|p\rangle \rightarrow$ expresses the fact that a particle has momentum p . It could also be more explicit: $|p=2\rangle$. the particle has momentum equal to 2.

- ② $|x=3\rangle$ would be the state of particle known to be at position $x=3$ cm.

- ③ $|x=3\text{ cm}, x=5\text{ cm}\rangle$ is "Not a possible state" - it has a contradiction. A particle cannot be in two places at once, even in quantum mechanics.

- ④ $|\psi\rangle$ represents a system in the state ψ and is therefore called the state vector.

"The ket can also be interpreted as the initial state in some transition or event."

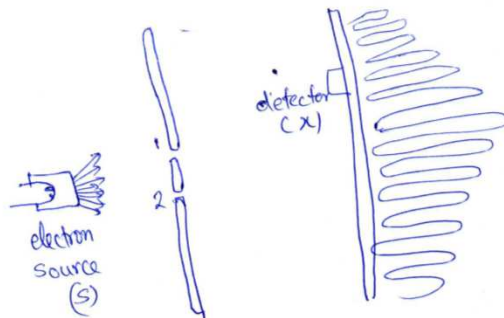
The bra $\langle 1$ represents the final state or the language in which you wish to express the content of the ket $| \rangle$.

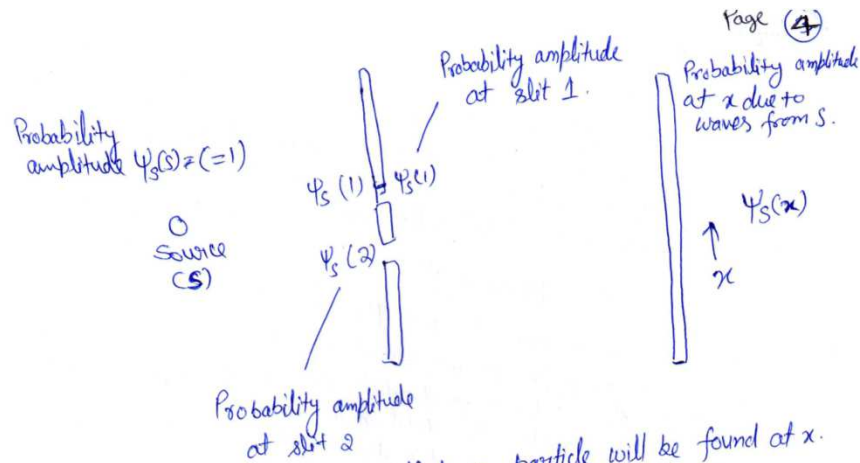
e.g. $\langle x=0.25 | \psi \rangle$ is the probability amplitude that a particle in state ψ will be found at $x=0.25$.
In conventional notation $\psi(x=0.25)$, the value of the function ψ at $x=0.25$.

We see that a bra-ket pair can represent an event, the result of an experiment. In quantum mechanics an experiment consists of two sequential observations - one that establishes the initial state (ket) and one that establishes the final state (bra).

$\langle x | \psi \rangle$ = The probability amplitude that a system in state $|\psi\rangle$ has position x . = $\psi(x)$

The Two slit experiment revisited





We ask for the probability that a particle will be found at x .

Our first general principle in quantum mechanics is that the probability that a particle will arrive at x , when let out at the source S , can be represented quantitatively by the absolute square of a complex number called a probability amplitude - in this case, the "amplitude that a particle from S will arrive at x ".

We will use such amplitudes so frequently and will write here in Dirac notation.

$$\begin{aligned} \text{Probability amplitude} &= \langle \text{Particle arrives at } x \mid \text{particle leaves } S \rangle \\ &\downarrow \\ &\langle \text{Final point} \mid \text{Initial point} \rangle \\ &\downarrow \\ &\langle \text{Final condition} \mid \text{Initial condition} \rangle \\ &\downarrow \\ &\langle x \mid S \rangle \end{aligned}$$

$\langle \rangle$ = "the amplitude that"

When there are two ways for the particle to reach the detector, the resulting probability is not the sum of the two probabilities, but must be written as the absolute square of the sum of two amplitudes. We had that the probability that an electron arrives at the detector when both paths are open is

$$P_{12} = |\Phi_1 + \Phi_2|^2$$

~~Now~~ we wish now to put this result in terms of our new notation. First, however, we want to state our second general principle of Q.M.: When a particle can reach a given state by two possible routes, the total amplitude for the process is the sum of the amplitudes for the two routes considered separately

$$\langle x | S \rangle_{\text{both holes are open}} = \langle x | S \rangle_{\text{through 1}} + \langle x | S \rangle_{\text{through 2}}$$

Now we want to write out in more detail what we can say about the amplitude for the process in which the electron reaches the detector at x by way of hole 1. We can do that by using our third general principle. When a particle goes by some particular route the amplitude for that route can be written as the product of the amplitude to go part way with the amplitude to go the rest of the way.

For give figure (1) the amplitude to go from S to x by way of hole 1 is equal to the amplitude to go from S to 1, multiplied by the amplitude to go from 1 to x

$$\langle x | S \rangle_{\text{via 1}} = \langle x | 1 \rangle \langle 1 | S \rangle$$

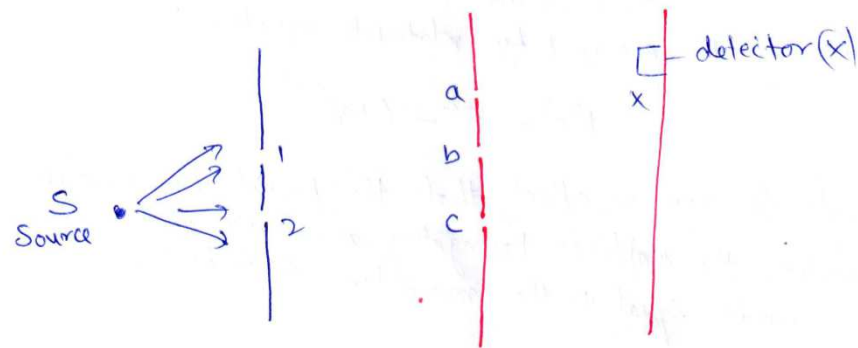
Similarly

$$\langle x | S \rangle_{\text{via 2}} = \langle x | 2 \rangle \langle 2 | S \rangle$$

from equation ① & ②

$$\langle x | s \rangle_{\text{both}} = \langle x | 1 \rangle \langle 1 | s \rangle + \langle x | 2 \rangle \langle 2 | s \rangle$$

if more complicated system



probability amplitude

$$\begin{aligned} \langle x | s \rangle = & \langle x | a \rangle \langle a | 1 \rangle \langle 1 | s \rangle + \langle x | a \rangle \langle a | 2 \rangle \langle 2 | s \rangle \\ & + \langle x | b \rangle \langle b | 1 \rangle \langle 1 | s \rangle + \langle x | b \rangle \langle b | 2 \rangle \langle 2 | s \rangle \\ & + \langle x | c \rangle \langle c | 1 \rangle \langle 1 | s \rangle + \langle x | c \rangle \langle c | 2 \rangle \langle 2 | s \rangle \end{aligned}$$

We can save writing by using the summation notation

$$\langle x | s \rangle = \sum_{\substack{i=1,2 \\ \alpha=a,b,c}} \langle x | \alpha \rangle \langle \alpha | i \rangle \langle i | s \rangle$$

Suppose a particle with a definite energy is going in empty space from a location q_1 to location q_2 . In other words, it is a free particle with no forces on it.

Amplitude to go from q_1 to q_2 is

$$\langle q_2 | q_1 \rangle = \frac{e^{i\vec{p} \cdot \vec{q}_{12}/\hbar}}{q_{12}} \quad \text{--- (3)}$$

where $q_{12} = q_2 - q_1$ and p is the momentum which is related to the energy E by relativistic equation

$$p^2 c^2 = E^2 - (m_0 c^2)^2$$

Equation (3) says in effect that the particle has wavelike properties, the amplitude propagating as a wave with a wave number equal to the momentum divide by \hbar .

The Postulates of Quantum Mechanics

Recall our position and momentum operators \mathbf{P} and \mathbf{R}

- They have corresponding eigenstate \mathbf{r} and \mathbf{k} $\mathbf{R}|\mathbf{r}\rangle = \mathbf{r}|\mathbf{r}\rangle, \quad \mathbf{P}|\mathbf{k}\rangle = \hbar\mathbf{k}|\mathbf{k}\rangle$

If we measure the position of a particle:

- The probability of finding it at \mathbf{r} is proportional to
- If it *is* found at \mathbf{r} , then afterwards it is in state

$$|\Psi(\mathbf{r})|^2 = |\langle \mathbf{r} | \Psi \rangle|^2$$

$$|\Psi^+\rangle = |\mathbf{r}\rangle$$

If we measure the momentum of a particle:

- The probability of momentum \mathbf{k} is proportional to
- After the measurement, it is in state

$$|\tilde{\Psi}(\mathbf{k})|^2 = |\langle \mathbf{k} | \Psi \rangle|^2$$

$$|\Psi^+\rangle = |\mathbf{k}\rangle$$

- This will generalize to *any* observable we might want to measure
- When we *aren't* doing measurements, we expect Schrödinger's Equation to work

Overview: Consider a quantum system in state $|\Psi\rangle$, and two observables A, B (with eigenvalues a, b and eigenvectors $|a\rangle, |b\rangle$).

A measurement of \hat{A} yields a with probability $|\langle a|\Psi\rangle|^2$. (Likewise for B .)

The *uncertainty* ΔA measures the overall spread in possible outcomes of the measurement (i.e., it measures the width of the probability distribution). It is defined as

$$\Delta A \equiv \langle (\hat{A} - \langle \hat{A} \rangle)^2 \rangle$$

So a system in a general quantum state $|\Psi\rangle$ lacks a well-defined a -value. The exception is if $|\Psi\rangle$ happens to be an eigenstate $|a\rangle$, in which case its a -value is unambiguous and hence the uncertainty ΔA associated with the measurement is zero. In this case we can say that the system is "in" the state with the definite observable value a .

Question: When is it possible to say that a quantum system is in a state with definite observable values a and b ? (i.e., zero uncertainty in either measurement value)