

# The Postulates of Quantum Mechanics

Some of the basic **postulates** of quantum mechanics will now be introduced.

The postulates are the fundamental assumptions on which quantum mechanics is based.

For example, Newton's three laws are postulates of classical mechanics.

# The Postulates of Quantum Mechanics

These postulates cannot be derived!

Newton's Laws, are postulates and are believed to be correct for macroscopic systems based on agreement with experiment.

The postulates of Quantum Mechanics also can not be derived. They too are believed to be correct for both microscopic and macroscopic worlds based on agreement with experiment.

The postulates of quantum mechanics can be expressed in many ways.

People present them in different order and the number of postulates is often different (some are combined)

The postulates are connected as a whole

They may be *very* strange at first. Applications will help us understand.

## Classical State Function

The first postulate deals with a state function, so let's examine the classical state function.

The classical mechanical state of a one-particle system at a particular time is given by 3 position coordinates and 3 velocities (or momenta)

The time evolution of the system is governed by Newton's second law:

$$F_x = m \frac{d^2x}{dt^2} \quad F_y = m \frac{d^2y}{dt^2} \quad F_z = m \frac{d^2z}{dt^2}$$

Usually, given the initial positions and momenta, we can integrate Newton's equations of motion to obtain the whole trajectory of the system and the state function. The the 3 coordinates and 3 velocities completely define the system.

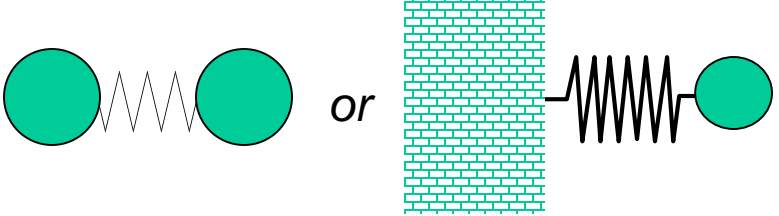
Heisenberg's uncertainty principle hints that this is not valid because we cannot simultaneously determine the position and momentum exactly.

## Postulate 1

The state of a quantum mechanical system is completely specified by a function  $\Psi(x,y,z,t)$  that depends on the coordinates and on time. This function is called the **wave function** of the system. **All possible information about the system can be derived from  $\Psi$ .**

## Example of a Wave function

The wave function for a one-dimensional harmonic oscillator is:

$$\Psi(x,t) = C e^{-\left(\frac{x}{a}\right)^2} e^{-\frac{i 2 \pi E t}{h}}$$


The diagram shows two representations of a harmonic oscillator. On the left, two red circles representing atoms are connected by a spring. On the right, a red circle representing an atom is connected to a vertical grid of small squares representing a crystal lattice by a spring.

where  $\alpha$  and  $C$  are constants and the variable  $x$  is the displacement of the diatomic from equilibrium.

Notice the wave function can be complex (and complicated)!  
More on the properties of the wave functions later.

*For this idealized system, we can derive any property of the system from the above function.*

## Postulate 1 (extended)

The state of a quantum mechanical system is completely specified by a function  $\Psi(x,y,z,t)$  that depends on the coordinates and on the time. This function is called the **wave function** of the system. All possible information about the system can be derived from  $\Psi$ .

The wave function  $\Psi(x,y,z,t)$  has an important property that its square is the probability distribution function for the system:

$$|\Psi(x, y, z, t)|^2 = \Psi^*(x, y, z, t)\Psi(x, y, z, t)$$

$$\Psi^*(x, y, z, t)$$

Complex conjugate of the wave function is obtained by replacing any imaginary numbers with their negative:  $i^* = -i$

e.g.

$$\Psi(x, t) = C \cdot e^{-\left(\frac{x}{a}\right)^2} \cdot e^{-\frac{i2\pi Et}{h}} \quad \Psi^*(x, t) = C \cdot e^{-\left(\frac{x}{a}\right)^2} \cdot e^{+\frac{i2\pi Et}{h}}$$

The probability of finding the particle at a time  $t$  near the position  $(x, y, z)$  is proportional to

$$P(x, y, z, t) = |\Psi(x, y, z, t)|^2 = |\Psi|^2$$

More precisely, the probability of finding the particle at time  $t$  within a given volume element  $dV = dx dy dz$  is:

$$= \int_V |\Psi(x, y, z, t)|^2 dx dy dz = \int_V \Psi^* \Psi dx dy dz$$

The probabilistic interpretation of the wave function was first developed by Max Born and it is sometimes referred to as the Born interpretation of the wave function.

Given this physical interpretation of the square of the wave function, the wave function must satisfy certain requirements.



Max Born

# Minimal Requirements for a Valid Wave Function

In general,  $\Psi(x,y,z,t)$  must satisfy the following conditions:

1.  $\Psi(x,y,z,t)$  must be a **continuous** function.

*There cannot be points in space where the wave function is “missing”. There must be a probability associated with every point in space.*

2.  $\Psi(x,y,z,t)$  must be **single-valued and bounded**.

- at a given  $x,y,z$  and  $t$ ,  $\Psi$  can only have one value.
- the value of the wave function cannot be infinite anywhere.

*There cannot be two or more probabilities of finding the particle at a single point in space.*

*There cannot be an infinite probability of finding the particle at a single point in space. The probability can at most be 1 which corresponds to 100%.*



## Examples

Which of the following functions are acceptable wave functions according to the first two criteria for the interval given?



$$\sin x \quad (-\infty, \infty)$$

$$\sin x - \frac{\cos x}{2} \quad (-\infty, \infty)$$

$$e^{-x} \cos x \quad (0, \infty)$$

$$e^x \quad (-\infty, \infty)$$

$$(1 - x^2)^{-1} \quad (-1, 1)$$

3.  $\Psi(x,y,z,t)$  should be normalizable such that the following integral is equal to one:

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

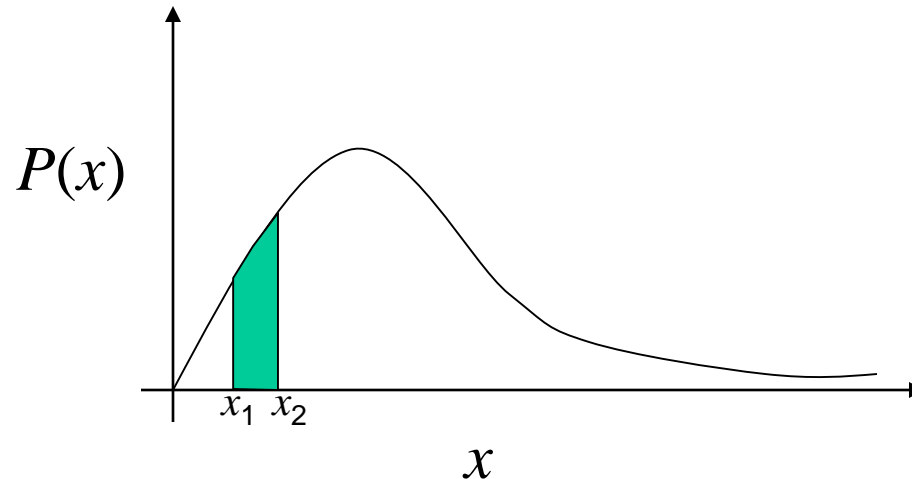
or

$$\int_{\substack{\text{all} \\ \text{space}}} \Psi^* \Psi d\tau = 1$$

Why?

The probability of finding the particle at an instant in time, “somewhere” in the universe must be equal to 100% or unity.

Consider the following probability distribution function that describes the probability of finding a single particle along the  $x$  coordinate:



To find the probability that the particle will be between  $x_1$  and  $x_2$  we would integrate  $P(x)$  between  $x_1$  and  $x_2$ .

$$\int_{x_1}^{x_2} P(x) dx$$

If we integrate over all space, then the probability must equal 1.

3.  $\Psi$  should be **normalized** such that the following integral is equal to one:

$$\int_{\substack{\text{all} \\ \text{space}}} \Psi^* \Psi d\tau = 1$$

If the wave function is not normalized, it should at least be **normalizable** such that the integral is equal to a real, finite value.

$$\int_{\substack{\text{all} \\ \text{space}}} \Psi^* \Psi d\tau = \begin{array}{l} \text{finite and real} \\ \text{valued} \end{array}$$

If the above integral is finite and real valued, the wave function  $\Psi$  can easily be normalized by multiplying by a normalization constant.

$$\int_{\text{all space}} \Psi^* \Psi d\tau = \begin{matrix} \text{finite and real-} \\ \text{valued} \end{matrix}$$

If the above is true then the **normalization constant** can be determined from the following:

$$N = \left( \frac{1}{\int \Psi^* \Psi d\tau} \right)^{\frac{1}{2}}$$

And our normalized wave function is then:

$$\Psi_{\text{normalized}} = N \cdot \Psi$$

## Examples

Normalize the following functions, *if possible*, for the intervals given.

$$\sin x \quad (-\infty, \infty)$$



$$\sin x \quad (0, 2\pi)$$

$$xe^{-x} \quad (0, \infty)$$

$$e^{-x^2} \quad (-\infty, \infty)$$

4.  $\Psi(x,y,z,t)$  should have partial derivatives

$$\frac{\partial \Psi}{\partial x} \quad \frac{\partial \Psi}{\partial y} \quad \frac{\partial \Psi}{\partial z}$$

that are **continuous** functions of  $x, y, z$ .

This is a looser requirement for a 'good' wave function. There are sometimes cases when this is relaxed. For example, when potential is ill-behaved. (e.g. Coulomb potential at the nucleus is infinite)

**Conditions 1 through 4 are the requirements for a 'well-behaved' function.**

## Minimal Requirements for a Valid Wave Function

1.  $\Psi(x,y,z,t)$  must be a continuous function.
2.  $\Psi(x,y,z,t)$  must be bounded and single-valued.
3.  $\Psi(x,y,z,t)$  must be normalizable.
4.  $\Psi(x,y,z,t)$  should be smooth. (The derivatives should be continuous).

These requirements arise from the Born-interpretation of the wave function. It is important to understand why they arise from the Born interpretation of the wave function.



## Postulate 2

To every “observable” in classical mechanics there corresponds an **operator** in quantum mechanics.

*More to come*

*What is an operator?*

An operator is a mathematical entity or symbol that tells you to do something to whatever follows the symbol.

let  $\hat{O} = \frac{d}{dx}$  and  $f(x) = x^2$

Then  $\hat{O}f(x) = \frac{d}{dx}(x^2) = 2x$

Operators usually denoted with a carat ^ over it, e.g.  $\hat{O}$

In these lecture notes will sometimes use (in the text) a bold underline, e.g. **O**

## Postulate 2 (Complete)

To every observable in classical mechanics there corresponds an operator in quantum mechanics. To find the operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates and linear momentum, and make the following replacements:

$$\begin{array}{ll} x \rightarrow \hat{x} = x & p_x \rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \\ y \rightarrow \hat{y} = y & p_y \rightarrow \hat{p}_y = -i\hbar \frac{\partial}{\partial y} \\ z \rightarrow \hat{z} = z & \\ t \rightarrow \hat{t} = t & p_z \rightarrow \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \end{array}$$

$$\hbar = \frac{h}{2\pi}$$

is the reduced Planck's constant  
and is pronounced 'h-bar'

Define the kinetic energy operator in one-dimension.



Define the kinetic energy operator in 3-dimensions.



The first postulate states that the wave function of a quantum mechanical system contains all information concerning the system.

The second postulate states that for every physical observable, there corresponds a quantum mechanical operator!

The 3rd postulate deals with measurements in quantum mechanics.

### Postulate 3

Any measurement of the observable associated with the operator  $\underline{\mathbf{A}}$ , the only values that will ever be observed are the eigenvalues 'a', which satisfy the following:

$$\hat{A}f = af$$

$f$  is an eigenfunction of the operator  $\mathbf{A}$   
(It is not necessarily the wave function)

# What are Eigenfunctions and Eigenvalues?

When a mathematical operation (such as multiplication, differentiation) is performed on a function, the result is generally some different function.

For example: differentiation of  $x^2$  yields a different function,  $2x$ .

For some combinations of operations and functions, the same function is regenerated, multiplied by a constant.

For example: differentiation of  $e^{2x}$  yields a different function,  $2e^{2x}$ .

The original function is simply multiplied by 2.

$$\begin{array}{ccc} \nearrow & \hat{A}f(x) = a \cdot f(x) & \nwarrow \\ \text{Operator acts on} & & \text{It gives the exact} \\ \text{function } \Psi & & \text{function back} \\ & & \text{multiplied by some} \\ & & \text{constant} \end{array}$$

The function is called an **eigenfunction** and the numeric constant is called the **eigenvalue**. The above is called an **eigenvalue equation**.

Determine if the function  $f$  is an eigenfunction of the operator  $\hat{A}$   
(if so, what is the eigenvalue?)



$$\hat{A} = \frac{d}{dx} \quad f(x) = \cos(\omega x)$$

$$\hat{A} = \frac{d^2}{dx^2} \quad f(x) = \cos(\omega x)$$

$$\hat{A} = \frac{d^2}{dx^2} \quad f(x) = e^{i\omega x}$$

$$\hat{A} = \frac{d}{dx} \quad f(x) = e^{Ax^2}$$

$$\hat{A} = \frac{\partial}{\partial y} \quad f(x, y) = y^2 e^{6x}$$

## Postulate 3

For any measurement of the observable associated with the operator  $\hat{\mathbf{A}}$ , the only values that will ever be observed are the eigenvalues  $a_n$  which satisfy:

$$\hat{A}f_n = a_n f_n$$

An operator generally has more than one valid eigenfunction so we index the eigenfunctions with a subscript  $n$ .

The eigenvalue 'a' can be discrete or continuous, depending on the operator.

If the eigenvalues are discrete then we usually index them from the smallest value to the largest value:

$$\hat{A}f_n = a_n f_n \quad n = (\text{sometimes}) 0, 1, 2, 3, \dots$$

If the eigenvalues are continuous, we usually drop the subscript.

$$\hat{A}f = af$$

In any experiment measuring the observable corresponding to the operator  $\underline{\mathbf{A}}$ , only the values  $a_1, a_2, a_3, \dots$  will be observed.

## Observables of the Linear Momentum, $p_x$

Consider the linear momentum,  $p_x$ , which is an observable we can often easily measure for a given single-particle system.

By the third postulate, we will only be able to measure values that are eigenvalues of the following equation:

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

It turns out that  $e^{ikx}$  is an eigenfunction of the operator  $\underline{p}_x$ . Check that this is true.





$$a = \hbar k$$

since  $k$  can be any constant, it turns out that linear momentum is an observable that is continuous and can take on any value.

## Observables of the Angular Momentum, $L_z$

The angular momentum operator (in the  $z$ -direction) is represented by the following operator in quantum mechanics:

$$\hat{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

The eigenfunctions of the angular momentum are given the symbol  $Y$ .

$$\hat{L}_z Y = \hbar m Y \quad m = 0, \pm 1, \pm 2, \pm 3 \dots$$

Don't worry about the explicit form of  $Y$  at this moment.

$$a = \hbar m \quad m = 0, \pm 1, \pm 2, \pm 3 \dots$$

Notice, however, that the constant ' $m$ ' can only take on discrete integer values. Thus, the eigenvalues of the angular momentum operator can only assume discrete values.

When we go to measure the angular momentum of any system, we will only be able to measure these discrete values.

It turns out that angular momentum is quantized. (More on the quantization of angular momentum much later in the course)

## Postulate 3

For any measurement of the observable associated with the operator  $\hat{A}$ , the only values that will ever be observed are the eigenvalues  $a_n$ , which satisfy:

$$\hat{A}f_n = a_n f_n$$

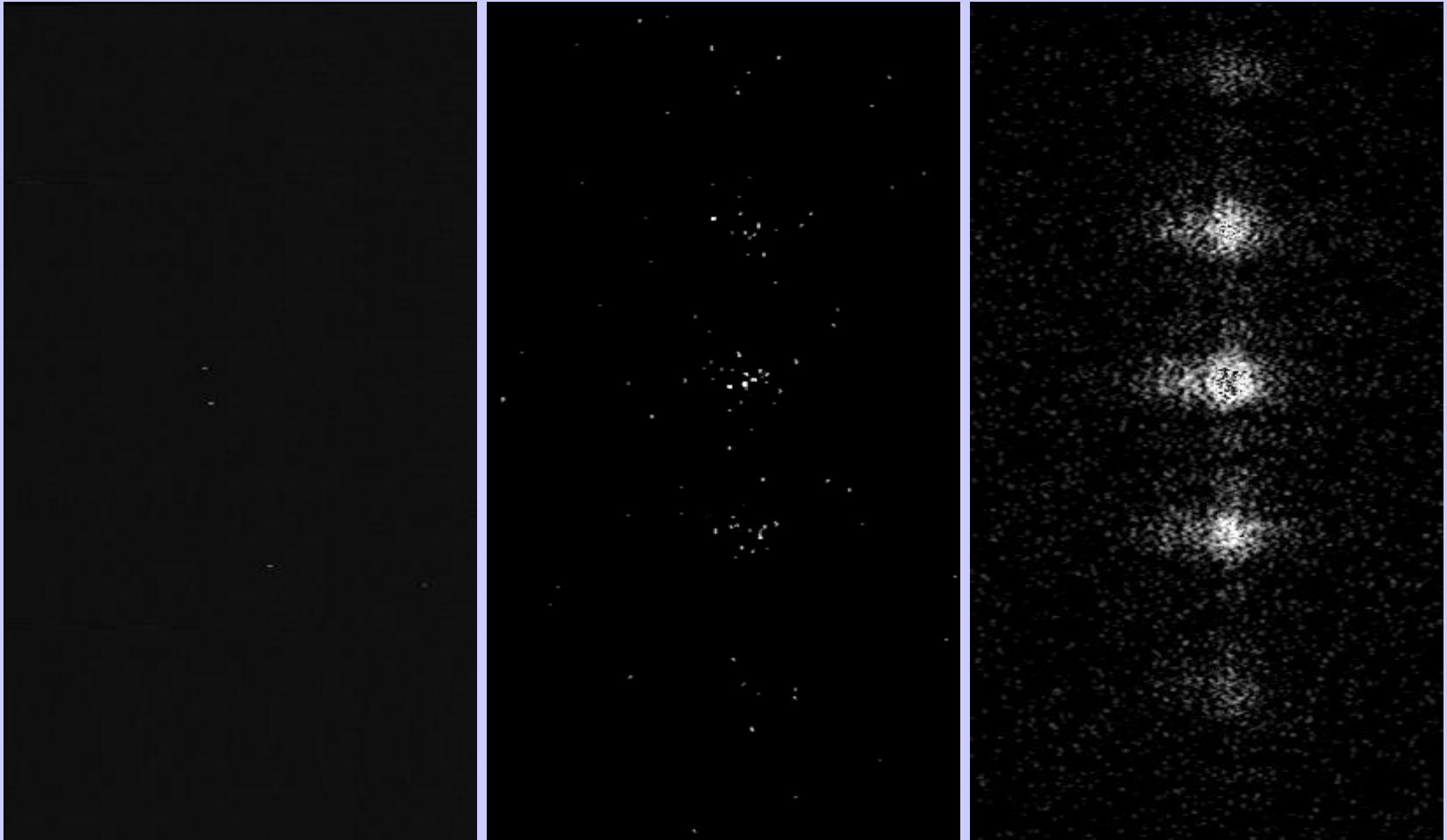
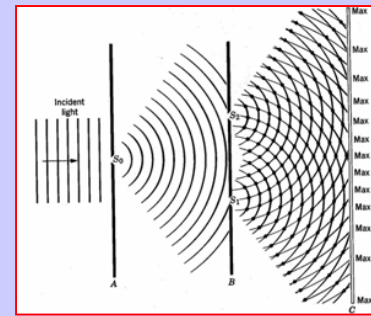
Postulate 3 tells us what values of a given observable are allowable. **But what value will we actually measure?**

If we have a system described by the wave function  $\Psi$ , the first postulate tells us that any information we can derive about the system is contained in the wave function.

Unfortunately, due to the probabilistic nature of quantum mechanics, we can't be sure which eigenvalue we will actually measure ( $a_1, a_5, a_{192}$ ?)

This is quite different from classical mechanics where if we knew the state function  $x(t)$ , we could tell exactly what one would measure at any given time.

# Young's Double-Slit Experiments with Single Photons



*Interference Pattern Made Up of Discrete Particle Detections!*

## Postulate 4

If a system is in a state described by a normalized wave function  $\Psi$ , then the **average** or **mean value** of the observable that will be measured corresponding to the operator  $\underline{A}$  is given by:

$$\langle a \rangle = \int_{\text{all space}} \Psi^* \hat{A} \Psi d\tau$$

The above is called the expectation value in quantum mechanics.

If we have a wave function and an operator corresponding to an observable we want to measure, the above tells us what the **average value** we will measure at a given time.

Let's write this out more explicitly:

$$\langle a \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^*(x, y, z, t) \left( \hat{A} \Psi(x, y, z, t) \right) dx dy dz$$

Brackets are used to emphasize that we apply the operator to  $\Psi$  before we integrate.

If the wave function  $\Psi$  is not normalized, then the expectation value is given by:

$$\frac{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^*(x, y, z, t) \left( \hat{A} \Psi(x, y, z, t) \right) dx dy dz}{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Psi^*(x, y, z, t) \Psi(x, y, z, t) dx dy dz}$$

## UNTIL NOW....

We have discussed some properties of the wave function  $\Psi$ . However, we have not discussed how we determine the wave function. The next postulate, which involves the famous Schrödinger equation, gives us this.



Erwin Schrödinger (1887-1961)

## Postulate 5

The wave function of a system evolves in time according to the time-dependent **Schrödinger equation**:

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

Where  $\hat{H}$  is the Hamiltonian operator given by:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z, t)$$

We can use the Schrödinger equation to solve for the wave function for any system. (in principle).



## Postulate 5 (alternative expression)

The wave function  $\Psi(x, y, z; t)$  of a system can be obtained by solving the time-dependent Schrödinger equation for that system:

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

where

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z, t)$$

The potential energy function  $V$  cannot be given in general because it depends on the system.

In this course, the systems we are interested in usually have a potential which does not depend on time.

$$V(x, y, z, t) \Rightarrow V(x, y, z)$$

In this case, we can simplify things.

It turns out that if the Hamiltonian (or the potential within it) does not change in time we can write the wave function as:



$$\Psi(x, y, z, t) = \psi(x, y, z) \cdot f(t) \quad \textit{Separation of variables}$$

## Addition to Postulate 5

If the potential does not change in time, the wave function can be obtained by solving for Schrödinger's time-independent equation.

$$\hat{H}\psi(x, y, z) = E\psi(x, y, z)$$

With the total wave function given by:

$$\Psi(x, y, z, t) = \psi(x, y, z) \cdot e^{-iEt/\hbar}$$

Thus, we don't have to solve the time-dependent wave equation, only the time-independent equation, because the time-dependent component of the total wave function is always the same.

We will use Schrödinger's time independent equation extensively in this course.

## Stationary State Wave Function

When the Hamiltonian does not change in time, the solutions to the time-independent wave equation are called **stationary states**.

$$\Psi(x, y, z, t) = \psi(x, y, z) \cdot e^{-iEt/\hbar}$$

The reason for this is that the probability density does not change in time, *i.e.* it is time independent.

This is easily shown (in 1-D):

$$\begin{aligned} P(x, t) &= |\Psi(x, t)|^2 = \Psi(x, t)^* \Psi(x, t) \\ &= \left( \psi(x) \cdot e^{-iEt/\hbar} \right)^* \psi(x) \cdot e^{-iEt/\hbar} \\ &= \psi(x)^* \psi(x) \cdot e^{+iEt/\hbar} \cdot e^{-iEt/\hbar} \\ &= \psi(x)^* \psi(x) \cdot e^0 \\ &= \psi(x)^* \psi(x) \leftarrow \text{independent of time} \end{aligned}$$

Notice that the time component of the total wave function of a stationary state simply oscillates:

$$\Psi(x, y, z, t) = \underbrace{\psi(x, y, z)} \cdot e^{-iEt/\hbar}$$

This is easier to see if we let:

$$\omega = E/\hbar = E/(2\pi\hbar) = \nu/2\pi$$

$$\begin{aligned}\Psi(x, y, z, t) &= \psi(x, y, z) \cdot e^{-i\omega t} \\ &= \psi(x, y, z) \cdot (\cos(\omega t) - i \sin(\omega t))\end{aligned}$$

$\omega$  is then the angular frequency of this oscillation.

*Because Schrödinger's equation has wave-like solutions, this is the reason Schrödinger's formulation of quantum mechanics is often called wave mechanics.*

# Summary of the Postulates of Quantum Mechanics

## Postulate 1

The state of a quantum mechanical system is completely specified by a function  $\Psi(x,y,z,t)$  that depends on the coordinates of the particle and on time. This function is called the **wave function** of the system. All possible information about the system can be derived from  $\Psi$ .

The wave function  $\Psi(x,y,z,t)$  has an important property that its square is the probability distribution function for the system:

$$|\Psi(x, yz, t)|^2 = \Psi^*(x, y, z, t)\Psi(x, y, z, t)$$

Due to the Born interpretation of the wave function  $\Psi(x,y,z,t)$  must be 'well behaved'. It must be a continuous function that is bound and single valued everywhere.  $\Psi(x,y,z,t)$  must be normalizable or quadratically integrable. Finally, the partial derivatives of  $\Psi$  w.r.t. to  $x$ ,  $y$  and  $z$  should be continuous.

## Postulate 2

To every observable in classical mechanics there corresponds a linear Hermitian operator in quantum mechanics. To find the operator, write down the classical-mechanical expression for the observable in terms of Cartesian coordinates and linear momentum, and make the following replacements:

$$\begin{array}{ll} x \rightarrow \hat{x} = x & p_x \rightarrow \hat{p}_x = -i\hbar \frac{\partial}{\partial x} \\ y \rightarrow \hat{y} = y & p_y \rightarrow \hat{p}_y = -i\hbar \frac{\partial}{\partial y} \\ z \rightarrow \hat{z} = z & \\ t \rightarrow \hat{t} = t & p_z \rightarrow \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \end{array}$$

This postulate gives us a simple recipe for obtaining quantum mechanical observables.

### Postulate 3

Any measurement of the observable associated with the operator  $\underline{\mathbf{A}}$ , the only values that will ever be observed are the eigenvalues  $a$ , which satisfy:

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

### Postulate 4

If a system is in a state described by a normalized wavefunction  $\Psi$ , then the average or mean value of the observable corresponding to operator  $\underline{\mathbf{A}}$  is given by:

$$\langle a \rangle = \int_{\text{all space}} \Psi^* \hat{A} \Psi d\tau$$

The above also called the expectation value in QM.



## Postulate 5

The wave function of a system evolves in time according to the time-dependent Schrödinger equation:

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

Where H is the Hamiltonian operator given by:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z; t)$$

If the potential does not change in time, the wave function can be obtained by solving for Schrodinger's time independent equation.

$$\hat{H}\psi(x, y, z) = E\psi(x, y, z)$$

Here, the the total wave function given by:

$$\Psi(x, y, z, t) = \psi(x, y, z) \cdot e^{-iEt/\hbar}$$

- The postulates of quantum mechanics replace Newton's and Hamilton's equations of motion for describing the behaviour of a given system.
- Postulate 5 furnishes the "equation of motion" that yields the wave function describing the possible states of the system.
- Once  $\Psi(x,y,z;t)$  are obtained - ALL of the properties (physical quantities) of the system can be calculated and interpreted by applying the other postulates.
- We will obtain an understanding of quantum mechanics by applying the postulates to a variety of chemical systems.