

## Matter Waves

In light waves, the Electric field (**E**) and Magnetic field (**B**) vary  
**What does vary in matter waves/de Broglie waves?**

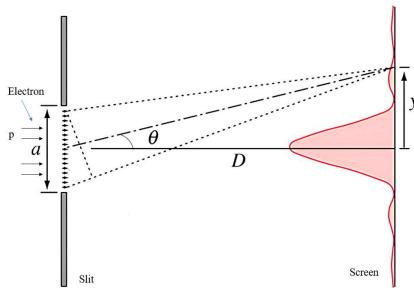
The wavefunction  $\Psi \rightarrow$

Related to the probability of finding a body at a point (x,y,z) in space at a time t.

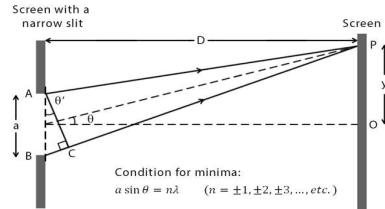
### Physical significance:

$|\Psi|^2 \rightarrow$  absolute value of wavefunction  $\rightarrow$  probability density  
 $\rightarrow$  proportional to the probability of experimentally finding the body described by the wavefunction  $\Psi$  at point (x, y, z) at time t

### Uncertainty principle demonstrated (single slit thought experiment)



A parallel beam of electrons, each having momentum  $p$ , is diffracted at a slit of width “ $a$ ”, forming a diffraction pattern on a screen.



At point P on the screen, the secondary waves interfere destructively, producing a dark fringe.

Assume that the screen is at a considerable distance from the slit,  $D \gg a$ , hence,  $\theta = \theta'$   
 $\Rightarrow \sin \theta \approx \tan \theta \approx \theta = y/D$

The path difference between the two rays AP and BP =  $\delta = BP - AP = BC$   
 In the right-angled triangle BCA,  
 $\sin \theta' = \sin \theta = BC/BA$

Condition for minima:  
 $a \sin \theta = n\lambda \quad (n = \pm 1, \pm 2, \pm 3, \dots, \text{etc.})$

The condition for minima or dark fringe →  
 Path difference = integral multiple of wavelength

$$\delta = n\lambda \quad (n = \pm 1, \pm 2, \pm 3, \dots, \text{etc.})$$

$$a \sin \theta = n\lambda$$

$$ay/D = n\lambda$$

$$y_n = n\lambda D/a$$

$\theta$ : Deflection angle to the 1<sup>st</sup> minima  
 $a \sin \theta = \lambda$

### Uncertainty principle demonstrated

When an electron arrives at the screen, one is not sure exactly where it has passed through the slit

Therefore, uncertainty in 'y' coordinate :  $\Delta y \approx a$

**What about uncertainty in the 'y-component' of the momentum of the electron?**

If we consider  $\theta$  to be the average diffraction angle, then  $\Delta p_y$  = Uncertainty in the y component of momentum.

$$\Delta p_y \approx p_y = p \sin \theta$$

$$\begin{aligned}\Delta y \cdot \Delta p_y &\approx ap \sin\theta \\ &= p\lambda && \text{as, } a \sin\theta = \lambda \\ \text{Using } \lambda &= \frac{h}{p} \\ \text{We get } \Delta y \cdot \Delta p_y &= h\end{aligned}$$

More rigorous calculation based on wave groups:

$$\begin{aligned}\Delta y \cdot \Delta p_y &\geq \frac{h}{4\pi} \\ \Delta x \cdot \Delta p_x &\geq \frac{h}{4\pi} \\ \Delta z \cdot \Delta p_z &\geq \frac{h}{4\pi}\end{aligned}$$

## The Uncertainty principle

Heisenberg *uncertainty principle*.

cannot simultaneously determine the exact value of a component of momentum,  $p_x$  say, of a particle and also the exact value of its corresponding coordinate,  $x$ . Instead, our precision of measurement is inherently limited by the measurement process itself such that

$$\Delta p_x \Delta x \geq \hbar/2$$

$$\hbar \equiv h/2\pi$$

$$\Delta p_y \Delta y \geq \hbar/2 \text{ and } \Delta p_z \Delta z \geq \hbar/2,$$

$\Delta p_x = 0, \Delta x = \infty$ ). Hence, *the restriction is not on the accuracy to which  $x$  or  $p_x$  can be measured, but on the product  $\Delta p_x \Delta x$  in a simultaneous measurement of both.*

$$\Delta p_x \Delta x \geq \hbar/2 \quad (\text{position-momentum uncertainty})$$

$$\Delta E \Delta t \geq \hbar/2 \quad (\text{Energy-time uncertainty})$$

where  $\Delta E$  is the uncertainty in our knowledge of the energy  $E$  of a system and  $\Delta t$  the time interval characteristic of the rate of change in the system.

**It is impossible to know both the exact position and the exact momentum of an object at the same time.**

Consider an electron moving along the x-axis with Energy

$$E = \frac{p^2}{2m} \quad \text{if } p_x \text{ is uncertain by } \Delta p_x$$

$$\Delta E = \frac{2p_x}{2m} \Delta p_x = v_x \Delta p_x$$

Here  $v_x$  can be interpreted as the recoil velocity of the electron along the x-axis when it is illuminated by a bright ray.  
If the time interval for the observation of the electron is  $\Delta t$ , then the uncertainty in position  $\Delta x = v_x \Delta t$

$$\Delta E \cdot \Delta t = \Delta x \cdot \Delta p_x \geq \frac{\hbar}{4\pi}$$

## Postulates of Quantum Mechanics

**The postulates of quantum mechanics are fundamental axioms that describe the behavior of quantum systems**

### 1. Description of the state of a system

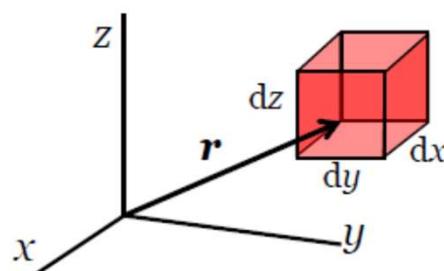
At a fixed time  $t$ , the state of a physical system is defined by its **wavefunction** or **state function**  $\Psi(\vec{r}, t)$

The wavefunction contains information about all the properties of the system that are subject to experimental determination.

The wavefunction depends on the spatial coordinates of all the particles that constitute the system and on time

The wavefunction itself has no physical meaning, but its square modulus,  $|\psi|^2$  (when real) or  $\psi^*\psi$  (when complex) represents the probability density or distribution for the system.

For a wavefunction  $\psi(\mathbf{r})$ , the probability of finding the particle in the volume element or volume of the infinitesimal region  $d\tau$  at  $\mathbf{r}$  is proportional to  $|\psi(\mathbf{r})|^2 d\tau$ . This is, however, valid only if the system contains only one particle.



$$d\tau = dx \, dy \, dz$$

The  $\psi(\mathbf{r})$  itself is known as probability amplitude.

Given the wavefunction  $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots)$ , the probability of finding particle 1 in  $d\tau_1$  at  $\mathbf{r}_1$  and particle 2 in  $d\tau_2$  at  $\mathbf{r}_2$  is  $|\psi(\mathbf{r})|^2 d\tau_1 d\tau_2, \dots$

### Wave function $\Psi$

- $\Psi \rightarrow$  Can be complex
- $|\Psi|^2 = \Psi^* \Psi \rightarrow$  probability density

For 1-D motion, the probability of finding a particle between  $x_1$  and  $x_2$  is  $P_{x1,x2} = \int_{x_1}^{x_2} |\Psi|^2 dx$

$$\int_{-\infty}^{\infty} |\Psi|^2 dv = N^2 \rightarrow \text{some finite quantity}$$

$N^2$  = Normalization constant

$$\int_{-\infty}^{\infty} \left| \frac{\Psi}{N} \right|^2 dv = 1 \quad \text{Normalization}$$

Any wave function that obeys the above condition is said to be **normalized**

The actual Probability of finding the particle anywhere within the volume

$$\text{For 1-Dimension} \quad N^2 \int_{-\infty}^{\infty} \psi(r)^* \psi(r) dx = 1$$

In general;

$$N^2 \int_{-\infty}^{\infty} \psi(r)^* \psi(r) d\tau = 1$$

$$\text{For 2-Dimensions} \quad N^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(r)^* \psi(r) dx dy = 1$$

In the case of multiple particles

$$\text{For 3-Dimensions} \quad N^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(r)^* \psi(r) dx dy dz = 1$$

$$N^2 \int_{-\infty}^{\infty} \psi(r)^* \psi(r) d\tau_1 d\tau_2 \dots = 1$$

Remember that when  $\psi$  real

$$\psi(r)^* \psi(r) = |\psi(r)|^2$$

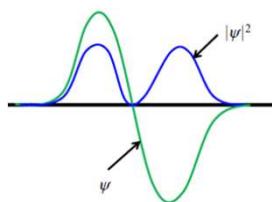
➤  $\Psi$  must also be single-valued since the probability of finding a particle at a certain time and particular place must be single-valued.

➤  $\Psi$  must be continuous

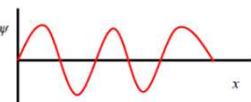
The Max Born interpretation of a wavefunction placed 4 restrictions on an acceptable wavefunction.

An acceptable wavefunction must:

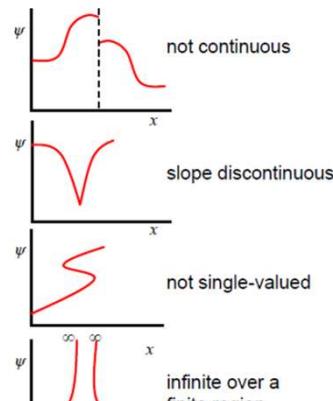
- (i) be continuous
- (ii) have a continuous slope
- (iii) be single-valued
- (iv) be square-integrable



The sign of a wavefunction has no direct physical importance: +ve and -ve regions of wavefunction both correspond to the same probability distribution.



An acceptable wavefunction



Unacceptable wavefunction

### Well-Behaved Wave Functions

1.  $\Psi$  must be continuous and single-valued everywhere.
  2.  $\frac{\partial \Psi}{\partial x}$ ,  $\frac{\partial \Psi}{\partial y}$ ,  $\frac{\partial \Psi}{\partial z}$  must be continuous and single-valued everywhere.
  3.  $\Psi$  must be normalizable, which means that  $\Psi$  must go to 0 as  $x \rightarrow \pm \infty$ ,  $y \rightarrow \pm \infty$ ,  $z \rightarrow \pm \infty$  in order that  $\int |\Psi|^2 dv$  over all space be a finite constant.
- Only wave functions with all these properties can yield physically meaningful results when used in calculations
  - So only such “well-behaved” wave functions are admissible as mathematical representations of real bodies.

## Postulates of Quantum Mechanics

### 2. Description of Physical quantities:

Every measurable physical quantity in quantum mechanics is described by a quantum mechanical operator

**All observables in classical mechanics have a corresponding linear, Hermitian operator in quantum mechanics**

An **operator** is something that carries out a mathematical operation on a function.

- A caret/cap/hat is placed over a mathematical symbol to designate an operator, e.g.,  $\widehat{\Omega}$  and  $\widehat{A}$ .
- All operators “operate” on a function written to their right and produce a new function,

$$\widehat{Q} f(x) = g(x)$$

↓  
 operator      ↑  
 function      “new” function

For  $f(x) = x^3$  and  $\widehat{Q} = d/dx$ , then

$$\widehat{Q}f(x) = \frac{d}{dx}(x^3) = 3x^2 = g(x)$$

A linear operator obeys the following condition:

$$\widehat{Q}[\alpha f(x) + \beta g(x)] = \alpha \widehat{Q} f(x) + \beta \widehat{Q} g(x)$$

where  $\alpha$  and  $\beta$  are constants;

All Hermitian operators have the eigenfunction-eigenvalue relationship:

$$\widehat{Q} f(x) = \omega f(x)$$

the function  $f(x)$ , the eigenfunction is the same on both sides  
 $\omega$ , the eigenvalue is a real number.

Physical Quantities:	Operator
Position Coordinate : $x$	$\hat{x}$
Position Vector : $\vec{r}$	$\hat{r}$
X component of momentum : $p_x$	$-i\hbar \frac{\partial}{\partial x}$
Momentum : $\vec{p}$	$-i\hbar \vec{\nabla}$
Kinetic Energy : $p^2/2m$	$-\frac{\hbar^2}{2m} \nabla^2$
Potential Energy : $V(\vec{r}, t)$	$\hat{V}(\vec{r}, t)$
Total Energy : $\frac{p^2}{2m} + V(\vec{r}, t)$	$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(\vec{r}, t)$

### 3. Eigenfunction-eigenvalue relationship

All observable values,  $\omega_n$ , for a system in state  $\psi_n$  obey the eigenfunction-eigenvalue relationship. The subscript  $n$  indicates a whole family of solutions, with each member given by a quantum number  $n$ .

$$\hat{Q} \psi_n = \omega_n \psi_n$$

eigenvalue equation

$$(operator)(function) = (constant factor) \times (function)$$

operator(function)      (constant factor) x (function)

eigenfunction,      eigenvalue  
eigenstate or  
eigenvector

An observable, a real number, is a quantity that is obtained from a single measurement of the system.

- Consider a six-sided die as a macroscopic system:  

 outcomes = observables = 1, 2, 3, 4, 5 and 6.

- For the hydrogen atom, each eigenfunction represents a particular atomic orbital and the operator gives the corresponding energy as the eigenvalue.
- Essentially, everything that is measurable in quantum mechanics is quantised.

**The only possible result of the measurement of a physical quantity is one of the *eigenvalues* of the corresponding observables**

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} = \text{Energy of a system}$$

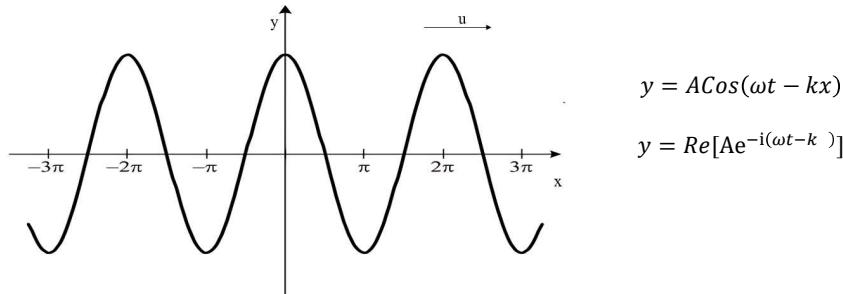
$$\hat{H}\Psi = E\Psi$$

eigenvalue equation  
 Energy operator (Hamiltonian)      Eigenvalue of the Hamiltonian operator : Energy

$\Psi$  → eigenfunction, eigenstate or eigenvector

**4. Evolution of the wave function/ wave-vector: governed by the Schrödinger equation that can have a variety of solutions, including complex ones**

Moving particle has a wave nature: De-Broglie  
[Wavefunction for a free particle]



$$\Psi = Ae^{-i(\omega t - kx)} \rightarrow \text{Solution of wave equation.}$$

**The wavefunction for a free particle**

$$\Psi = Ae^{-i(\omega t - kx)} \rightarrow \text{Solution of wave equation.}$$

$$\text{Replace } \omega \rightarrow \omega = 2\pi\nu ; k = \frac{2\pi}{\lambda}$$

$$\begin{aligned} \text{We know } E &= h\nu \\ &= 2\pi\hbar\nu \\ &= \hbar\omega & k &= \frac{2\pi}{\lambda} = \frac{2\pi p}{h} & \rightarrow & p &= \hbar k \end{aligned}$$

$$\Psi = Ae^{-\frac{i}{\hbar}(Et - px)}$$

Wave function of a free particle moving in +x direction

$\Psi = Ae^{-\frac{i}{\hbar}(Et-p)}$  : Wave function of a free particle moving in  $+x$  direction.

$$\frac{\partial \Psi}{\partial x} = \frac{ip}{\hbar} \Psi$$

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

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{ip}{\hbar} \frac{\partial \Psi}{\partial x}$$

$$= -\frac{p^2}{\hbar^2} \Psi$$

$$\frac{\partial \Psi}{\partial t} = -\frac{iE}{\hbar} \Psi \quad \rightarrow \quad \hat{E} = i\hbar \frac{\partial}{\partial t}$$

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \quad \hat{E} = i\hbar \frac{\partial}{\partial t}$$

At speeds  $\ll c$

$$\text{Total energy of a particle: } E = \frac{p^2}{2m} + V = \text{K.E.} + \text{P.E.}$$

$$\hat{E}\Psi = \frac{\hat{p}^2}{2m} \Psi + \hat{V}\Psi$$

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + \hat{V}\Psi \quad \leftarrow \text{1-D Time-dependant Schrödinger equation (TDSE)}$$

In 3-D

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} \right] + \hat{V}\Psi$$

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + \hat{V}\Psi \quad \leftarrow \quad \text{3-D Time-dependent Schrödinger equation (TDSE)}$$

**Schrödinger's equation cannot be derived from other basic principles of physics, it is a basic principle in itself.**

- We started from the wave function of a freely moving particle, i.e.,  $V=0$
- Extend this to a general case of having potential.
- There is no way to tell if this procedure is right or wrong.
- The only way is to calculate for the real cases and compare them with the experiments.
- Schrodinger's equation cannot be "derived" but can be established empirically.

Once we know potential  $V$ , we solve the Schrodinger equation to get  $\Psi$

### Time independent Schrodinger equation (Steady state Schrodinger equation in 1D)

$$\Psi = A e^{-\frac{i}{\hbar}(Et - \frac{p^2}{2m}x)} = A e^{\frac{ip}{\hbar}x} e^{\frac{-iE}{\hbar}t} = \psi e^{\frac{-iE}{\hbar}t}$$

Substituting in TDSE  $V = V(x,y,z)$  [independent of time]

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + \hat{V}\Psi$$

$$E\Psi e^{\frac{-iEt}{\hbar}} = -\frac{\hbar^2}{2m} \left( e^{\frac{-iE}{\hbar}t} \right) \frac{\partial^2 \Psi}{\partial x^2} + \hat{V}\Psi e^{\frac{-iEt}{\hbar}}$$

$$E\psi e^{-\frac{iEt}{\hbar}} = -\frac{\hbar^2}{2m} \left( e^{-\frac{iEt}{\hbar}} \right) \frac{\partial^2 \psi}{\partial x^2} + \hat{V}\psi e^{-\frac{iEt}{\hbar}}$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} [E - V]\psi = 0$$

Time Independent/ Steady state Schrodinger equation in 1D

In 3D Schrodinger equation is written as:

$$\nabla^2 \psi + \frac{2m}{\hbar^2} [E - V]\psi = 0$$

### 5: Average or Expectation value

$\rho(\vec{r}, t)dv = \Psi^*(\vec{r}, t)\Psi(\vec{r}, t)dv$   
= the probability of finding the particle in the volume element  $dv$  about point  $\vec{r}$ , at time  $t$ .

The expectation value (or average value) of the position vector of the particle.

$$\begin{aligned} \langle \vec{r} \rangle &= \int \vec{r} \rho(\vec{r}, t)dv \\ &= \int \Psi^*(\vec{r}, t) \hat{r} \Psi(\vec{r}, t)dv \end{aligned}$$

$$\begin{aligned} \bar{x} &= \frac{x_1 N_1 + x_2 N_2 + \dots}{N_1 + N_2 + \dots} \\ &= \frac{x_1 N_1}{N_1 + N_2 + \dots} + \frac{x_2 N_2}{N_1 + N_2 + \dots} \\ &= \sum_i x_i p_i \end{aligned}$$

#### Physical Meaning:

It is the value of the measurement of  $\vec{r}$  on a very large number of equivalent identically prepared independent systems represented by the wave function  $\Psi$ .

## REMEMBER PREVIOUS DISCUSSION

### Derivation of the average energy in Planck's formula

Average energy:  $\bar{\mathcal{E}} = \frac{\sum_{n=0}^{\infty} \mathcal{E} P(\mathcal{E})}{\sum_{n=0}^{\infty} P(\mathcal{E})}$

$$P(\mathcal{E}) = \frac{e^{-\mathcal{E}/kT}}{kT}$$

$P(\mathcal{E}) d\mathcal{E}$  is the probability of finding a given entity of a system with energy in the interval between  $\mathcal{E}$  and  $\mathcal{E} + d\mathcal{E}$ ,

$\mathcal{E} = nh\nu$  where  $n = 0, 1, 2, 3, \dots$

## REMEMBER PREVIOUS DISCUSSION

### Continuing: Average or Expectation value

The expectation value of an arbitrary function  $f(\vec{r}, t) = f(x, y, z, t)$  is

$$\langle f(\vec{r}, t) \rangle = \int \Psi^*(\vec{r}, t) f(\vec{r}, t) \Psi(\vec{r}, t) dv \quad (\text{provided that integral exists}).$$

Similarly, for expectation value of A is

$$\langle A \rangle = \int \Psi^*(\vec{r}, t) \hat{A} \Psi(\vec{r}, t) dv$$

$$\langle p_{x,y,z} \rangle = \int \Psi^*(\vec{r}, t) \left( -i\hbar \frac{\partial}{\partial x, y, z} \right) \Psi(\vec{r}, t) dv$$

$$\langle \vec{p} \rangle = \int \Psi^*(\vec{r}, t) (-i\hbar \vec{\nabla}) \Psi(\vec{r}, t) dv$$

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

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* \left( \frac{\hbar}{i} \frac{\partial}{\partial x} \right) \Psi \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial x} \, dx$$

$$\langle E \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{E} \Psi \, dx = \int_{-\infty}^{\infty} \Psi^* \left( i\hbar \frac{\partial}{\partial t} \right) \Psi \, dx = i\hbar \int_{-\infty}^{\infty} \Psi^* \frac{\partial \Psi}{\partial t} \, dx$$

Let us see why expectation values involving operators have to be expressed in the form

$$\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi \, dx$$

The other alternatives are  $\int_{-\infty}^{\infty} \hat{p} \Psi^* \Psi \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \frac{\partial}{\partial x} (\Psi^* \Psi) \, dx = \frac{\hbar}{i} [\Psi^* \Psi]_{-\infty}^{\infty} = 0$

since  $\Psi^*$  and  $\Psi$  must be 0 at  $x = \pm\infty$ , and

$$\int_{-\infty}^{\infty} \Psi^* \Psi \hat{p} \, dx = \frac{\hbar}{i} \int_{-\infty}^{\infty} \Psi^* \Psi \frac{\partial}{\partial x} \, dx$$

which makes no sense. In the case of algebraic quantities such as  $x$  and  $V(x)$ , the order of factors in the integrand is unimportant, but when differential operators are involved, the correct order of factors must be observed.

- A Hermitian operator, like a wavefunction, can also be complex and therefore all Hermitian operators obey the following condition:

$$\int_{-\infty}^{\infty} \psi_i^* \hat{\Omega} \psi_j \, d\tau = \int_{-\infty}^{\infty} \psi_i \hat{\Omega}^* \psi_j^* \, d\tau$$

where  $\hat{\Omega}^*$  = the complex conjugate of the operator  $\hat{\Omega}$ ,  
 $\psi_i^*$  = the complex conjugate of the wavefunction  $\psi_i$   
and  $\psi_j^*$  = the complex conjugate of the wavefunction  $\psi_j$

- Again, the eigenfunctions of Hermitian operators are orthonormal, i.e. the product of the functions integrate over all space to either 0 or 1.

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, d\tau = \delta_{ij} \text{ (Kronecker delta)}$$

$$\delta_{ij} = \begin{cases} 0 & \text{when } i \neq j \text{ (orthogonal)} \\ 1 & \text{when } i = j \text{ (normal)} \end{cases}$$

Find  $\langle \hat{x}\hat{p}_x - \hat{p}_x\hat{x} \rangle$

$$\begin{aligned}
 \langle \hat{x}\hat{p}_x - \hat{p}_x\hat{x} \rangle &= \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) (\hat{x}\hat{p}_x - \hat{p}_x\hat{x}) \Psi(\vec{r}, t) dx \\
 &= -i\hbar \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) \left[ \frac{x\partial\Psi}{\partial x} - \frac{\partial(x\Psi)}{\partial x} \right] dx \\
 &= -i\hbar \int_{-\infty}^{+\infty} \Psi^*(\vec{r}, t) \left[ \frac{x\partial\Psi}{\partial x} - \psi - x \frac{\partial(\Psi)}{\partial x} \right] dx \\
 &= i\hbar \int_{-\infty}^{+\infty} \Psi^* \Psi dx \\
 &= i\hbar
 \end{aligned}$$

### Conservation of probability

If a particle is described by a normalized wavefunction,  $\Psi(\vec{r}, t)$ , then the probability of finding the particle at a time  $t$  within a volume element  $dV$  about the point  $\vec{r}(x, y, z)$

$$\rho(\vec{r}, t)dV = |\Psi(\vec{r}, t)|^2 dV \rightarrow \int_V |\Psi(\vec{r}, t)|^2 dV = 1$$

Considering the probability of finding the particle within a finite volume  $V$

$$\int_V \rho(\vec{r}, t)dV = \int_V |\Psi(\vec{r}, t)|^2 dV$$

**The rate of change of probability**

$$\frac{\partial}{\partial t} \int_V \rho(\vec{r}, t) dV = \frac{\partial}{\partial t} \int_V \Psi^* \cdot \Psi dV \\ = \int_V [\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}] dV$$

Now refer to TDSE

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V(\vec{r}) \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

Complex conjugate of TDSE

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi^* + V(\vec{r}) \Psi^* = -i\hbar \frac{\partial \Psi^*}{\partial t} \\ -\frac{\hbar^2}{2m} \Psi^* \nabla^2 \Psi + \Psi^* V \Psi = i\hbar \Psi^* \frac{\partial \Psi}{\partial t} \\ -\frac{\hbar^2}{2m} \Psi \nabla^2 \Psi^* + \Psi V \Psi^* = -i\hbar \Psi \frac{\partial \Psi^*}{\partial t}$$

Subtracting the above equations

$$-\frac{\hbar^2}{2m} [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] = i\hbar [\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}]$$

**The rate of change of probability** =  $\frac{\partial}{\partial t} \int_V \rho(\vec{r}, t) dV = \frac{\partial}{\partial t} \int_V \Psi^* \cdot \Psi dV$

$$= \int_V [\Psi^* \frac{\partial \Psi}{\partial t} + \Psi \frac{\partial \Psi^*}{\partial t}] dV$$

Analogous to the continuity equation of charge conservation in electrodynamics :

$$\left[ \frac{\partial \rho(\text{Charge density})}{\partial t} + \vec{v} \cdot \vec{j}(\text{current density}) \right] = 0$$

$$= \frac{i\hbar}{2m} \int_V [\Psi^* \nabla^2 \Psi - \Psi \nabla^2 \Psi^*] dV$$

**J is interpreted as the probability current density**

Where

$$\vec{j} = \frac{\hbar}{2mi} [\Psi^* \vec{\nabla} \Psi - \Psi \vec{\nabla} \Psi^*] \\ = \frac{i\hbar}{2m} [\Psi \vec{\nabla} \Psi^* - \Psi^* \vec{\nabla} \Psi]$$

= Probability Current Density

### Look at the Time Dependent Schrodinger Equation

If the potential  $V \neq V(t)$ ;  $V = V(x, y, z)$  then the Hamiltonian  $H = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r})$  is not a frame of time.  
Then the time-dependent Schrodinger equation simplifies considerably.

$$\text{Time Dependent Schrodinger Equation} \quad i\hbar \frac{\partial \Psi}{\partial t} = \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + \hat{V}(\vec{r}) \right] \Psi(\vec{r}, t)$$

$$\text{Assume} \quad \Psi(\vec{r}, t) = \Psi(\vec{r})f(t)$$

$$i\hbar \Psi(\vec{r}) \frac{\partial f}{\partial t} = \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi(\vec{r}) + \hat{V}(\vec{r}) \Psi(\vec{r}) \right] f(t)$$

$$\text{Divide both sides by} \quad \Psi(\vec{r}, t) = \Psi(\vec{r})f(t)$$

$$\frac{i\hbar}{f(t)} \frac{\partial f}{\partial t} = \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi(\vec{r}) + \hat{V}(\vec{r}) \Psi(\vec{r}) \right] \frac{1}{\Psi(\vec{r})}$$

$$\frac{i\hbar}{f(t)} \frac{\partial f}{\partial t} = \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi(\vec{r}) + \hat{V}(\vec{r}) \Psi(\vec{r}) \right] \frac{1}{\Psi(\vec{r})}$$

LHS only depends on the  $t$  and RHS only depends on  $r$

→ both sides must be equal to a constant.

This constant should have the dimension of Energy (denoted by E)

$$i\hbar \frac{\partial f}{\partial t} = Ef(t) \quad \left[ -\frac{\hbar^2}{2m} \vec{\nabla}^2 + \hat{V}(\vec{r}) \right] \Psi(\vec{r}) = E\Psi(\vec{r})$$

Time-Independent Schrödinger Equation  
(TISE)

Solving the energy part:  $i\hbar \frac{\partial f}{\partial t} = Ef(t)$

$$f(t) = Ce^{-i\frac{Et}{\hbar}}$$

$$\Psi(\vec{r}, t) = C\Psi(\vec{r})e^{-i\frac{Et}{\hbar}}$$

While normalizing the wavefunction, C can be made as 1