

## Section 1. The concepts and postulates of quantum mechanics

- Set up formal approach to quantum theory, based on a series of postulates
- Discuss wavefunctions, operators, eigenvalues and eigenfunctions
- Show how we can predict the results of measurements of a quantum system
- Discuss the uncertainty principle
- Discuss the time dependence of quantum systems

## 1.1 Postulate 1

The state of a quantum system is completely defined by its wavefunction  $\psi$ . Everything we can know about the system can be derived from  $\psi$ .

One particle in one dimension:  $\psi(x, t)$

One particle in three dimensions:  $\psi(\underline{r}, t)$

Two particles in three dimensions:  $\psi(\underline{r}_1, \underline{r}_2, t)$

In general,  $\psi$  is a **complex** function. The probability  $P$  of finding a particle at a point in space is proportional to  $|\psi|^2$  ( $=\psi^* \psi$ )

1 particle in 1-D:  $P(x, t)dx = |\psi(x, t)|^2 dx$

1 particle in 3-D:  $P(\underline{r}, t)d^3r = |\psi(\underline{r}, t)|^2 d^3r$

Cartesians:  $d^3r = dx dy dz$

Spherical polars:  $d^3r = r^2 \sin \theta dr d\theta d\phi$

Wavefunctions are **normalised**:

$$1 \text{ particle in 1-D: } \int |\psi(x,t)|^2 dx = 1$$

$$1 \text{ particle in 3-D: } \iiint |\psi(\underline{r},t)|^2 d^3r = 1$$

Integrate over the region of space available to the particle

## 1.2 Postulate 2

Every measurable quantity (observable) has a corresponding operator.

- **Operators** are mathematical “rules” that act on a function to give another function, e.g.

$$\hat{A} f(x) = g(x)$$

### Examples

Let  $f(x) = x + x^2$

**Differential operator:**  $\hat{A} = \frac{d}{dx} \rightarrow g(x) = 1 + 2x$

**Multiplicative operator:**  $\hat{A} = x^2 \rightarrow g = x^3 + x^4$

**Parity operator:**  $\hat{A} f(x) = f(-x) \rightarrow g = -x + x^2$

Products of operators are defined as

$$\hat{A}\hat{B} f(x) = \hat{A}(\hat{B}(f(x)))$$

The order of operators is important:

$$\hat{A}\hat{B} \text{ is not necessarily } \hat{B}\hat{A}$$

In general,  $\hat{A}$  and  $\hat{B}$  do not commute

### Example

$$\text{Let } f(x) = x + x^2, \quad \hat{A} = \frac{d}{dx}, \quad \hat{B} = x$$

$$\hat{A}\hat{A} f(x) = \hat{A}^2 f(x) = 2 \quad (\hat{A}^2 \equiv d^2/dx^2)$$

$$\hat{A}\hat{B} f(x) = 2x + 3x^2$$

$$\hat{B}\hat{A} f(x) = x + 2x^2$$

$$\hat{A}\hat{B} \neq \hat{B}\hat{A} \text{ in this case}$$

- Operators in quantum mechanics are **linear** and **Hermitian**.

Linear:  $\hat{A}(c_1 f_1 + c_2 f_2) = c_1 \hat{A} f_1 + c_2 \hat{A} f_2$

( $c_1, c_2$  are constants,  $f_1, f_2$  are functions)

see problems sheet for  
examples

Hermitian:

$$\int f_1^*(x) (\hat{A} f_2(x)) dx = \int (\hat{A} f_1(x))^* f_2(x) dx$$

(integrate over region available to the particle)

- Some important operators (Postulate 2A)

**Position:**  $\hat{x} = x, \quad \hat{y} = y, \quad \hat{z} = z$  ie  $\underline{\hat{r}} = \underline{r}$

**Momentum:**

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x}, \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y}, \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z}$$

i.e.  $\underline{\hat{p}} = -i\hbar \underline{\nabla}$

Gradient operator

- Other operators are derived from these and the classical definitions:

**Kinetic energy**, classically  $T = \frac{1}{2}mv^2 = \frac{p^2}{2m}$

→ in QM:  $\hat{T} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$

Particle mass

Laplacian operator

**Potential energy**:  $\hat{V}(\underline{r}) = V(\underline{r})$

**Total energy (i.e. Hamiltonian)**:  $\hat{H} = \hat{T} + \hat{V}$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) \quad \text{in 3D}$$

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x) \quad \text{in 1D}$$

Check that these operators are Hermitian

$$\int f_1^*(x) (\hat{A} f_2(x)) dx = \int (\hat{A} f_1(x))^* f_2(x) dx$$

1. **Position** operator:  $\hat{A} \equiv \hat{x} = x$

Multiplicative operator is obviously Hermitian  
( $x$  is real, so  $x = x^*$ )

2. **Momentum** operator:  $\hat{A} \equiv \hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$$\int f_1^*(x) (\hat{p}_x f_2(x)) dx = -i\hbar \int f_1^*(x) \frac{\partial f_2(x)}{\partial x} dx$$

Integrate by parts

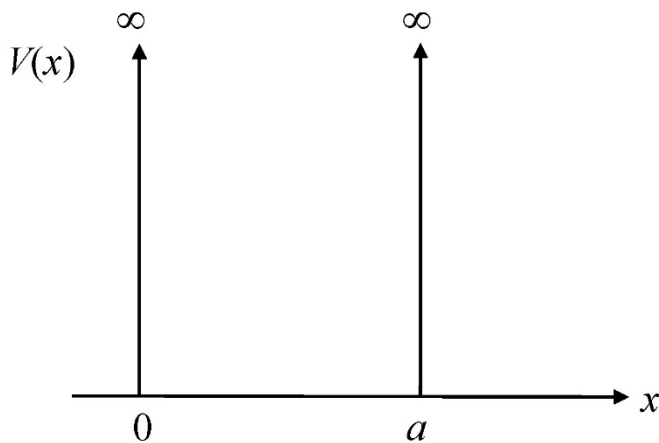
$$\rightarrow \left[ -i\hbar f_1^*(x) f_2(x) \right] + i\hbar \int \frac{\partial f_1^*}{\partial x} f_2(x) dx$$

Assume functions are well behaved at the boundaries of the region **i.e. they vanish**



$$i\hbar \int \frac{\partial f_1^*}{\partial x} f_2(x) dx = \int (\hat{p}_x f_1)^* f_2(x) dx \quad \therefore \text{Hermitian}$$

For example, consider a particle in an infinite square well potential



Wavefunction  
vanishes at  $x = 0$  and  
 $x = a \because$  no probability  
of finding particle at  
 $x \leq 0$  or  $x \geq a$

Box width can be made arbitrarily large (cf. free particle)  $\rightarrow$  wavefunction still vanishes at the boundaries of the accessible region (box normalisation of a free particle).

3. For **kinetic energy** see problems sheet

### 1.3 Postulate 3

The only possible result of a measurement is an eigenvalue of the relevant operator. Whatever the state of the system before the measurement, the state immediately after is the corresponding eigenfunction.

#### Eigenvalues and eigenfunctions

For a general operator  $\hat{A}$ , the equation

$$\hat{A}\phi = \alpha\phi$$

A diagram illustrating the equation  $\hat{A}\phi = \alpha\phi$ . A green box labeled "function" has an arrow pointing to the symbol  $\phi$ . Another green box labeled "constant" has an arrow pointing to the symbol  $\alpha$ .

(with relevant boundary conditions) has non-zero solutions only for special values of  $\alpha$ . We write these solutions as

$$\hat{A}\phi_n = \alpha_n\phi_n$$

$\alpha_n$  are the **eigenvalues** of  $\hat{A}$

$\phi_n$  are the **eigenfunctions** of  $\hat{A}$

The label  $n$  can be discrete or continuous

## Examples

- **Momentum operator in 1D:**  $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

$$-i\hbar \frac{\partial}{\partial x} \exp(ikx) = \hbar k \exp(ikx)$$

$$\hat{A} \phi = \alpha \phi$$

Eigenvalues:  $\hbar k$  (where  $k$  is a constant)

Eigenfunctions:  $\exp(ikx)$

In this case, the eigenvalues are continuous

Physical interpretation: the wave  $\exp(ikx)$  represents a particle moving in the  $x$  direction with a momentum  $p = \hbar k$

de Broglie wavelength

(Consistent with de Broglie relation  $\lambda = h/p$ )

- If we measure the momentum of a quantum particle we obtain a value  $p = \hbar k$  and immediately after the measurement the wavefunction is  $\psi = \exp(ikx)$

- Infinite square well

Potential energy  $V(x) = 0$  for  $0 < x < a$  and is infinity elsewhere

Total energy operator in the region available to the particle:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

Eigenvalues and eigenfunctions given by:

$$\underbrace{-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}}_{\hat{H}} \underbrace{\sin\left(\frac{n\pi x}{a}\right)}_{\phi_n} = \underbrace{\frac{\hbar^2 \pi^2 n^2}{2ma^2}}_{\alpha} \underbrace{\sin\left(\frac{n\pi x}{a}\right)}_{\phi_n}$$

Eigenvalues:  $E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2}$  ( $n$  is an integer)  
 $n = 1, 2, 3, \dots$

Eigenfunctions:  $\phi_n(x) \propto \sin\left(\frac{n\pi x}{a}\right)$

eigenfunctions should be normalised

In this case, the eigenvalues are discrete

If we measure the energy of a particle in an infinite square well, the result will be one of the eigenvalues  $E_n$ . Immediately after the measurement the wavefunction is  $\psi = \phi_n(x)$ .

As a result of the measurement, the wavefunction “collapses” into one of the eigenfunctions.

### “Quantum Measurement Problem”

How (and if) wavefunction collapse occurs.

Schrödinger’s cat: Cat is in a mixed state of being either “dead” or “alive” with a non-zero probability. Don’t know the actual state until the box is opened.

But how are the probabilities of “dead” and “alive” states converted into a well-defined outcome or observation?

## 1.4 Properties of Hermitian operators

Start with

$$\hat{A}\phi_n = \alpha_n \phi_n$$

eigenfunction

eigenvalue

Multiply both sides by  $\phi_m^*$  and integrate over relevant range:

$$\int \phi_m^* \hat{A} \phi_n = \alpha_n \int \phi_m^* \phi_n$$

Because  $\hat{A}$  is Hermitian, this becomes:

$$\int \underbrace{(\hat{A}\phi_m)^*}_{=\alpha_m^* \phi_m^*} \phi_n = \alpha_n \int \phi_m^* \phi_n \quad (1)$$

Taking complex conjugate of  $\hat{A}\phi_m = \alpha_m \phi_m$  gives  $(\hat{A}\phi_m)^* = \alpha_m^* \phi_m^*$ , so (1) becomes:

$$(\alpha_n - \alpha_m^*) \int \phi_m^* \phi_n = 0$$

- If  $n = m$ , then  $\alpha_n = \alpha_n^*$  so  $\alpha_n$  is **real**
- If  $n \neq m$ , then  $\int \phi_m^* \phi_n = 0$  so  $\phi$ 's are **orthogonal**
- If eigenfunctions are normalised we can write

$$\int \phi_m^* \phi_n = \delta_{mn}$$

Kronecker delta  
 $\delta_{mn} = 0$  if  $m \neq n$   
 $= 1$  if  $m = n$

The eigenvalues of Hermitian operators are real and the eigenfunctions corresponding to different eigenvalues are orthogonal

- The eigenfunctions of Hermitian operators form a **complete set**, so that any function (in the relevant region of space) can be written as a **linear combination**:

$$F = c_1 \phi_1 + c_2 \phi_2 + \dots = \sum_n c_n \phi_n$$

arbitrary function

constant coefficients

- We have assumed that there is **no degeneracy** (i.e. that all eigenvalues are different). Everything works OK if there are degenerate eigenvalues.



## 1.5 Postulate 4

Quantum mechanics is not deterministic. We can only predict the probability of the result of a measurement and the average over a series of measurements.

How do we calculate these probabilities?

Assume  $\psi$  is known

Assume we make a measurement, where the sets of eigenvalues and eigenfunctions of the corresponding operator  $\hat{A}$  are  $\{\alpha_n\}$  and  $\{\phi_n\}$

At the time of the measurement the normalised wavefunction of the system is  $\psi$

We can write  $\psi = \sum_n c_n \phi_n$

The probability of measuring  $\alpha_m$  (and collapsing the system into  $\phi_m$ ) is  $|c_m|^2$

Because  $\psi$  and  $\{\phi_n\}$  are normalised:  $\sum_n |c_n|^2 = 1$

see problems sheet

How can we find the coefficients  $c_m$ ?

Start with:

$$\psi = \sum_n c_n \phi_n$$

Multiply both sides by  $\phi_m^*$  and integrate

$$\int \phi_m^* \psi = \sum_n c_n \int \phi_m^* \phi_n$$

Use orthogonality

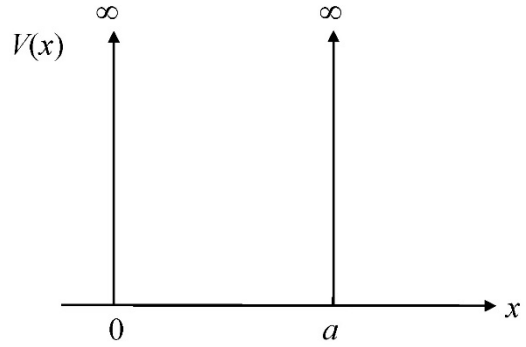
$$\int \phi_m^* \psi = \sum_n c_n \delta_{mn} = c_m$$

$$c_m = \int \phi_m^* \psi$$

$c_m$  gives the “amount” of  $\phi_m$  contained in  $\psi$

Example: Infinite square well in 1-D

Suppose wavefunction is constant at the time of the measurement



$$\psi(x) = \frac{1}{\sqrt{a}}$$

$$\int_0^a |\psi|^2 dx = 1$$

We measure the total energy of the particle; the corresponding eigenvalues and eigenvectors are

$$E_n = \frac{\hbar^2 \pi^2 n^2}{2ma^2} \quad \phi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right)$$

The coefficients are:

normalisation constant

$$c_m = \int \phi_m^* \psi = \frac{\sqrt{2}}{a} \int_0^a \sin\left(\frac{m\pi x}{a}\right) dx$$

$$\rightarrow \begin{aligned} c_m &= \frac{2\sqrt{2}}{m\pi} \quad \text{for } m \text{ odd} \\ c_m &= 0 \quad \text{for } m \text{ even} \end{aligned}$$

Probability of measuring  $E_1 = \frac{\hbar^2 \pi^2}{2ma^2}$  is  $\frac{8}{\pi^2}$

Probability of measuring  $E_2 = \frac{4\hbar^2 \pi^2}{2ma^2}$  is 0

Probability of measuring  $E_3 = \frac{9\hbar^2 \pi^2}{2ma^2}$  is  $\frac{8}{9\pi^2}$

- Expectation values

Suppose we have a large number of identical systems. What would be the average value of a measurement taken on each these systems?

Average, or **expectation value** of the measurements with corresponding operator  $\hat{A}$

$$\langle \hat{A} \rangle = \sum_n |c_n|^2 \alpha_n$$

notation for expectation value

eigenvalue

probability of measuring  $\alpha_n$

- This can be expressed in a more useful form

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi$$

Show that these are equivalent:

$$\langle \hat{A} \rangle = \int \underbrace{\left( \sum c_m^* \phi_m^* \right)}_{\psi^*} \hat{A} \underbrace{\left( \sum c_n \phi_n \right)}_{\psi}$$

$$\hat{A} \phi_n = \alpha_n \phi_n$$

$$= \int \left( \sum c_m^* \phi_m^* \right) \left( \sum c_n \alpha_n \phi_n \right)$$

$$= \sum_m \sum_n c_m^* c_n \alpha_n \int \phi_m^* \phi_n$$

$$= \sum_n |c_n|^2 \alpha_n$$

$$\delta_{mn}$$

as above

- Note that all our analysis has assumed that the eigenvalues are discrete. Everything works OK if the eigenvalues are continuous.

Expectation value of position:

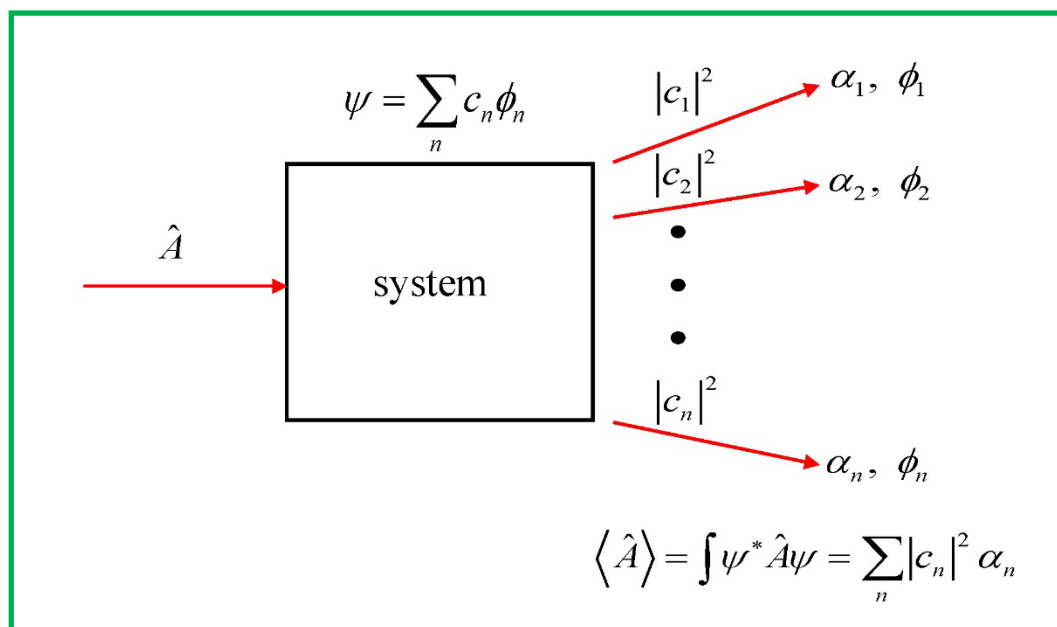
$$\langle \hat{x} \rangle = \int \psi^* x \psi dx$$

Expectation value of momentum:

$$\langle \hat{p}_x \rangle = -i\hbar \int \psi^* \frac{\partial \psi}{\partial x} dx$$

See year 2  
quantum  
notes and  
problems  
sheets

## Schematic summary



## 1.6 Commutators and compatibility

- The **commutator** of two operators  $\hat{A}$  and  $\hat{B}$  is defined by

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

In general,  
result is an  
operator

If  $[\hat{A}, \hat{B}] = 0$  then  $\hat{A}$  and  $\hat{B}$  commute

If  $[\hat{A}, \hat{B}] \neq 0$  then  $\hat{A}$  and  $\hat{B}$  do not commute  
and the order of their application matters

### Examples

- If  $\hat{A} = \hat{p}_x$  and  $\hat{B} = \hat{x}$

$$[\hat{p}_x, \hat{x}] \psi = \hat{p}_x \hat{x} \psi - \hat{x} \hat{p}_x \psi$$

$$= -i\hbar \frac{\partial}{\partial x} (x \psi) - x \left( -i\hbar \frac{\partial \psi}{\partial x} \right)$$

$$= -i\hbar \left( x \frac{\partial \psi}{\partial x} + \psi \right) + i\hbar x \frac{\partial \psi}{\partial x} = -i\hbar \psi$$

$$\rightarrow [\hat{p}_x, \hat{x}] \psi = -i\hbar \psi$$

Commutation relation:  $[\hat{p}_x, \hat{x}] = -i\hbar$

If  $\hat{A} = \hat{x}$  and  $\hat{B} = \hat{p}_x$  we find  $[\hat{x}, \hat{p}_x] = i\hbar$

If  $\hat{A} = \hat{p}_x$  and  $\hat{B} = \hat{y}$

$$[\hat{p}_x, \hat{y}] \psi = -i\hbar \frac{\partial}{\partial x} (y \psi) - y \left( -i\hbar \frac{\partial \psi}{\partial x} \right)$$

$$= -i\hbar y \frac{\partial \psi}{\partial x} + i\hbar y \frac{\partial \psi}{\partial x} = 0$$

$\rightarrow$   $[\hat{p}_x, \hat{y}] = 0$



## Why do commutators matter?

Two observables are **compatible** if their corresponding operators have a common set of eigenfunctions, e.g.

$$\hat{A}\phi_n = \alpha_n\phi_n$$

$$\hat{B}\phi_n = \beta_n\phi_n$$

If observable corresponding to  $\hat{A}$  is measured the wavefunction will become an eigenfunction eg  $\phi_m$ . If observable corresponding to  $\hat{B}$  is then measured, the result will be certain (i.e.  $\beta_m$ ).

A set of compatible observables can be known precisely, i.e. measured simultaneously

With non-compatible observables we can only predict the probabilities of the results of measurements. Measuring one observable affects the measurement of the others.

If  $\hat{A}$  and  $\hat{B}$  commute then their corresponding observables are compatible (and vice versa)

## Proof

Consider compatible observables as above:

$$\hat{A}\phi_n = \alpha_n\phi_n \quad \hat{B}\phi_n = \beta_n\phi_n$$

A general wavefunction can be written as

$$\psi = \sum_n c_n \phi_n$$

Calculate commutator of  $\hat{A}$  and  $\hat{B}$

$$\begin{aligned} [\hat{A}, \hat{B}]\psi &= \sum_n c_n \left( \hat{A} \hat{B} \phi_n - \hat{B} \hat{A} \phi_n \right) \\ &= \sum_n c_n \left( \hat{A} \beta_n \phi_n - \hat{B} \alpha_n \phi_n \right) \\ &= \sum_n c_n \left( \alpha_n \beta_n \phi_n - \beta_n \alpha_n \phi_n \right) = 0 \\ &\rightarrow [\hat{A}, \hat{B}] = 0 \end{aligned}$$

If  $\hat{A}$  and  $\hat{B}$  do not commute then the corresponding observables are not compatible

### Example

$$[\hat{p}_x, \hat{x}] = -i\hbar$$

$\hat{p}_x$  and  $\hat{x}$  are **not compatible**, so the position and momentum of a particle cannot both be known precisely

- This is closely associated with **Heisenberg's uncertainty principle**

Consider measurements corresponding to an operator  $\hat{A}$  on set of systems with wavefunction  $\psi$ . The average value will be

$$\langle \hat{A} \rangle = \int \psi^* \hat{A} \psi$$

The quantity

$$\Delta A^2 = \int \psi^* \left( \hat{A} - \langle \hat{A} \rangle \right)^2 \psi$$

$\langle \hat{A} \rangle$  is a  
constant

$$= \int \psi^* \left( \hat{A}^2 - 2\hat{A}\langle \hat{A} \rangle + \langle \hat{A} \rangle^2 \right) \psi$$

$$= \langle \hat{A}^2 \rangle - 2\langle \hat{A} \rangle^2 + \langle \hat{A} \rangle^2$$

$$= \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2$$

Similar to variance

gives a measure of the amount of spread (i.e. uncertainty) in the measurements

It can be shown that for measurements corresponding to two operators  $\hat{A}$  and  $\hat{B}$

Heisenberg  
Uncertainty  
Principle

$$\Delta A \Delta B \geq \frac{1}{2} \left| \int \psi^* [\hat{A}, \hat{B}] \psi \right|$$

See text  
books for  
proof

If  $\hat{A}$  and  $\hat{B}$  do not commute, there must be “uncertainty” in the measurements of the corresponding observables (i.e. both  $\Delta A$  and  $\Delta B$  must be non-zero)

Example: If  $\hat{A} = \hat{p}_x$  and  $\hat{B} = \hat{x}$ ,  $[\hat{p}_x, \hat{x}] = -i\hbar$

$$\rightarrow \Delta x \Delta p \geq \frac{\hbar}{2}$$

## 1.7 Postulate 5

Between measurements, the evolution of the wavefunction is governed by

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

TDSE

i.e., the **Time-Dependent Schrodinger Equation**

$\hat{H}$  is the total energy (Hamiltonian) operator, so the TDSE can be written

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

in 3D

Note that knowledge of  $\psi$  at one time allows prediction of  $\psi$  for all future times

Follows  $\because$  TDSE is a linear equation

Measurements will disrupt this evolution of  $\psi$ . A measurement collapses the wavefunction into an eigenfunction of the relevant operator.  $\psi$  is then “reset” and the TDSE takes over again.

Quantum Measurement problem: Measurement  $\rightarrow$  eigenfunction  $\phi_m$ . Time evolution of  $\phi_m$  determined by the TDSE

## 1.8 Stationary states

An important case arises if the potential energy  $V(\underline{r}, t)$  in the TDSE is **not dependent on time**  $t$

$V(\underline{r})$  only

The energy eigenvalues and eigenfunctions given by

not time dependent

$$\hat{H}(\underline{r}) \phi_n(\underline{r}) = E_n \phi_n(\underline{r})$$

do not depend on time

An arbitrary wavefunction at time  $t$  can be expanded as

$$\psi(\underline{r}, t) = \sum_n c_n(t) \phi_n(\underline{r})$$

As seen in section 1.4,  
but the coefficients are  
now time dependent



This is substituted into the TDSE to give

$$\underbrace{i\hbar \sum_n \frac{dc_n}{dt} \phi_n(\underline{r})}_{d\psi/dt} = \underbrace{\sum_n c_n(t) \hat{H}(\underline{r}) \phi_n(\underline{r})}_{\hat{H}\psi}$$

$$= \sum_n c_n(t) E_n \phi_n(\underline{r})$$

So

$$\sum_n \left( i\hbar \frac{dc_n}{dt} - E_n c_n(t) \right) \phi_n(\underline{r}) = 0$$

which can be satisfied for a given value of  $n$  only if

$$i\hbar \frac{dc_n}{dt} = E_n c_n(t)$$

Solution is

$$c_n(t) = c_n(0) \exp(-iE_n t / \hbar)$$

↑  
value of coefficient at  $t = 0$

So, wavefunction is given by

$$\psi(\underline{r}, t) = \sum_n c_n(0) \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

At  $t = 0$  we have

$$\psi(\underline{r}, 0) = \sum_n c_n(0) \phi_n(\underline{r})$$

and the coefficients can be found from (see section 1.5)

$$c_m(0) = \int d^3r \phi_m^*(\underline{r}) \psi(\underline{r}, 0)$$

If the potential energy is not time dependent, then all information about the wavefunction can be derived from the energy eigenvalues and eigenfunctions, i.e. from solutions of

$$\hat{H}(\underline{r}) \phi_n(\underline{r}) = E_n \phi_n(\underline{r})$$

$$\left( -\frac{\hbar^2}{2m} \nabla^2 + V(\underline{r}) \right) \phi_n(\underline{r}) = E_n \phi_n(\underline{r})$$

TISE

Time-Independent Schrodinger Equation

If  $\psi$  starts in an energy eigenfunction [e.g.  $\phi_m(\underline{r})$ ] then

i.e.  $c_m(0) = 1$ , all other  $c_n(0) = 0$

$$\psi(\underline{r}, t) = \phi_m(\underline{r}) \exp(-iE_m t / \hbar) \quad (1)$$

i.e.,  $\psi$  remains in an energy eigenfunction and a later measurement of the energy will give  $E_m$

These energy eigenfunctions (i.e., solutions of the TISE) are called **stationary states**.

Note that  $\psi(\underline{r}, t)$  is time dependent because the particle can move.

From (1), the probability of finding the particle at time  $t$  in volume element  $d^3r$  at  $\underline{r}$  is  $|\psi(\underline{r}, t)| d^3r = |\phi_m(\underline{r})| d^3r$  which is independent of time.

[ Note that if an eigenfunction is multiplied by an arbitrary phase factor, then it remains an eigenfunction.

Likewise,  $\psi(\underline{r}, t)$  can be multiplied by an arbitrary phase factor  $e^{i\theta}$ , but this does not change the physics e.g.  $|\psi|^2$  does not change. Could also multiply  $\psi(\underline{r}, t)$  by  $-1$  with the same effect. ]

## 1.9 Spreading of a wave packet

Superposition of plane waves  $\rightarrow$  Gaussian wavepacket representing the localised state of a particle.

i.e.  $V(x) = 0$

Consider a 1D quantum system in free space is described by a Gaussian wavefunction. At  $t = 0$ ,

$$\psi(x, 0) = \left(\frac{a}{\pi}\right)^{1/4} \exp\left(-\frac{1}{2}ax^2\right)$$

Calculate  $\psi(x, t)$

constant

This example nicely demonstrates several of the concepts and postulates we have looked at so far. It also shows how we handle systems with **continuous eigenvalues**.

## Notes on $\psi(x, 0)$ :

$$\int_{-\infty}^{\infty} |\psi|^2 dx = \left(\frac{a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-ax^2} dx = 1$$

1.  $\psi(x, 0)$  is normalised, because

$$\int_{-\infty}^{\infty} dx \exp(-ax^2) = \left(\frac{\pi}{a}\right)^{1/2}$$

standard integral

2. Expectation value of  $\hat{x}$

see section 1.5

$$\langle \hat{x} \rangle = \int_{-\infty}^{\infty} dx \psi^*(x, 0) x \psi(x, 0) = 0$$

3. Expectation value of  $\hat{x}^2$

$$\langle \hat{x}^2 \rangle = \int_{-\infty}^{\infty} dx \psi^*(x, 0) x^2 \psi(x, 0) = \frac{1}{2a}$$

standard integral

4. Uncertainty in measurements of  $x$  (i.e. width of the “wavepacket”)

$$\Delta x = \sqrt{\langle \hat{x}^2 \rangle} = \sqrt{\frac{1}{2a}}$$

See section 1.6.

In this case

$$\begin{aligned} \Delta x^2 &= \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2 \\ &= \langle \hat{x}^2 \rangle \because \langle \hat{x} \rangle = 0 \end{aligned}$$

# Eigenfunctions

The Hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

In this case (because  $V(x) = 0$ ) the momentum operator  $\hat{p}_x$  commutes with  $\hat{H}$

$$\hat{p}_x = -i\hbar \frac{d}{dx} \Rightarrow [\hat{p}_x, \hat{H}] = 0$$

$\hat{p}_x$  and  $\hat{H}$  are **compatible** and therefore have a common set of eigenfunctions:  $\exp(ikx)$

$$\hat{p}_x : -i\hbar \frac{d}{dx} \exp(ikx) = \hbar k \exp(ikx)$$

obvious in this case

momentum eigenvalue

$$\hat{H} : -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \exp(ikx) = \frac{\hbar^2 k^2}{2m} \exp(ikx)$$

energy eigenvalue

## Aside

If we measure momentum on the initial wavepacket  $\psi(x,0)$ , what is the probability of obtaining a particular value  $\hbar k$ ?

In section 1.5 we saw that any wavefunction can be expanded in eigenfunctions as

$$\psi = \sum_n c_n \phi_n$$

and the probability of measuring  $\alpha_m$  (i.e. the eigenvalue corresponding to  $\phi_m$ ) is  $|c_m|^2$ . How does this work with continuous eigenvalues?

Use results of **Fourier transforms**

$$\underbrace{f(x)}_{\text{arbitrary function}} = \int_{-\infty}^{\infty} dk \underbrace{F(k) \exp(ikx)}_{\text{Fourier transform}}$$

$$F(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx f(x) \exp(-ikx)$$

Fourier  
transform  
pair



In our case

$$\psi(x, t=0) = \sum_n c_n(t=0) \phi_n(x)$$

can be re-written as

$$\psi(x, 0) = \int_{-\infty}^{\infty} dk \underbrace{c(k)}_{\text{coefficients: now } k \text{ labels the state}} \underbrace{\exp(ikx)}_{\text{momentum eigenfunctions}}$$

integral instead of sum

Fourier analysis gives us  $c(k)$ :

$$c(k) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dx \psi(x, 0) \exp(-ikx)$$

$$= \frac{1}{2\pi} \left( \frac{a}{\pi} \right)^{1/4} \int_{-\infty}^{\infty} dx \exp\left(-\frac{1}{2}ax^2\right) \exp(-ikx)$$

$$= \left( \frac{1}{2\pi} \right)^{1/2} \left( \frac{1}{\pi a} \right)^{1/4} \underbrace{\exp\left(-\frac{k^2}{2a}\right)}_{\text{Gaussian distribution of momentum}}$$

standard  
Fourier  
integral

Probability of measuring momentum  $p = \hbar k$  is

$$\propto |c(k)|^2 \propto \exp(-k^2 / a)$$

Uncertainty in measurement of  $p$  is

$$\Delta p = \hbar \sqrt{\frac{a}{2}}$$

haven't derived  
this but  
analogous to  $\Delta x$

In this case

$$\Delta x \Delta p = \frac{\hbar}{2}$$

Heisenberg!  
(see section 1.6)

## Back to the problem....[i.e. spreading of a wavepacket]

In section 1.8, we saw that the time dependence of a wavefunction is given by

$$\psi(\underline{r}, t) = \sum_n c_n(0) \phi_n(\underline{r}) \exp(-iE_n t / \hbar)$$

$\phi_n$  are energy eigenfunctions

$c_n(0)$  are expansion coefficients at  $t = 0$

In our case the energy eigenfunctions are the same as the momentum eigenfunctions (i.e.,  $\exp(ikx)$ ), so the coefficients are just the  $c(k)$  calculated above

We find

$$\psi(x, t) = \left( \frac{1}{2\pi} \right)^{1/2} \left( \frac{1}{\pi a} \right)^{1/4} \times \int_{-\infty}^{\infty} dk \exp\left(-\frac{k^2}{2a}\right) \underbrace{\exp(ikx)}_{\phi(x)} \exp\left(-\frac{i\hbar k^2 t}{2m}\right)$$

43

Integral can be performed to give

$$\psi(x,t) = \left(\frac{1}{\pi a}\right)^{1/4} (2\pi a')^{1/2} \exp\left(-\frac{1}{2}a'x^2\right)$$

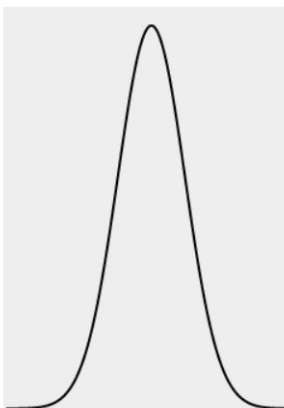
$$\text{where } \frac{1}{a'} = \frac{1}{a} + \frac{i\hbar t}{m}$$

The wavefunction stays Gaussian, with width given by

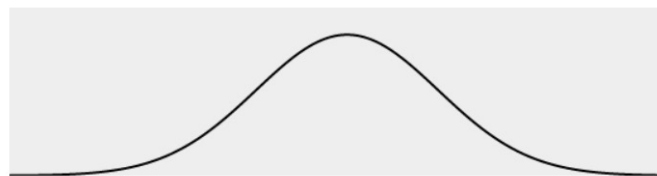
$$\Delta x = \sqrt{\langle \hat{x}^2 \rangle}$$
$$\because \langle \hat{x} \rangle = 0$$

$$\Delta x(t) = \sqrt{\frac{1}{2a} + \frac{\hbar^2 a t^2}{2m^2}}$$

Note how the wavefunction spreads out over time (see problems sheet for example)



$t = 0$



$t > 0$

At  $t = 0$  we cannot localise the particle more than is allowed by the Uncertainty Principle.

## 1.10 Dirac notation

This is a useful shorthand for writing down the integrals that arise in quantum mechanics

We write

$$\int \psi_1^*(\underline{r}) \psi_2(\underline{r}) d^3 r \equiv \langle \psi_1 | \psi_2 \rangle$$

(and similarly for 1D integrals)

$\langle \psi_1 |$  is a “bra”

$|\psi_2 \rangle$  is a “ket”

$\langle \psi_1 | \psi_2 \rangle$  is a bra(c)ket!

Integrals involving operators are written as:

$$\int \psi_1^*(\underline{r}) \hat{A} \psi_2(\underline{r}) d^3 r \equiv \langle \psi_1 | \hat{A} | \psi_2 \rangle$$

For example, repeat our analysis in section 1.5.  
Expand wavefunction in eigenfunctions

$$|\psi\rangle = \sum_n c_n |\phi_n\rangle$$

Diagram illustrating the expansion of a wavefunction ket  $|\psi\rangle$  into a sum of eigenfunction kets  $|\phi_n\rangle$  with coefficients  $c_n$ . The components are labeled: wavefunction ket, coefficient, and eigenfunction ket.

“Close” with  $\langle\phi_m|$

$$\langle\phi_m|\psi\rangle = \sum_n c_n \underbrace{\langle\phi_m|\phi_n\rangle}_{\delta_{mn}} = \sum_n c_n \underbrace{\delta_{mn}}_{\text{orthogonality}} = c_m$$

Diagram illustrating the inner product of the expansion with a bra state  $\langle\phi_m|$ . The result is  $c_m$ , where the orthogonality of the eigenfunctions is used to simplify the expression.

So we can write

$$|\psi\rangle = \sum_n \langle\phi_n|\psi\rangle |\phi_n\rangle$$

So far, we have discussed wavefunctions in space, i.e.  $\psi(\underline{r})$ . There are other representations of wavefunctions, e.g. a matrix representation. **Dirac notation stays the same in all cases, so it is a more general formulation of quantum mechanics.**

## 1.11 Matrix representation

This is a rather different way to set up problems in QM. Later, we shall see examples of its use.

Consider an observable with operator  $\hat{A}$ . We want to find its eigenfunctions and eigenvalues, i.e. solutions of

$$\hat{A}\phi(\underline{r}) = \alpha \phi(\underline{r}) \quad \text{or} \quad \hat{A}|\phi\rangle = \alpha |\phi\rangle \quad (1)$$

eigenfunction

eigenvalue

We try to find a solution by expanding  $\phi$  in a set of **orthogonal** and **normalised** functions:

$$\phi(\underline{r}) = \sum_n a_n u_n(\underline{r}) \quad \text{or} \quad |\phi\rangle = \sum_n a_n |u_n\rangle \quad (2)$$

constant coefficients

Note that the functions  $u_n(\underline{r})$  can be **any complete set of orthogonal functions that “span” the relevant region of space**. They are not the eigenfunctions of  $\hat{A}$ .

Substitute (2) into (1) to give (using Dirac notation)

$$\sum_n a_n \hat{A} |u_n\rangle = \alpha \sum_n a_n |u_n\rangle$$

“Close” with  $\langle u_m |$  (i.e. multiply both sides by  $u_m^*(\underline{r})$  and integrate over space) and use orthogonality property  $\langle u_m | u_n \rangle = \delta_{mn}$ :-

$$\sum_n \underbrace{\langle u_m | \hat{A} | u_n \rangle}_{A_{mn}} a_n = \alpha \sum_n a_n \underbrace{\langle u_m | u_n \rangle}_{\delta_{mn}}$$

$$\Rightarrow \sum_n A_{mn} a_n = \alpha a_m \quad \text{where} \quad A_{mn} = \langle u_m | \hat{A} | u_n \rangle$$

This is a **matrix eigenvalue problem**

$$\underbrace{\begin{pmatrix} A_{11} & A_{12} & \cdots & \cdots \\ A_{21} & A_{22} & \cdots & \cdots \\ \vdots & \vdots & \ddots & \\ \vdots & \vdots & & \ddots \end{pmatrix}}_{\text{matrix}} \underbrace{\begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{pmatrix}}_{\text{eigenvector}} = \alpha \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{pmatrix} \quad (3)$$

↑  
eigenvalue



## Notes

- This is not a new problem – it's the same problem in a different representation. All the results we've seen so far have an equivalent in matrix representation.
- There are often infinitely many “basis states”  $|u_n\rangle$ . Matrix representation is often used in practical QM computations, in which case the basis is truncated to give a finite matrix.

- Dirac notation can also be used in the matrix representation. Equation 3 can be written as

$$\hat{A} \underbrace{|a\rangle}_{\boxed{\text{ket}}} = \alpha \underbrace{|a\rangle}_{\boxed{\text{ket}}}$$

**Operators** are now **matrices**

**Kets** are now **column vectors**

**Bras** are now **row vectors**

$\langle \mid \rangle$  now implies **matrix multiplication**

$$\langle a|b\rangle \equiv \begin{pmatrix} a_1^* & a_2^* & \cdots & \cdots \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \\ \vdots \\ \vdots \end{pmatrix} = a_1^* b_1 + a_2^* b_2 + \cdots$$

$$\langle b|a\rangle^* \equiv (b_1 \quad b_2 \quad \cdots \quad \cdots) \begin{pmatrix} a_1^* \\ a_2^* \\ \vdots \\ \vdots \end{pmatrix} = a_1^* b_1 + a_2^* b_2 + \cdots$$

$$\text{So } \langle a|b\rangle = \langle b|a\rangle^*$$

The **conjugate transpose** (or **Hermitian conjugate**) of a ket is the corresponding bra and vice versa:  $|a\rangle^\dagger = \langle a|$ ,  $\langle a|^\dagger = |a\rangle$

## Example

The complex conjugate of the ket

$$|a\rangle = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ \vdots \end{pmatrix}$$

is given by

$$|a\rangle^* = \begin{pmatrix} a_1^* \\ a_2^* \\ \vdots \\ \vdots \end{pmatrix}$$

and  $|a\rangle^\dagger$  is the matrix transpose of this complex conjugate, i.e.,

$$|a\rangle^\dagger = \langle a| = \begin{pmatrix} a_1^* & a_2^* & \cdots & \cdots \end{pmatrix}$$