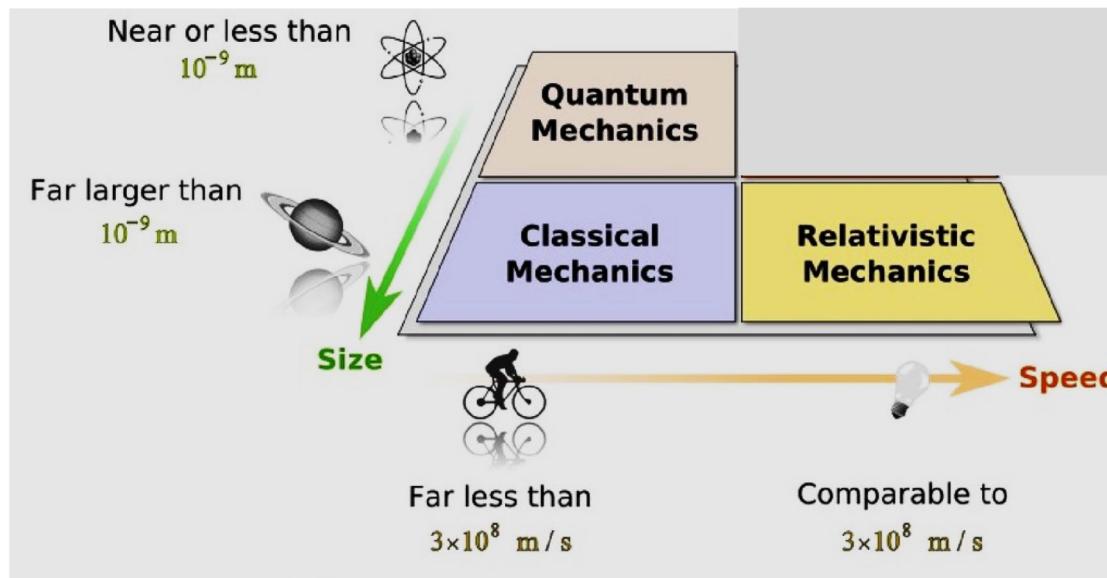


# Quantum Mechanics

Quantum Physics is a branch of physics which deals with the theories of atoms and subatomic particles at very small scales .



# The early development of the quantum Mechanics

- In the early years of the twentieth century, Max Planck, Albert Einstein, Louis de Broglie, Neils Bohr, Werner Heisenberg, Erwin Schrodinger, Max Born, Paul Dirac and others created the theory now known as quantum mechanics.
- The discovery of quantum Physics is nearly a total surprise.
- It described the physical world in a way that was fundamentally new.
- The fundamental difference between the classical (Newtonian) mechanics and quantum mechanics lies in what they describe.
- In quantum mechanics, the kind of certainty about the future characteristics of classical mechanics is impossible because the initial state of a particle can not be established with sufficient accuracy.

- The quantum mechanics was not developed in a strictly logical way, but, gradually with a series of guesses inspired by previous theories, as follows:

### 1900 (Planck):

- Max Planck proposed that light with frequency  $\nu$  is emitted in quantized lumps of energy that come in integral multiples of the quantity,

$$E = \hbar\omega$$

where  $h = 6.63 \times 10^{-34} J.s$  is Plank's constant, and  $\hbar = \frac{h}{2\pi} = 1.06 \times 10^{-34} J.s$

- Planck's hypothesis simply adds the information of how many lumps of energy a wave contains.

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### 1905 (Einstein):

- Albert Einstein stated that the quantization was in fact inherent to the light, and that the lumps can be interpreted as particles, which we now call "photons". So Planck's relation  $E = \hbar\omega$  becomes:

$$\begin{aligned} E &= \hbar\omega \\ \Rightarrow pc &= \hbar(ck) \end{aligned}$$

$E = pc$  and  $\omega = ck$  for a light wave.

$$p = \hbar k$$

- This result relates the momentum of a photon,  $p$ , to the wavenumber of the wave,  $k$ , it is associated with.

## De Broglie Hypothesis: de-Broglie waves

- Inspired with Planck and Einstein, Louis de-Broglie, a French Physicist, suggested that, *all moving matters or material particles have particle-wave duality and exhibits wave-like nature.*
- The wave associated with the moving matter is known as *matter wave or de-Broglie waves.*



Keeping the dual nature of matter waves, Broglie combined Einstein's equation which dealt with the energy of matter, and Planck's equation which dealt with the energy of waves and gave a relation between the momentum of moving matters (p) and wavelength of matter waves ( $\lambda$ ) as

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

**De-Broglie wavelength of matter waves**

- As in the case of electromagnetic waves, the wave and particle aspects of moving bodies can never be observed at the same time. In certain situations a moving body resembles a wave and in others resembles a particle.
- Which set of properties is most prominent, depends on how its de Broglie wavelength compares with its dimensions and the dimensions of whatever it interacts with.

Problems: Find the de Broglie wavelength of (a) a 46-g golf ball with a velocity of 30m/s, and (b) an electron with a velocity of  $10^7$ m/s.

Solution:

(a) Since  $v \ll c$ , we can take  $m = m_0$ , hence

$$\lambda = \frac{h}{mv}$$

$$\lambda = \frac{6.63 \times 10^{-34} J.s}{(0.046 \text{ kg})(30 \text{ m/s})} = 4.8 \times 10^{-34} \text{ m}$$

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(b)

$$\lambda = \frac{h}{mv} = \frac{6.63 \times 10^{-34} J.s}{(9.2 \times 10^{-31} \text{ kg})(10^7 \text{ m/s})} = 7.3 \times 10^{-11} \text{ m}$$

The wavelength of electron is comparable to the dimensions of atoms. Here, we can expect wave character of moving electron.

## Experimental evidence of the de Broglie hypothesis

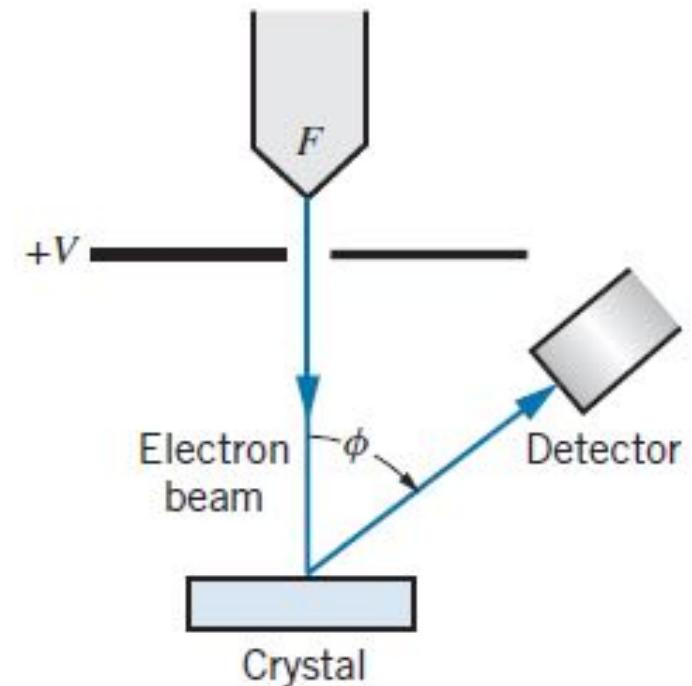
- There is no experiment that can be done to reveal the wave nature of macroscopic (laboratory-sized) objects. Experimental verification of de Broglie's hypothesis comes only from experiments with objects on the atomic scale.
- The indications of wave behavior come mostly from interference and diffraction experiments. To show the evidence of de-Broglie waves. we'll discuss diffraction of light waves with electrons.
- The experiments that first verified de Broglie's hypothesis involve *electron diffraction through the atoms of a crystal*.

## Experimental evidence of the de Broglie waves

- The indications of wave behavior come mostly from interference and diffraction experiments. To show the evidence of de-Broglie waves. we'll discuss diffraction of light waves with electrons.
- The experiments that first verified de Broglie's hypothesis involve *electron diffraction* through the atoms of a crystal.
- An electron diffraction experiment gave the first experimental confirmation of the wave nature of electrons (and the quantitative confirmation of the de Broglie relationship  $\lambda = h/p$ ) soon after de Broglie's original hypothesis.
- In 1926, at the Bell Telephone Laboratories, Clinton Davisson and Lester Germer were investigating the reflection of electron beams from the surface of nickel crystals.

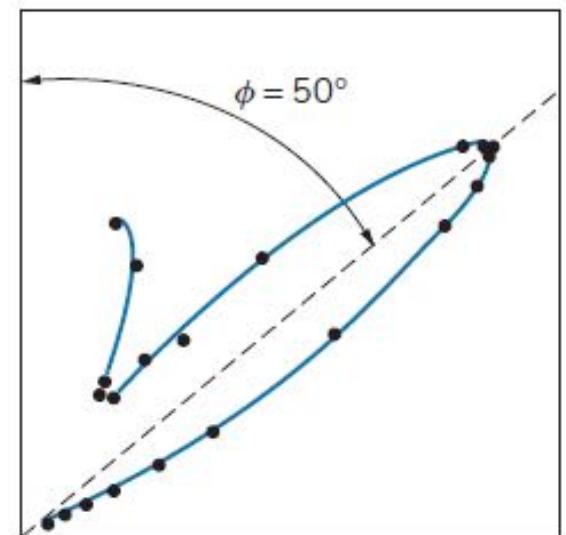
Apparatus used by Davisson and Germer to study electron diffraction.

- A beam of electrons from a heated filament is accelerated through a potential difference  $V$ .
- After passing through a small aperture, the beam strikes a single crystal of nickel.
- Electrons are scattered in all directions by the atoms of the crystal, some of them striking a detector, which can be moved to any angle  $\phi$  relative to the incident beam and which measures the intensity of the electron beam scattered at that angle.



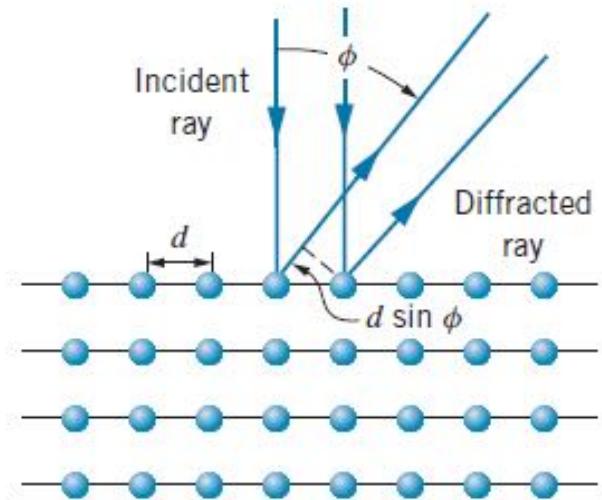
## Results of Davisson and Germer.

- Figure shows the results of one of the experiments of Davisson and Germer.
- Each point on the plot represents the relative intensity when the detector, is located at the corresponding angle  $\varphi$  measured from the vertical axis.
- Constructive interference causes the intensity of the reflected beam to reach a maximum at  $\varphi = 50^0$  for  $V = 54$  V.



Let's see how these results give confirmation of the de Broglie wavelength.

- Figure shows a simplified representation of the nickel crystal used in the Davisson-Germer experiment.
- Each of the atoms of the crystal can act as a scatterer, so the scattered *electron waves* can interfere, and we have a crystal diffraction grating for the electrons.
- Because the electrons were of low energy, they did not penetrate very far into the crystal, and it is sufficient to consider the diffraction to take place in the plane of atoms on the surface.



The crystal surface acts like a diffraction grating with spacing  $d$ .

- Similar to a reflection-type diffraction grating for light; the spacing  $d$  between the rows of atoms on the crystal is analogous to the spacing between the slits in the optical grating.
- The maxima for a diffraction grating occur at angles  $\phi$  such that the path difference between adjacent rays  $d \sin \phi$  is equal to a whole number of wavelengths:

$$d \sin \phi = n\lambda \quad n = 1, 2, 3, \text{ the order number of the maximum}$$

- From independent data, it is known that the spacing between the rows of atoms in a nickel crystal is  $d = 0.215 \text{ nm}$ . The peak at  $\phi = 50^\circ$  must be a first-order peak ( $n = 1$ ), because no peaks were observed at smaller angles.
- If this is indeed an interference maximum, the corresponding wavelength is,

$$\lambda = d \sin \phi = (0.215 \text{ nm})(\sin 50^\circ) = 0.165 \text{ nm}$$

We can compare this value with that expected on the basis of the de Broglie theory.

- An electron accelerated through a potential difference of 54 V has a kinetic energy of 54 eV and therefore a momentum of

$$p = \sqrt{2mK} = \frac{1}{c} \sqrt{2mc^2K} = \frac{1}{c} \sqrt{2(511,000eV)(54eV)} = \frac{1}{c} (7430eV)$$

- The de Broglie wavelength is  $\lambda = \frac{h}{p} = \frac{hc}{pc}$ .

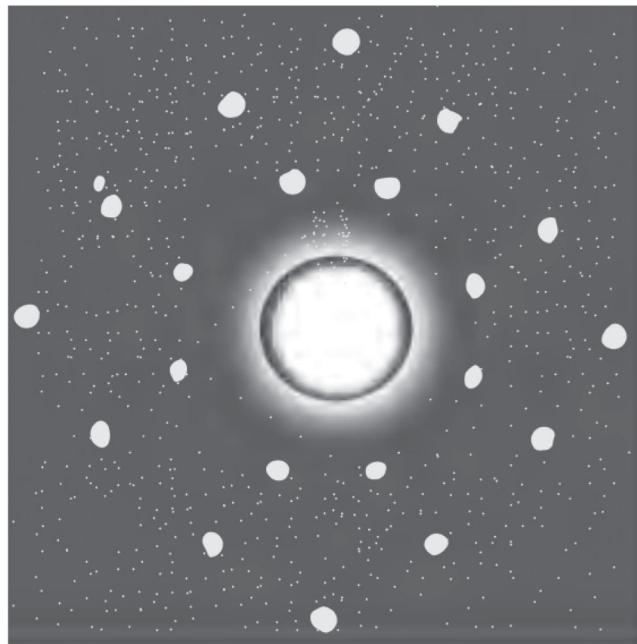
Using  $hc = 1240 \text{ eV} \cdot \text{nm}$ ,

$$\lambda = \frac{hc}{pc} = \frac{1240 \text{ eV} \cdot \text{nm}}{7430 \text{ eV}} = 0.167 \text{ nm}$$

## Conclusion and Remarks:

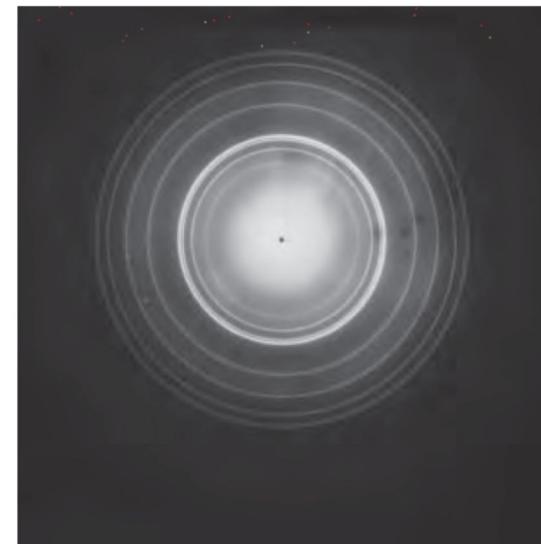
- This is in excellent agreement with the value found from the diffraction maximum, and provides strong evidence in favor of the de Broglie theory.
- For this experimental work, Davisson shared the 1937 Nobel Prize with G. P. Thomson.
- The wave nature of particles is not exclusive to electrons; *any* particle with momentum  $p$  has de Broglie wavelength  $h/p$ .

## The de Broglie hypothesis: Further experimental proofs



Diffraction of neutrons  
By a sodium chloride  
crystal

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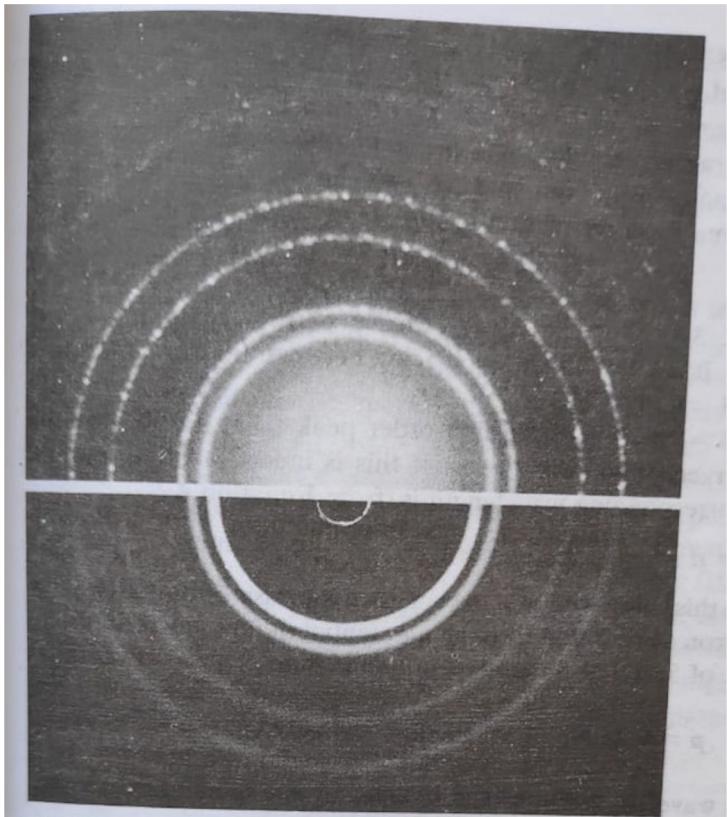


Diffraction of electrons by  
Polycrystalline  
beryllium

Dr V.S. Gayathri

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## Comparison of X-ray diffraction and electron diffraction



Upper half of the figure shows the result of scattering of 0.071 nm X rays by an aluminium foil.

Lower half shows the result of scattering of 600 eV electrons by aluminium.

Problems: What will be the ratio of DB wavelength of proton to  $\alpha$ - particle if they are accelerated with a same potential,  $V$ ?

Solution:

If a charged particle is accelerated by a potential difference of  $V$  volts, then the DB wavelength is given by  $\lambda = \frac{h}{\sqrt{2mqV}}$

Then, the ratio of DB wavelength of proton to  $\alpha$ - particle is

$$\frac{\lambda_p}{\lambda_\alpha} = \frac{\sqrt{2m_\alpha q_\alpha V_\alpha}}{\sqrt{2m_p q_p V_p}}$$

Putting  $V_\alpha = V_p$ ,  $\frac{\lambda_p}{\lambda_\alpha} = \frac{\sqrt{4 \times 2}}{\sqrt{1 \times 1}} = \sqrt{8} = 2\sqrt{2}$

The ratio of DB wavelength of proton to  $\alpha$ - particle is  $2\sqrt{2}$

## The de Broglie hypothesis and the Bohr's quantization rule

An immediate success of de Broglie's hypothesis was that it gave an explanation of the quantization condition, that angular momentum of an electron circulates in orbits of radius r

$$L = \frac{nh}{2\pi}$$

where v: speed of the electron

m: mass of the electron, and

n: a positive integer (now referred to as a quantum number)

These orbits would be stable and the hydrogen atom was said to be in a stationary state

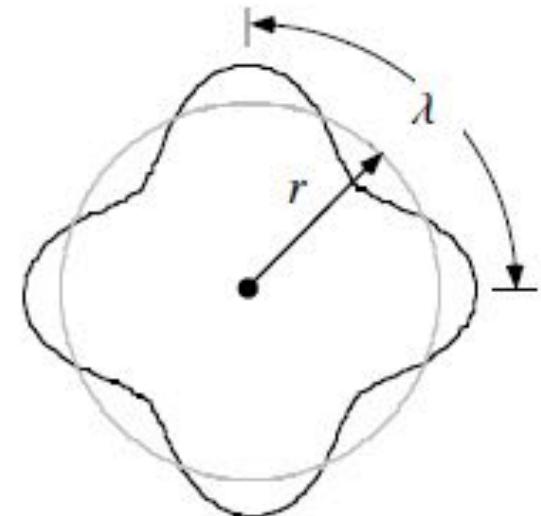
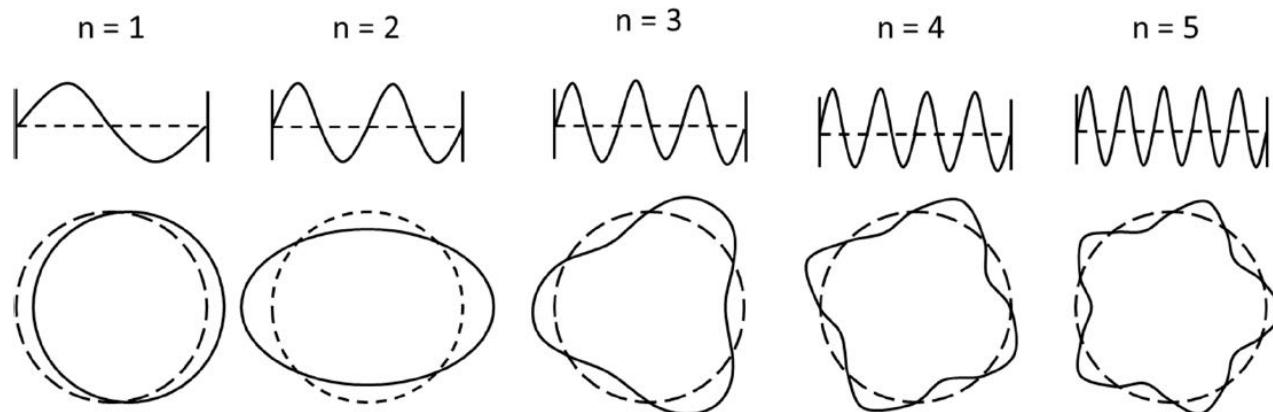
Now, according to Bohr, electrons in atoms have wavelike properties. If the electron circulating around the nucleus is associated with a wave of wavelength  $\lambda$ , then for the wave not to destructively interfere with itself, there must be a whole number of waves fitting into one circumference of the orbit,i.e.

Using the de Broglie wavelength relation  $p = \frac{h}{\lambda}$

The angular momentum of electron,

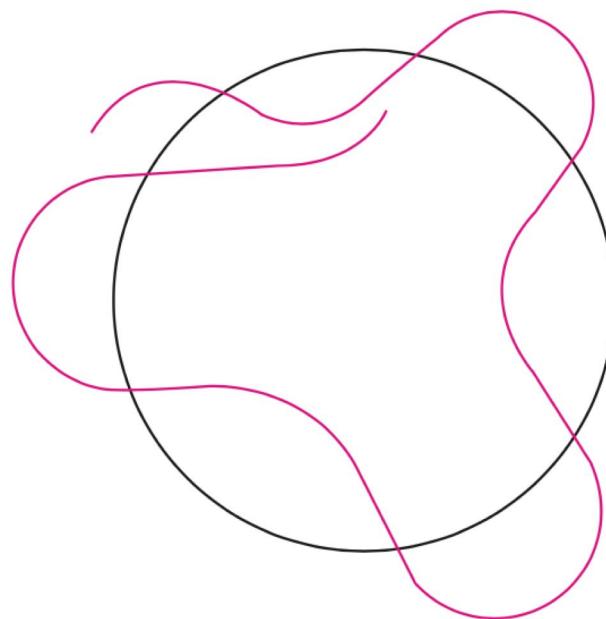
$$L = mvr = pr = \frac{h}{\lambda}r = \frac{nh}{2\pi}$$

which is just Bohr's quantization condition.



*De Broglie wave for which four wavelengths  $\lambda$  fit into a circular orbit of radius  $r$ .*

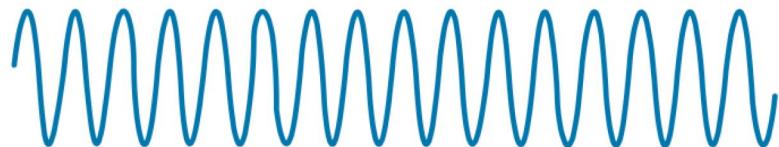
The diagram shows a visual representation of De Broglie's theory



A fractional number of wavelength cannot persist because destructive interference will occur.

# Heisenberg Uncertainty principle

- How to represent a moving particle as a de Broglie wave?
- What are the limitations of such a representation?



(a)



(b)

A pure sine wave extending from  $-\infty$  to  $+\infty$ .

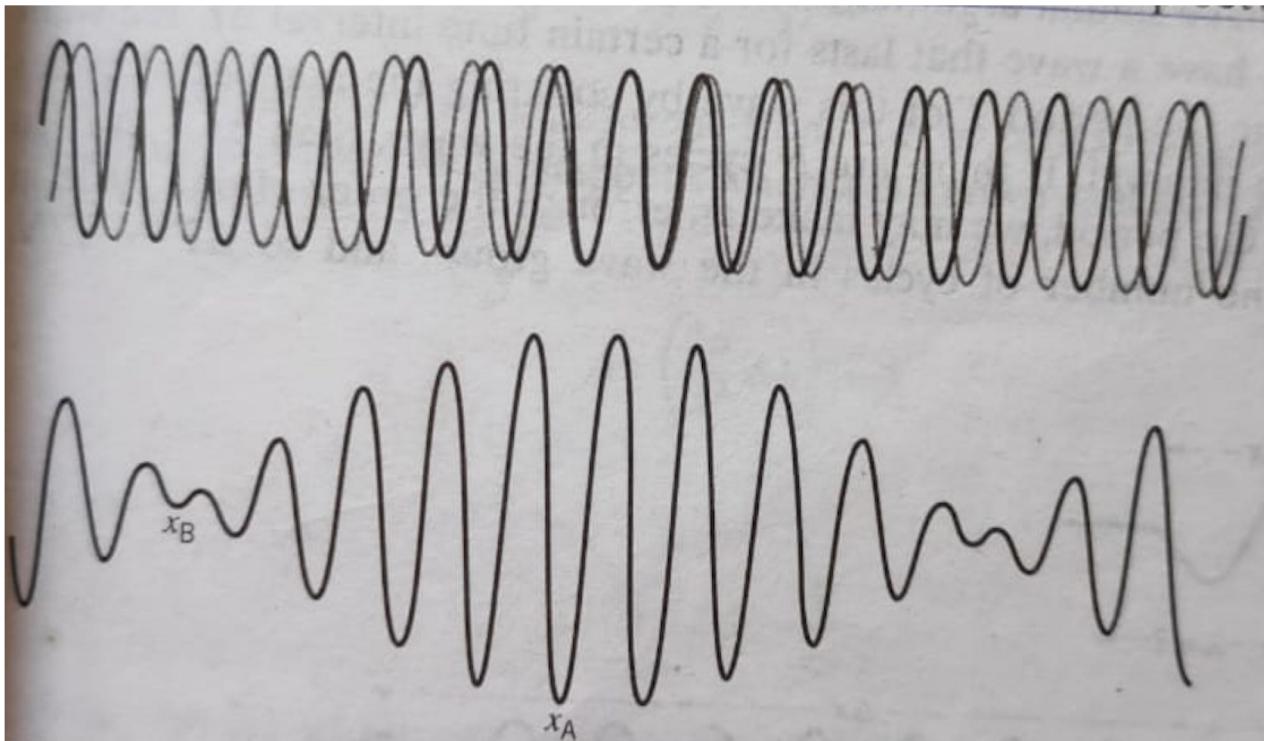
Wavelength  $\lambda = \frac{2\pi}{k}$  (precisely determined)

$\therefore p = \frac{h}{\lambda}$  (precisely determined)

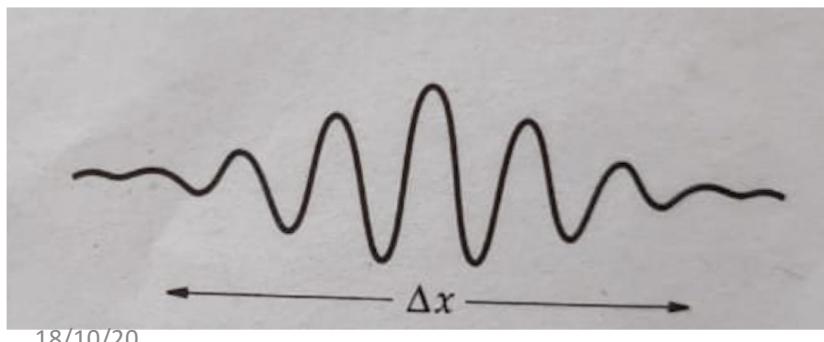
But “**where is the wave located?**”

A short wave pulse describes the **position** of the particle **more precisely**.

But **what is the value of  $\lambda$ ?**



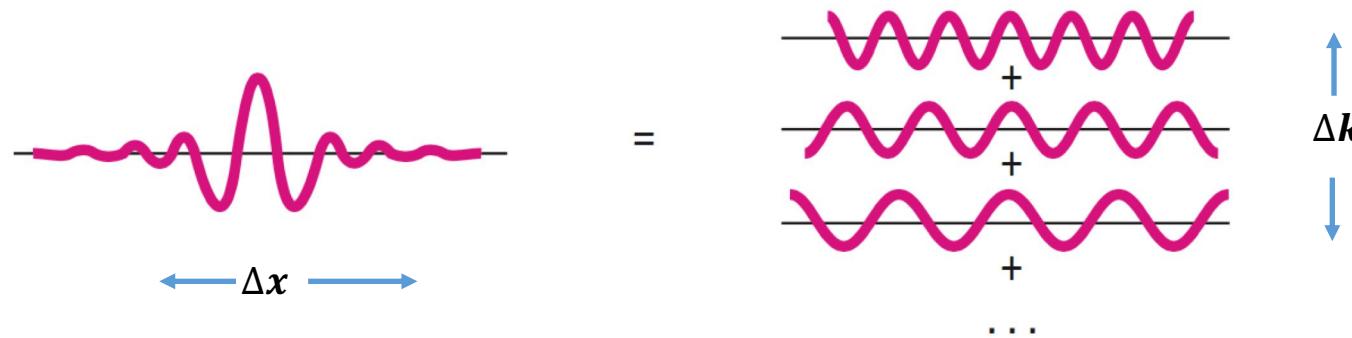
Superposition of nearly equal  $\lambda$  (or  $k$ ) give beats.



The resultant of the addition of many sine waves (of different  $\lambda$  and possibly different Amplitudes) is a **wave group**.

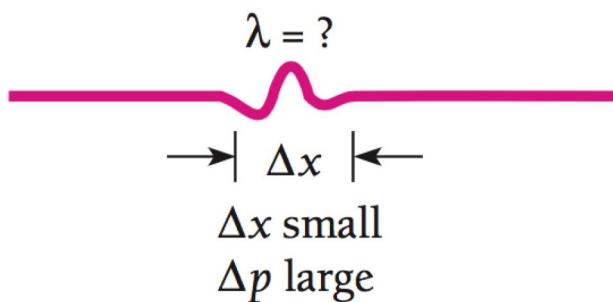
- ✓ An isolated wave group is the result of superposing an infinite number of waves with different wavelengths(or wave numbers).
- ✓ The narrower the wave group ( $\Delta x$ ), the greater the range of wavelengths involved( $\Delta k$ ).

Hence  $\Delta x$  and  $\Delta k$  have **inverse** relationship.



A **moving particle** can be described as a **wave group**. This implies that there are **fundamental limits** to the **accuracy** with which we can measure **particle properties** such as its position, momentum etc.,

## Comparison of different de Broglie wave groups



For a narrow de Broglie wave group:

Particle's position can be specified more precisely.

Not enough waves to measure wavelength  $\lambda$  accurately : ∴  $\lambda$  not well defined.

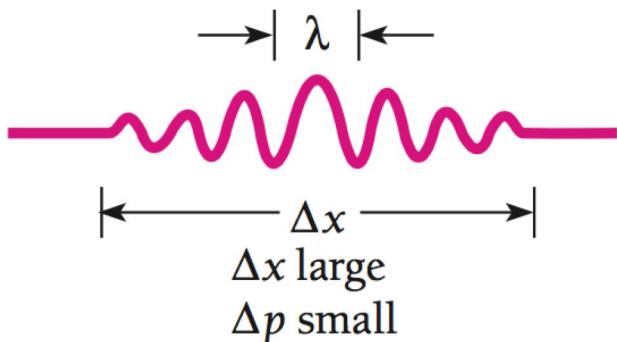
Since  $\lambda = \frac{h}{\gamma mv}$ , particle's momentum is not a precise quantity.

**A well-defined position ( $\Delta x$  smaller), large uncertainty  $\Delta p$  in the momentum of the particle the group represents**

## Comparison of different de Broglie wave groups

For a wide de Broglie wave group:

It has a clearly defined  $\lambda$ .



∴ Particle's momentum is a precise quantity.

The width of the group is too great : So, we can't locate the particle exactly at a given time.

**“More precise momentum but a less precise position”**

## **Mathematical representation of wave group**

At a certain time t, the wave group  $\Psi(x)$  can be represented by

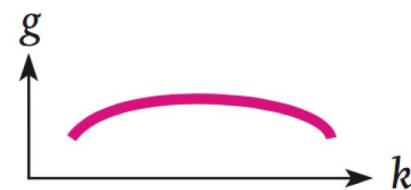
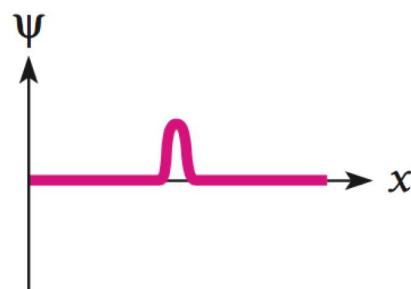
$$\Psi(x) = \int_0^{\infty} g(k) \cos kx \, dk \quad \text{“Fourier integral”}$$

g(k):

- Fourier transform of  $\Psi(x)$  .
- describes how the amplitudes of the waves that contribute to  $\Psi(x)$  vary with wave number k.
- Specifies the wave group as completely as  $\Psi(x)$ .

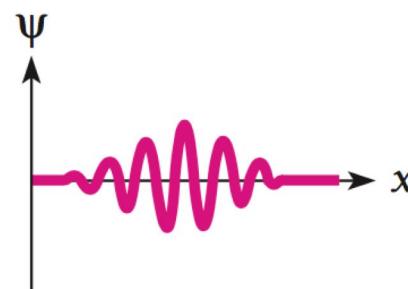
## The wave functions and Fourier transforms

A brief disturbance needs a broader range of frequencies to describe it than a disturbance of greater duration. The narrower the wave group broader the range of wave numbers needed to describe them & vice versa.



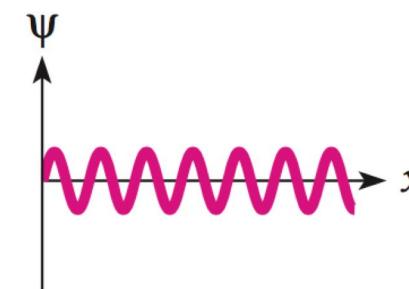
(a)

A pulse



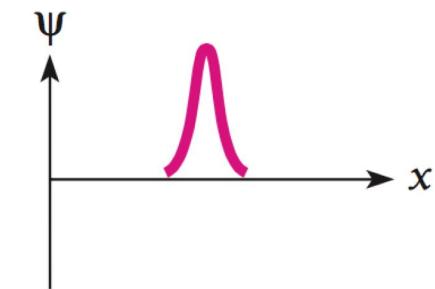
(b)

A wave group



(c)

A wave train



(d)

A Gaussian distribution

The minimum value of the product  $\Delta x \Delta k$  occurs when the envelope of the wave group is a Gaussian function.

If  $\Delta x$  and  $\Delta k$  are taken as the standard deviations of the respective functions  $\Psi(x)$  and  $g(k)$ , then this minimum value is

$$\Delta x \Delta k = \frac{1}{2}$$

Since wave groups, in general, do not have Gaussian forms,

$$\Delta x \Delta k \geq \frac{1}{2}$$

The de Broglie wavelength of a particle of momentum  $p$  is,

$$\lambda = h/p$$

The corresponding wave number:  $k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$

$$p = \frac{hk}{2\pi} \quad (\text{in terms of wave number } k)$$

$$\therefore \Delta p = \frac{h\Delta k}{2\pi} \quad (\text{relation between uncertainties})$$

Since  $\Delta x \Delta k \geq \frac{1}{2}$ ,

$$\Delta x \Delta p_x \geq \frac{h}{4\pi}$$

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$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad (\hbar = h/2\pi)$$

- ❖ If we arrange matters so that  $\Delta x$  is small (corresponding to a narrow wave group), then  $\Delta p_x$  will be large.
- ❖ If we reduce  $\Delta p_x$ ,  $\Delta x$  will be large (as a broad wave group is inevitable).
- ❖ These uncertainties are not due to inadequate apparatus, but due to the imprecise character in nature of the quantities involved.
- ❖ Any instrumental or statistical uncertainties that arise during a measurement only increase the product  $\Delta x \Delta p_x$ .

## Uncertainty principle : Energy & time

Suppose we wish to measure the energy  $E$  (in the form of electromagnetic waves) emitted during the time interval  $\Delta t$  in an atomic process.

Let the minimum uncertainty in the number of waves  
we count in a wave group = 1 wave

Uncertainty in the frequency measurement is

$$\Delta\nu \geq \frac{1}{\Delta t}$$

The corresponding energy uncertainty is

So,

$$\Delta E \geq \frac{h}{\Delta t}$$

or

$$\Delta E \Delta t \geq h$$

A more precise calculation based on the nature of wave groups changes this result to

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

## Heisenberg Uncertainty Relationships

- (i)  $\Delta x \Delta p_x \geq \frac{\hbar}{2}$  ;  $\Delta y \Delta p_y \geq \frac{\hbar}{2}$  ;  $\Delta z \Delta p_z \geq \frac{\hbar}{2}$
- (ii)  $\Delta E \Delta t \geq \frac{\hbar}{2}$

## Heisenberg Uncertainty Principle

- It is impossible to know both the exact position and exact momentum of an object at the same time.
- It is not possible to make a simultaneous determination of the energy and the time coordinate of a particle with unlimited precision.

## **Conclusion:**

Since it is not possible to make a simultaneous determination of the exact position and momentum of a particle, we can't say anything definite about its future values.

**“We cannot know the future for sure because we cannot know the present for sure”**

The indeterminacy is inherent in the nature of a moving body.

## Problem1

An electron moves in the x direction with a speed of  $3.6 \times 10^6 \text{ m/s}$ . We can measure its speed to a precision of 1% . (a) With what precision can we simultaneously measure its position? (b) What can we say about its motion in the y direction?

### Solution:

(a) The electron's momentum is

$$\begin{aligned} p_x &= m v_x = (9.11 \times 10^{-31} \text{ kg}) \left( 3.6 \times 10^6 \frac{\text{m}}{\text{s}} \right) \\ &= 3.3 \times 10^{-26} \text{ kg.m/s} \end{aligned}$$

The uncertainty  $\Delta p_x$  is 1% of  $3.3 \times 10^{-26} \text{ kg.m/s}$ .

The uncertainty in position is then

$$\Delta x \sim \frac{\hbar}{\Delta p_x} = \frac{1.05 \times 10^{-34} \text{ J.s}}{3.3 \times 10^{-26} \text{ kg.m/s}} = 3.2 \text{ nm}$$

(b) If the electron is moving in the x direction, then we know its speed in the y direction precisely; thus  $\Delta p_y = 0$ . The uncertainty relationship  $\Delta y \Delta p_y \sim \hbar$  then requires that  $\Delta y$  be infinite. We can therefore know nothing at all about the electron's y coordinate.

## Problem2

An excited atom gives up its excess energy by emitting a photon of characteristic frequency. The average period that elapses between the excitation of an atom and the time it radiates is  $1.0 \times 10^{-8} \text{ s}$ . Find the inherent uncertainty in the frequency of the photon.

### Solution:

The photon energy is uncertain by the amount

$$\begin{aligned}\Delta E &\geq \frac{\hbar}{2\Delta t} \geq \frac{1.054 \times 10^{-34} \text{ J.s}}{2(1.0 \times 10^{-8} \text{ s})} \\ &\geq 5.310^{-27} \text{ J}\end{aligned}$$

The corresponding uncertainty in the frequency of light is

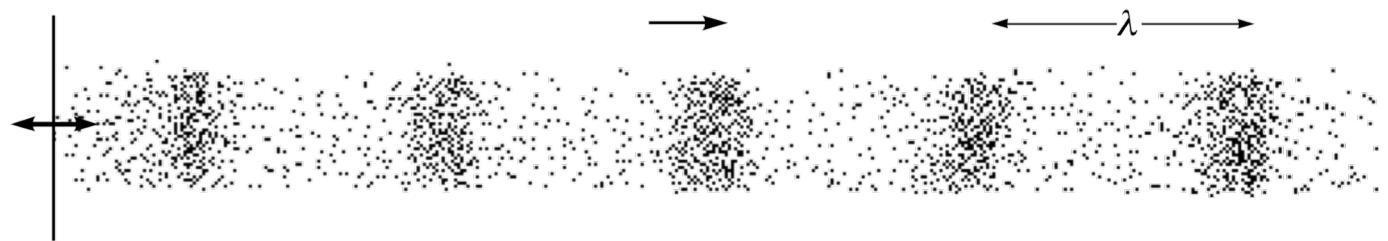
$$\Delta\nu \geq \frac{\Delta E}{h} \geq 8 \times 10^6 \text{ Hz}$$

This is the irreducible limit to the accuracy with which we can determine the frequency of the radiation emitted by an atom.

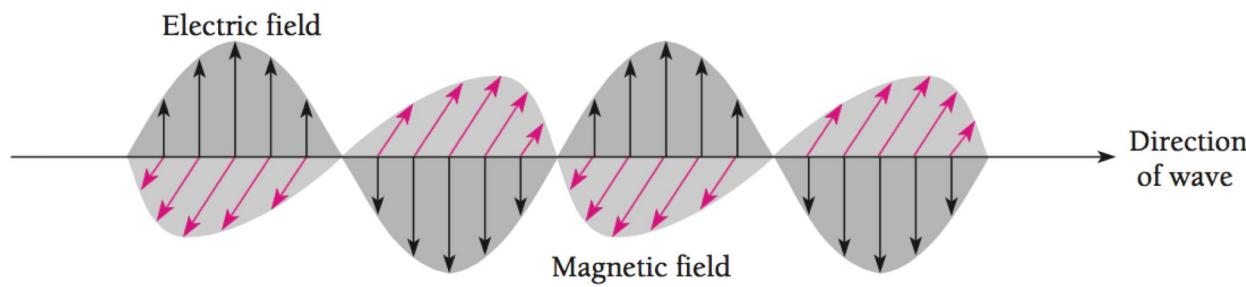
# Matter Waves: Waves of What?



Periodic variation  
of **height** of water surface



Periodic variation  
of **pressure**



Periodic variation  
of E & B fields

In matter waves, what varies periodically?  
What is the physical property that varies as the de Broglie wave propagates?

The quantity whose variations make up matter waves is called the **wave function  $\Psi(x, y, z, t)$** .

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

- is the **amplitude** of the de Broglie waves.
- can be positive or negative, it can't be an observable quantity.
- are usually complex with both real and imaginary parts.

So,  **$\Psi(x, y, z, t)$  itself has no physical interpretation.**

Every complex function  $\Psi$  can be written in the form:

$$\Psi = A + iB \quad (\text{where } A \text{ & } B \text{ are real functions})$$

The complex conjugate  $\Psi^*$  of  $\Psi$  is :  $\Psi^* = A - iB$

So,

$$\begin{aligned} |\Psi|^2 &= \Psi^* \Psi \\ &= A^2 - i^2 B^2 \\ &= A^2 + B^2. \quad (\text{as } i^2 = -1) \end{aligned}$$

Hence,  $|\Psi|^2 = \Psi^* \Psi$  is always a positive real quantity.

## What does the amplitude of de Broglie wave represent?

The **probability** of finding the particle at any point depends on the **amplitude** of its de Broglie wave at that point.

In classical physics,

$$\text{Intensity of any wave} \propto |\text{amplitude}|^2$$

In quantum physics,

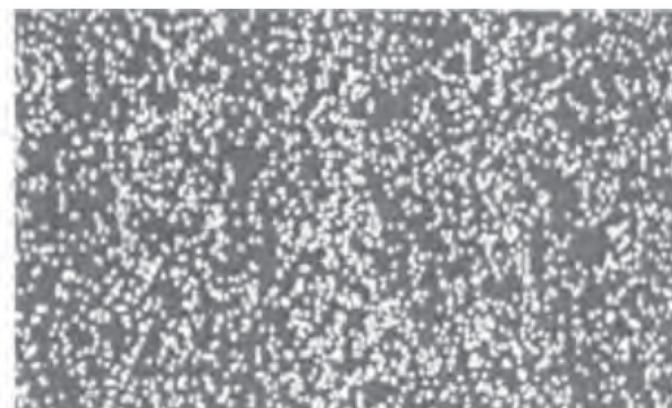
$$\text{Probability to observe particles} \propto |\text{de Broglie wave amplitude}|^2$$

## Regions of High & Low Probability

Consider the characteristic interference fringes produced by the electrons in a double-slit type experiment. The path of each electron is guided by its de Broglie wave towards the regions of high probability. This statistical effect is apparent ONLY when a large number of electrons has been detected.



(a) 100 electrons.



(b) 3000 electrons



(c) 70,000 electrons

## Interpretation of $|\Psi|^2$ by Max born :

- ❖ The square of the absolute value of the wave function  $\Psi$  is known at the **probability density**.
- ❖ The **probability** of experimentally finding the body described by the wave function  $\Psi(x, y, z, t) \propto |\Psi|^2$ .
- ❖ A large value of  $|\Psi|^2$  means the strong possibility of the body's presence and vice versa.
- ❖ As long as  $|\Psi|^2$  is not 0 somewhere, there is a definite chance of detecting the body.

**“∴ Matter waves are waves of probability”**

The interpretation of  $|\psi(x)|^2$  helps us to understand the **continuity condition of  $\psi(x)$** :

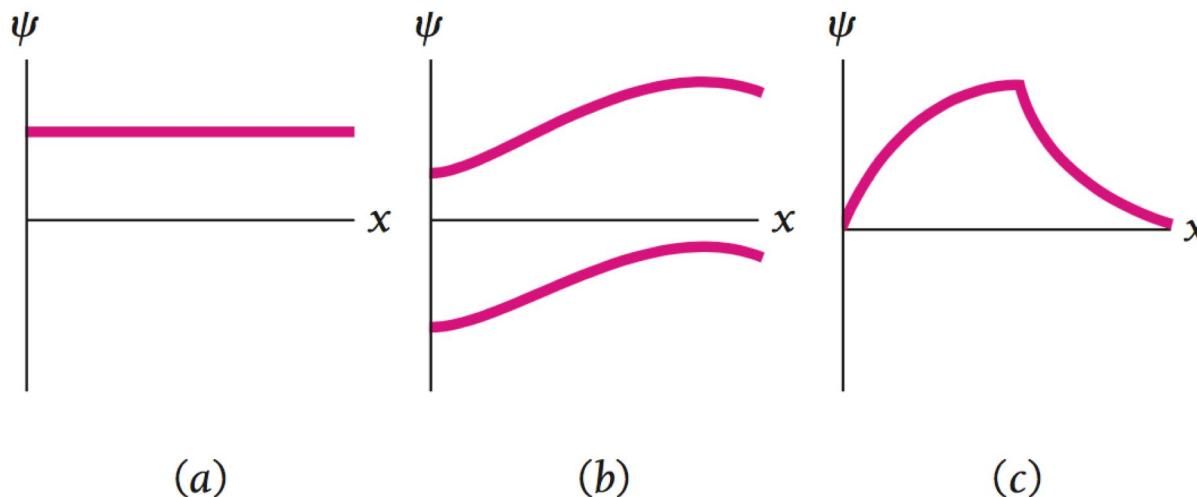
- We must not allow the probability to change discontinuously.
- The probability to locate the particle varies smoothly and continuously.

## Condition for a Well-Behaved Wave Functions

1.  $\Psi$  must be continuous and single-valued(since P can have only one value at a particular place and time) 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  $\Psi$  must go to 0 as  $x \rightarrow \pm\infty$ ,  $y \rightarrow \pm\infty$ ,  $z \rightarrow \pm\infty$  in order that  $\int_{-\infty}^{\infty} |\Psi|^2 dV$  over all space be a finite constant.

## Problem

Which of the wave functions cannot have physical significance in the interval shown? Why not?

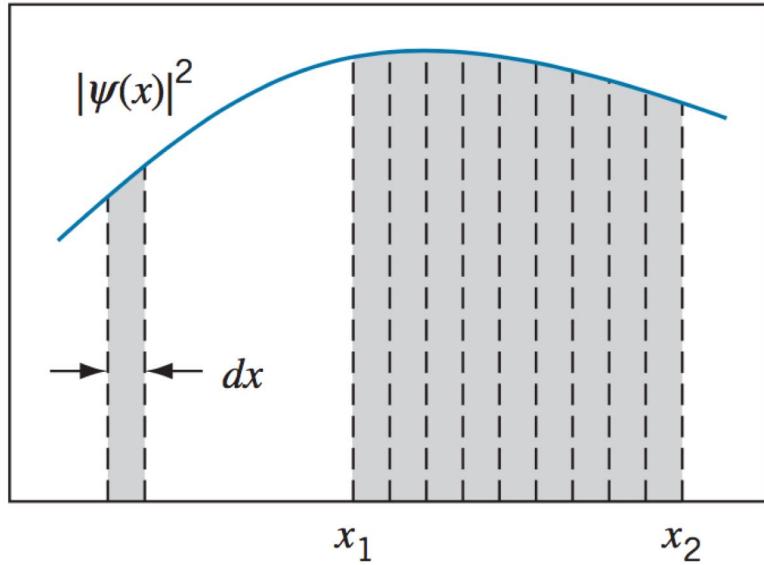


Wave functions without physical significance are:

- (i) Fig (b). As the function  $\psi$  is double valued
- (ii) Fig (c). As the derivative  $\frac{\partial\psi}{\partial x}$  is discontinuous.

## Normalization

Suppose the interval between two points  $x_1$  and  $x_2$  is divided into a series of infinitesimal intervals of width  $dx$ .



The probability to find the particle in a small region of width  $dx$  = area of the strip under  $|\psi(x)|^2$  curve

The total probability to find the particle between  $x_1$  and  $x_2$  = sum of the area of the strips.

**Probability** of finding it between [ ]

$x_1$  and  $x_2$

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We require a 100% probability of finding the particle somewhere along the x-axis, thus

$$\int_{-\infty}^{\infty} |\Psi(x)|^2 dx = 1 \dots \dots 2 \quad \text{“Normalization condition”}$$

- A wave function in which the arbitrary multiplicative constant is determined according to equation 2, is said to be normalized; else it is unnormalized.
- Only a properly normalized wave function may be used for physically meaningful calculations.
- If it is done correctly, equation 1 will always yield a probability that lies between 0 and 1.

## Expectation value

In quantum mechanics, due to the inherent uncertainty, we can only calculate the probability associated with any coordinate. Suppose we wish to find the average location  $\bar{x}$  of a number of identical particles distributed along the  $x$  axis, in such a way that there are  $N_1$  particles at  $x_1$ ,  $N_2$  particles at  $x_2$  and so on?

The **average position** in this case is the same as the **center of mass of the distribution**. So,  $\bar{x} = \frac{N_1x_1 + N_2x_2 + \dots}{N_1 + N_2 + \dots} = \frac{\sum N_i x_i}{\sum N_i}$

For a **single particle**, we must replace the number  $N_i$  of particles at  $x_i$  by the probability  $P_i$ .

The probability  $P_i$  that the particle be found in an interval  $dx$  at  $x_i$ :

$$P_i = |\Psi_i|^2 dx$$

Making the above substitution and changing summation to integration,

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} x |\Psi|^2 dx}{\int_{-\infty}^{\infty} |\Psi|^2 dx}$$

If  $\Psi$  is a normalized wave function,  $\int_{-\infty}^{\infty} |\Psi|^2 dx = 1$

“Expectation value  
For position”

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$$\langle x \rangle = \int_{-\infty}^{\infty} x |\Psi|^2 dx$$

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By analogy, the expectation (or average) value of any function  $G(x)$  of a particle described by a wave function  $\Psi$  is :

$$\langle G(x) \rangle = \int_{-\infty}^{\infty} G(x) |\Psi|^2 dx$$

**Note:**

- In classical mechanics, solving a problem gives us the entire future course of the body's motion. In quantum mechanics, the **future** course of the **particle's motion** is a matter of **probabilities** instead of certainties.
- We can't find the expectation value for momentum  $\langle p \rangle$  and energy  $\langle E \rangle$  with the procedure above, as according to uncertainty principle we cannot define such functions as  $p(x)$  and  $E$ .

## Problem

A particle limited to the x-axis has the wavefunction  $\Psi = ax$  between  $x = 0$  and  $x = 1$ ;  $\Psi = 0$  elsewhere. (a) Find the probability that the Particle can be found between  $x = 0.45$  and  $x = 0.55$ . (b) Find the expectation value  $\langle x \rangle$  of the particle's position.

## **Solution:**

$$\begin{aligned}\text{(a) The probability is } & \int_{x_1}^{x_2} |\Psi|^2 dx = a^2 \int_{0.45}^{0.55} x^2 dx \\ &= a^2 \left[ \frac{x^3}{3} \right] = 0.0251a^2\end{aligned}$$

(b) The expectation value is

$$\langle x \rangle = \int_0^1 x |\Psi|^2 dx = a^2 \int_0^1 x^3 dx$$

$$= a^2 \frac{x^4}{4} = \frac{a^2}{4}$$

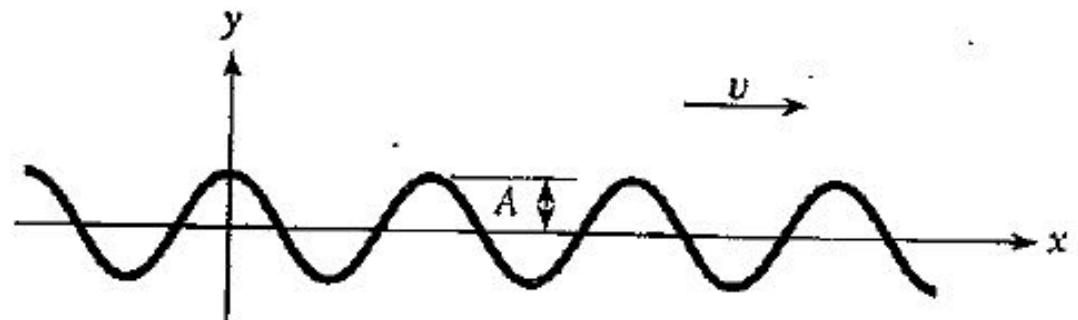
# The Schrödinger Equation

*A basic physical principle that cannot be derived from anything else*

# The classical wave equation

The wave equation :

$$\frac{\partial^2 y}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 y}{\partial t^2}$$



which governs a wave whose variable is  $y$  that propagates in the  $x$  direction with the speed  $v$ .

Can this wave equation be used for **matter waves**?

# The wave equation for matter waves: The Schrödinger equation

- For **matter waves**, we use a wave equation which is known as *Schrödinger equation*.
- *Schrödinger* equation (SE) is a fundamental equation of quantum mechanics, formulated by Erwin Schrodinger in 1926 that governs how matter waves evolve in space and time.
- *Schrödinger* equation is analogous to the **second law of motion of Newtonian mechanics** and describes the motion and behaviour of a system on atomic and subatomic levels using a variable  $\psi$ .



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- **Erwin Schrödinger** (1887 – 1961)
- American physicist
- Best known as one of the creators of quantum mechanics

Before discussing *Schrödinger* equation, let us start with a **review of the wave equation,**

which governs a wave whose **variable is  $y$**  that propagates in the  $x$  direction with the speed  $v$ .

In the case of a wave in a stretched string → y is displacement of the string from the x-axis.

In the case of sound wave → y is the pressure difference

In the case of light wave → y is either the electric or the magnetic field magnitude.

Wave equation 1 can be derived from the second law of motion for mechanical waves and from Maxwell's equations for electromagnetic waves.

Let us consider the wave equation of a free particle that is not under the influence of any force and is pursuing a straight path at constant speed.

This wave is described by the general solution of eq. 1 for undamped (constant A), monochromatic (constant  $\omega$ ) harmonic wave in x-direction:

here  $y$  is complex quantity with both real and imaginary parts, because  $e^{-i\theta} = \cos \theta - i \sin \theta$ .

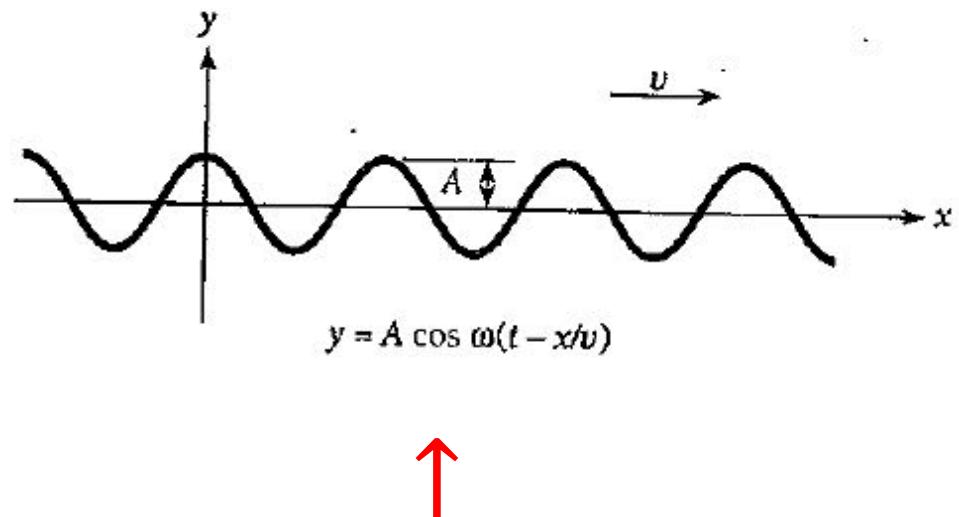
Now, equation 2 can be written in form

**Only real part has significance in the case of waves in stretched string.**

So, the solution is:

$$y = A \cos \omega(t - x/v).$$

There  $y$  represents the displacement of the string from its normal position.



Waves in xy-plane travelling in the x-direction along a stretched string lying on the x-axis.

# The Schrödinger Equation (SE)

- Schrödinger Equation: Time-dependent form
- Schrödinger Equation : Steady-state form

# Schrödinger Equation: Time-dependent form

- In quantum mechanics the wave function  $\psi$  corresponds to the wave variable.
  - $\psi$  is not itself a measurable quantity (unlike  $y$  of wave motion in general) and may be complex.
  - So, we assume that  $\psi$  for a moving free particle in x-direction is specified by

Replacing  $\omega = 2\pi\nu$  and  $v = \lambda\nu$ , we have

Replacing  $\nu$  and  $\lambda$  in terms of total energy E and momentum p of the particle, as

$$E = h\nu = 2\pi\hbar\nu \Rightarrow \nu = E/2\pi\hbar$$

$$\text{and } \lambda = \frac{h}{p} \Rightarrow \lambda = \frac{2\pi\hbar}{p}$$

We have,

Eq. 6 describes the wave equivalent of an unrestricted particle of total energy  $E$  and momentum  $p$  moving in  $x$ -direction (same as eq. 2 for a stretched string).

Equation 6 is correct only for freely moving particles.

What about, if particle is subject to certain restrictions/boundaries?

For example: *An electron bound to an atom by the electric field of its nucleus.*

We must obtain the fundamental differential equation for  $\psi$  which we can then solve for  $\psi$  in a specific situation.



## Schrödinger Equation

The Schrödinger equation can be arrived at in various ways , but it **can not be derived** from existing physical principles. It represents something new.

## The properties that the Schrodinger equation must have:

- We are seeking an equation that describes non-relativistic particles, so we take  $K = \frac{1}{2}mv^2 = \frac{p^2}{2m}$
- It must conserve energy. We therefore take

$$\text{Kinetic energy}(K) + \text{potential energy } (U) = \text{Total energy } (E)$$

Note: E is not the relativistic total energy.

- The equation must be consistent with the de Broglie hypothesis. Thus the kinetic energy associated with the free-particle de Broglie wave is

$$K = \frac{\hbar^2 k^2}{2m}$$

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- The equation must be “well-behaved” in the mathematical sense.
- The solution must also be **linear**, so that the de Broglie waves have the important **superposition property** we expect for waves.

Now to get the wave equation for  $\psi$ , we start by differentiating eq. 6 for  $\psi$  twice w.r.t. x, which gives:

$$\frac{\partial^2 \psi}{\partial x^2} = -\frac{p^2}{\hbar^2} \psi$$

or  $p^2\psi = -\hbar^2 \frac{\partial^2\psi}{\partial x^2}$  ..... 7

Differentiation eq.6 once w.r.t  $t$  gives:

$$\frac{d\psi}{dt} = - \frac{iE}{\hbar} \psi$$

or  $E\psi = -\frac{\hbar}{i} \frac{d\psi}{dt}$  ..... 8

At  $v \ll c$ , the total energy  $E$  of a particle is the sum of its kinetic energy  $p^2/2m$  and its potential energy  $U(x,t)$ :

The function  $U$  represents the influence of the rest of the universe on the particle. Of course , only a small part of the universe interacts with the particle to any extent (In the case of the electron in a hydrogen atom, only the electric field of the nucleus must be taken into account).

In equation 9, multiplying both side with  $\psi$  gives

Now, we substitute for  $E\psi$  and  $p^2\psi$  from eq. 7 and 8, we get

$$-\frac{\hbar}{i} \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$$

..... 11

# Time-dependent Schrödinger equation in one dimension.

$$-\frac{\hbar}{i} \frac{d\psi}{dt} = -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U(x, y, z, t)\psi$$

Time-dependent Schrödinger equation (TDSE) in three dimensions.

### Note:

- Any restrictions that may be present on the particle's motion will affect  $U$ .
- Once  $U$  is known, SE may be solved for the wave function  $\psi$  of the particle, from which its probability density  $|\psi|^2$  may be determined for a specified  $x, y, z, t$ .

- Schrödinger Equation **can not be derived** from other basic principles of physics, It is **itself a basic principle**.
- The time dependent Schrödinger equation is one of the **postulates of quantum mechanics**.
- It has been shown to be consistent with all experiments.

The one-dimensional time-dependent *Schrödinger equation (TDSE)* for a particle of mass  $m$  moving along the  $x$  axis and interacting with its environment through a potential energy function  $U(x,t)$  is

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x, t)\psi = -\frac{\hbar}{i} \frac{d\psi}{dt}$$

## Hamiltonian operator ( $\hat{H}$ )

LHS of TDSE can be written as:

$$\begin{aligned} & -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U(x, t)\psi \\ &= \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x, t) \right] \psi \\ &= \hat{H}\psi \end{aligned}$$

where  $\hat{H}$  is called the **Hamiltonian operator** which is the differential operator that *represents the total energy of the particle*.

Thus, the shorthand for TDSE is:

$$\hat{H}\psi = i\hbar \frac{d\psi}{dt}$$

## Momentum operator( $\hat{p}$ )

Hamiltonian operator,  $\hat{H}$  can be written as,

$$\hat{H} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U \right] = \frac{\hat{p}_x^2}{2m} + \hat{U}$$

where the ***momentum operator*** is:  $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$

## Operators associated with various observable quantities

Quantity	Operator
Position, $x$	$x$
Linear momentum, $p$	$i\hbar \frac{\partial}{\partial x}$
Potential energy, $U(x)$	$U(x)$
Kinetic energy, $KE = \frac{p^2}{2m}$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
Total energy, $E$	$i\hbar \frac{\partial}{\partial t}$
Total energy (Hamiltonian form), $H$	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x)$

## Linearity and superposition

The Schrödinger's equation

- 1) has terms that contain  $\Psi$  and its derivatives
- 2) does not contain terms independent of  $\Psi$  or that involves higher powers of  $\Psi$  or its derivatives.

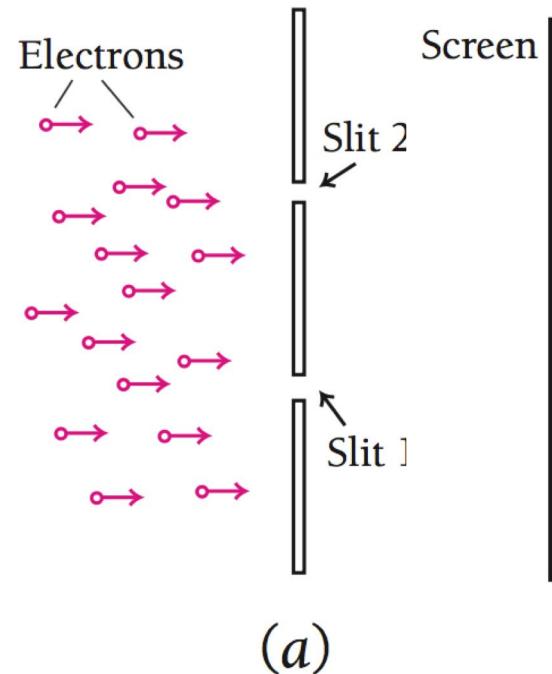
Thus, **Schrödinger equation is linear in the wave function  $\Psi$ .**

If  $\Psi_1$  and  $\Psi_2$  are two solutions of the equation, then

$$\Psi = a_1\Psi_1 + a_2\Psi_2 \quad (a_1, a_2 : \text{constants})$$

is also a solution. Thus the wave functions  $\Psi_1$  and  $\Psi_2$ , obey **superposition principle**. We can conclude that interference effects can occur for wave functions just as they can for light, sound, water and electromagnetic waves.

## Applying superposition principle to electron diffraction



Consider a pair of slits through which a parallel beam of monoenergetic electrons pass.

In this double-slit experiment, when both slits are open, **do wave functions add or the probability densities add to produce the resultant intensity?**

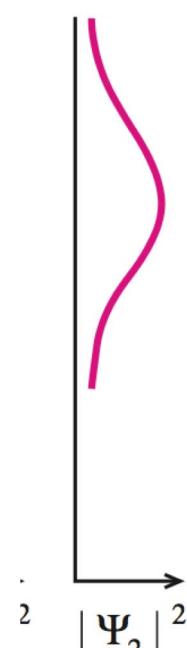
## The resultant electron intensities at the screen

**Only slit 1 open**



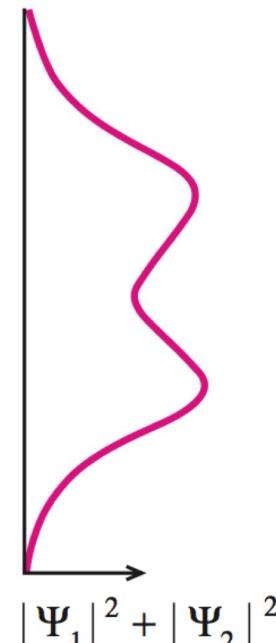
(b)

**Only slit 2 open**

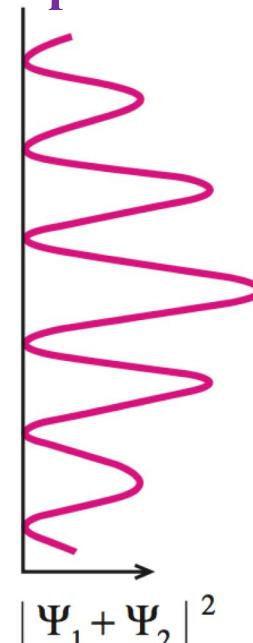


(c)

**Both slits 1 & 2 open**



(d)



(e)

Probability density  
 $P_1 = |\Psi_1|^2 = \Psi_1^* \Psi_1$   
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Probability density  
 $P_2 = |\Psi_2|^2 = \Psi_2^* \Psi_2$   
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**Which is the actual intensity--(d) or (e) ?**

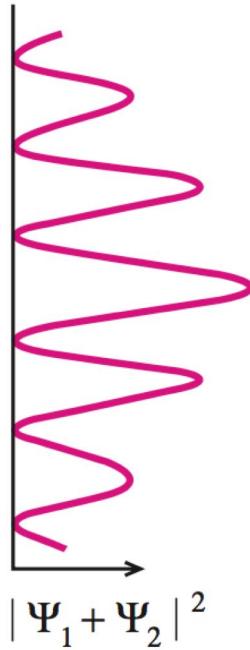
The diffraction pattern arises from the superposition  $\Psi$  of the wave functions  $\Psi_1$  and  $\Psi_2$  of the electrons that have passed through slits 1 and 2:

$$\Psi = \Psi_1 + \Psi_2$$

The probability density at the screen is therefore

$$\begin{aligned} P &= |\Psi|^2 = |\Psi_1 + \Psi_2|^2 \\ &= (\Psi_1^* + \Psi_2^*)(\Psi_1 + \Psi_2) \\ &= \Psi_1^*\Psi_1 + \Psi_2^*\Psi_2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \\ &= P_1 + P_2 + \Psi_1^*\Psi_2 + \Psi_2^*\Psi_1 \end{aligned}$$





(e)

This is the **actual intensity** at the screen when both the slits are open.

**The wave functions  $\Psi_1$  and  $\Psi_2$  add** to produce the intensity at the screen, **not the probability densities  $|\Psi_1|^2$  and  $|\Psi_2|^2$**

## Operators and Expectation values

We can use the operators to obtain expectation values for momentum p and energy E.

The expectation value for p:  $\langle p \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{p} \Psi \, dx$

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

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

The expectation value for E:

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

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

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

Every observable quantity  $G$  characteristic of a physical system may be represented by a suitable quantum-mechanical operator  $\hat{G}$ . To obtain this operator, we express  $G$  in terms of  $x$  and  $p$  and then replace  $p$  by  $\frac{\hbar}{i} \frac{\partial}{\partial x}$ . If the wave function  $\Psi$  of the system is known,

The expectation value of an operator :  $\langle G(x, p) \rangle = \int_{-\infty}^{\infty} \Psi^* \hat{G} \Psi \, dx$

## Schrödinger Equation: Steady-state form

- In many situations **the potential energy of a particle does not depend on time explicitly.**
- 
- The forces that act on it, and hence  $U$ , vary with the position of the particle only.
- In these situations, Schrödinger's equation may be simplified by removing all reference to  $t$  and then it is referred as **Steady-state form**.

Let us start discussing from one-dimensional wave function of an unrestricted particle:

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

$$\Psi = A e^{-(\frac{i}{\hbar}E)t} e^{+(\frac{i}{\hbar}p)x}$$

Evidently,  $\Psi$  is the product of a time-dependent function  $e^{-(\frac{i}{\hbar}E)t}$  and a position dependent function  $\psi$ .

- As it happens, the time variations of all wave functions of particles acted on by forces independent of time have the same form as that of an unrestricted particle.
- Substituting the of Eq. 1 into the time-dependent form of Schrödinger's equation, we have:

$$E\psi e^{-(\frac{i}{\hbar}E)t} = -\frac{\hbar^2}{2m} e^{-(\frac{i}{\hbar}E)t} \frac{\partial^2 \psi}{\partial x^2} + U\psi e^{-(\frac{i}{\hbar}E)t}$$

or       $E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + U\psi$

or  $\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$

Steady-state Schrödinger equation in one dimension

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{2m}{\hbar^2} (E - U) \psi = 0$$

In three dimensions:

An important property of Schrödinger's steady-state equation:

If it has one or more solutions for a given system, each of these wave functions corresponds to a specific value of the energy  $E$ .

- In wave mechanics: Energy quantization appears as a natural element of the theory.
- In the physical world: Energy quantization is revealed as a universal phenomenon characteristic of *all* stable systems.

# Eigenvalue equation

The *Schrödinger Equation* is the form of an *Eigenvalue Equation*:

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

where  $\hat{H}$  is the *Hamiltonian operator*,

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

- $\psi$  is the wave function and is an *eigen function* of  $\hat{H}$
- $E$  is the total energy ( $T + U$ ) and an *eigenvalue* of  $\hat{H}$ .  $E$  is just a constant!

## A problem on Eigen values

An eigen function of the operator  $\frac{d^2}{dx^2}$  is  $\psi = e^{2x}$ . Find the corresponding eigenvalue.

Solution:

Eigenvalue Equation:  $\hat{H}\psi = E\psi$

Here,  $\hat{H} = \frac{d^2}{dx^2}$ , so

$$\begin{aligned}\hat{H}\psi &= \frac{d^2(e^{2x})}{dx^2} \\ &= \frac{d}{dx} \left[ \frac{d}{dx^2}(e^{2x}) \right] \\ &= 4e^{2x}\end{aligned}$$

But,  $\psi = e^{2x}$ , so  $\hat{H}\psi = 4\psi$

Here, corresponding eigen value E is 4