

Foundation of Quantum Mechanics

Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

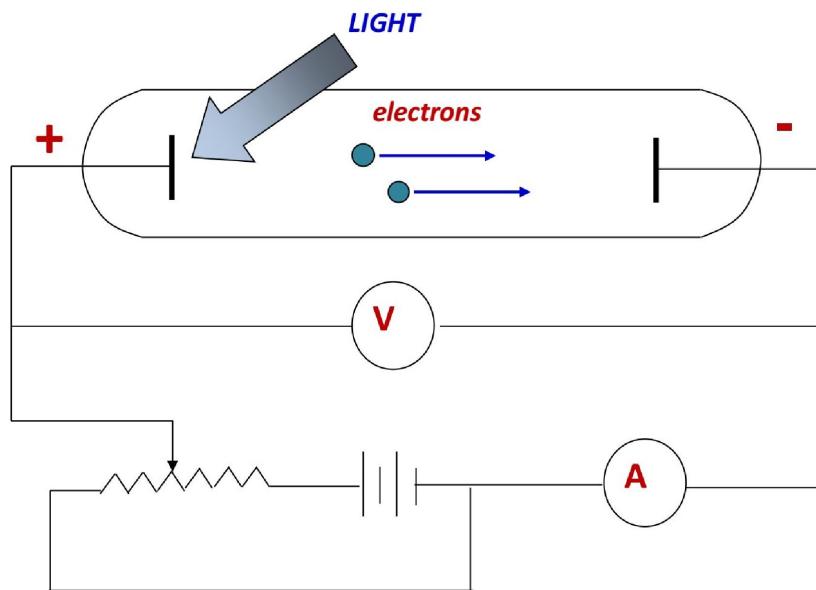
PHOTOELECTRIC EFFECT

In an evacuated vessel, if light of suitable frequency is allowed to fall on a clean metal surface, electrons are emitted from the metal surface.

This phenomenon, discovered by **HERTZ** in 1887, is known as Photoelectric effect.

Usually a *radiation in the UV-region* produces the effect.

PHOTOELECTRIC EFFECT



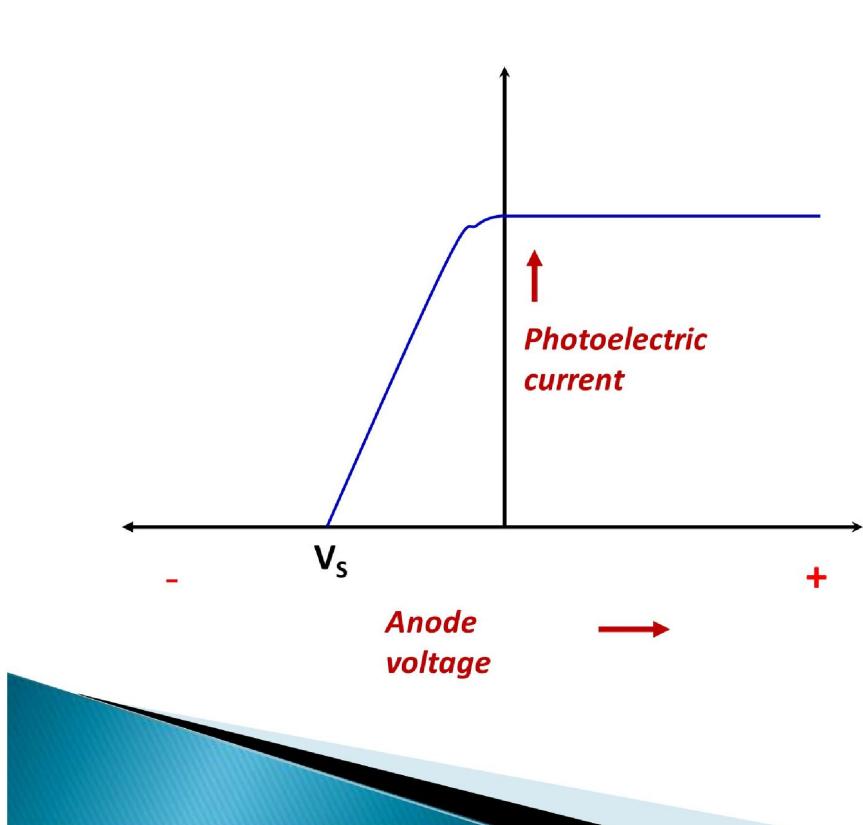
PHOTOELECTRIC EFFECT

Some of the photoelectron that emerges from this surface have enough energy to reach the cathode despite its negative polarity; they are responsible for the measured current.

The slower photoelectrons are repelled before they get to the cathode.

When the voltage is increased to a certain value, V_s , no more photoelectrons arrive at the cathode, the current dropping to zero. V_s is called the *stopping potential* for the particular frequency of the incident light.

PHOTOELECTRIC EFFECT



By measuring the V_s , maximum kinetic energy of the photoelectrons for incident radiation of a particular frequency $(K.E.)_{\max}$ of the photoelectrons may be estimated.

At the stopping potential, the initial kinetic energy of the electrons is equal to the potential energy, i.e. $\frac{1}{2}mv^2 = -eV_s$

PHOTOELECTRIC EFFECT

Experimental characteristics of the photoelectric effect

➤ Within the limits of experimental accuracy ($\sim 10^{-9}$ s), there is no time-lag between the incidence of light on the metal surface and the emission of photoelectrons.

➤ No electrons are ejected, regardless of the intensity of the radiation, unless the frequency of the radiation exceeds a threshold value characteristic of the metal. This limiting frequency is called the *threshold frequency* (v_0) of the metal.

PHOTOELECTRIC EFFECT

Experimental characteristics of the photoelectric effect

- No electrons are ejected, regardless of the intensity of the radiation, unless the frequency of the radiation exceeds a threshold value characteristic of the metal. This limiting frequency is called the *threshold frequency*(v_0) of the metal.
- A bright light (i.e. more intense light) yields more photoelectrons than a dim one (i.e. light with lower intensity) of the same frequency, but the electron energies remain the same.

These observations strongly suggest that ejection of electrons occurs when it is involved in a collision with a particle-like projectile that carries enough energy to eject the electron from the metal surface.

PHOTOELECTRIC EFFECT

In the year 1905, **Einstein** realized that photoelectric effect could be understood if the energy in light is not spread over wave-fronts but is concentrated in small packets or photons of energy hv , where, v is the frequency of incident radiation.

Then the conservation of energy requires that the kinetic energy of the ejected electron should be,

$$\frac{1}{2}mv^2 = hv - \phi$$

ϕ is a characteristic of the metal called its *work function*, the energy required to remove an electron from the metal surface to infinity.

PHOTOELECTRIC EFFECT

$$\frac{1}{2}mv^2 = hv - \phi$$

Photo-ejection occurs if $hv > \phi$

Photo-ejection cannot occur if $hv < \phi$

Work function, ϕ , is the minimum energy for an electron to escape from a particular metal surface, and is related to v_o by the formula,

$$\Phi = h v_o$$

The greater the ϕ of a metal, the more the energy is needed for an electron to leave the metal surface and higher v_o for photoelectric emission to occur

PHOTOELECTRIC EFFECT

Metal	Φ (in electron volt)
Cs	1.9
K	2.2
Na	2.3
Li	2.5
Ca	3.2
Cu	4.7
Ag	4.7
Pt	6.4

$$1 \text{ coulomb} \times 1 \text{ volt} = 1 \text{ Joule}$$

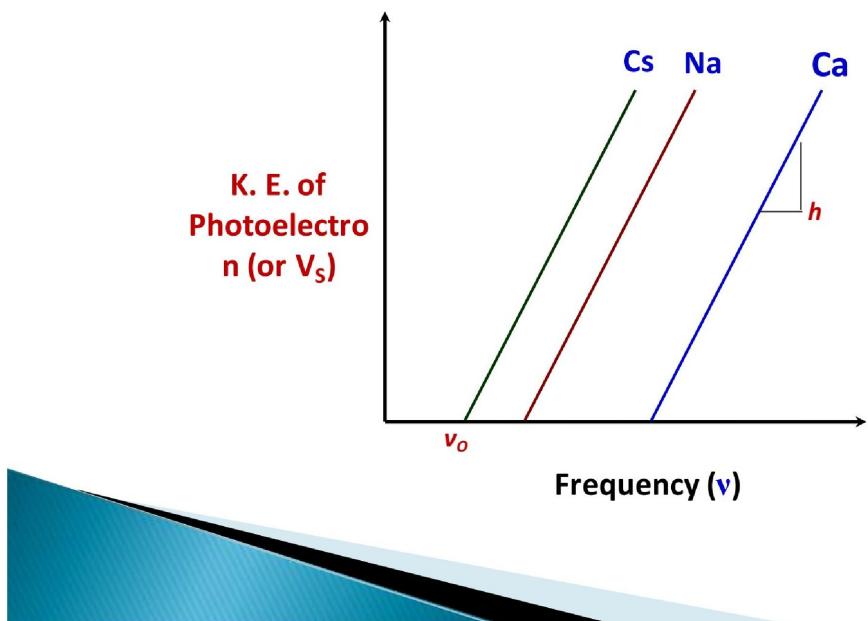
$$1 \text{ eV} = (1.602 \times 10^{-19} \text{ coulomb}) \times (1 \text{ volt}) \\ = 1.602 \times 10^{-19} \text{ J}$$

To pull an electron from a metal surface generally takes about half as much energy as that needed to pull out an electron from a free atom of the metal in gaseous phase.

For instance, the ionization energy of cesium is 3.9 eV compared with its work function of 1.9 eV.

PHOTOELECTRIC EFFECT

$$\begin{aligned} & \frac{1}{2}mv^2 = h\nu - \phi \\ \text{or, } & \frac{1}{2}mv^2 = h\nu - h\nu_0 \\ \text{or, } & -eV_s = h\nu - h\nu_0 \end{aligned}$$



Using the known value of "e", *Einstein* obtained a value of "h" in close agreement with Planck's value deduced from the blackbody radiation formula.

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Dr. Subhabrata Banerjee
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Department of Chemistry
Ramakrishna Mission V. C. College
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PHOTOELECTRIC EFFECT

$$\begin{aligned} \text{or, } & \frac{1}{2}mv^2 = hv - \phi \\ \text{or, } & \frac{1}{2}mv^2 = hv - hv_0 \\ & -eV_s = hv - hv_0 \end{aligned}$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$c = \text{velocity of light} = 3 \times 10^8 \text{ m.s}^{-1}$$

$$h = 6.626 \times 10^{-27} \text{ erg.s}$$

$$c = \text{velocity of light} = 3 \times 10^{10} \text{ cm.s}^{-1}$$

$$\begin{aligned} 1 \text{ eV} &= (1.602 \times 10^{-19} \text{ coulomb}) \times (1 \text{ volt}) \\ &= 1.602 \times 10^{-19} \text{ J} \end{aligned}$$

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PHOTOELECTRIC EFFECT

Numerical Problem – 1: The work function for sodium metal is 1.82 eV. Calculate the threshold frequency for sodium.
[C.U. 2002]

$$\begin{aligned} \text{Work function, } \phi &= 1.82 \text{ eV} \\ &= (1.82 \times 1.602 \times 10^{-19}) \text{ J} \\ &= 2.92 \times 10^{-19} \text{ J} \\ \text{We know, } \Phi &= h v_0 \\ \text{or, } v_0 &= \phi/h \\ &= (2.92 \times 10^{-19} \text{ J}) / (6.626 \times 10^{-34} \text{ Js}) \\ &= 4.40 \times 10^{14} \text{ s}^{-1} \\ &= 4.40 \times 10^{14} \text{ Hz} \end{aligned}$$

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PHOTOELECTRIC EFFECT

Numerical Problem – 2: When lithium is irradiated with light, the kinetic energy of the ejected electrons is $2.935 \times 10^{-19} \text{ J}$ for $\lambda = 300 \text{ nm}$ and $1.280 \times 10^{-19} \text{ J}$ for $\lambda = 400 \text{ nm}$. Calculate the Planck constant. [C.U. 2004]

$$\frac{1}{2}mv^2 = hv - hv_0$$

or, $\frac{1}{2}mv^2 = h(c/\lambda) - h(c/\lambda_0)$

For, for $\lambda = 300 \text{ nm}$ $2.935 \times 10^{-19} = \frac{hc}{300 \times 10^{-9}} - \frac{hc}{\lambda_0}$ (1)

For, for $\lambda = 400 \text{ nm}$ $1.280 \times 10^{-19} = \frac{hc}{400 \times 10^{-9}} - \frac{hc}{\lambda_0}$ (2)

Eqn. (1) – eqn. (2) $1.655 \times 10^{-19} = \frac{hc}{10^{-9}} \left[\frac{1}{300} - \frac{1}{400} \right]$

or, $1.655 \times 10^{-19} = \frac{(h)(3 \times 10^8)}{10^{-9}} \left[\frac{1}{300} - \frac{1}{400} \right]$

or, $h = 6.62 \times 10^{-34} \text{ Js}$

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PHOTOELECTRIC EFFECT

Numerical Problem – 3: When lithium is irradiated with light, the kinetic energy of the ejected electrons is $2.935 \times 10^{-19} \text{ J}$ for $\lambda = 300 \text{ nm}$ and $1.280 \times 10^{-19} \text{ J}$ for $\lambda = 400 \text{ nm}$. Calculate (i) the threshold frequency; (ii) the work function of lithium.

$$\frac{1}{2}mv^2 = hv - hv_0 = hv - \phi$$

For, for $\lambda = 300 \text{ nm}$ $2.935 \times 10^{-19} = \frac{hc}{300 \times 10^{-9}} - \frac{hc}{\lambda_0}$ (1)

Substituting this value in equation – (i), $2.935 \times 10^{-19} = \frac{hc}{300 \times 10^{-9}} - \frac{hc}{\lambda_0}$

or, $\frac{c}{\lambda_0} = v_o = 5.564 \times 10^{14} \text{ Hz}$

Work function, $h\nu_o = (6.62 \times 10^{-34}) (5.564 \times 10^{14}) = 3.687 \times 10^{-19} \text{ J}$

or, $\varphi = 3.687 \times 10^{-19} \text{ J}$

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PHOTOELECTRIC EFFECT

Numerical Problem – 4: Cs has a work function of 2 eV. Find: (a) its threshold wavelength; (b) the maximum energy of the liberated electron when the metal is irradiated with light of $\lambda = 4.5 \times 10^{-7}$ m; (c) the stopping potential [Given: 1 eV = 1.609×10^{-19} J].

$$\begin{aligned}\text{Work function, } \phi &= 2.00 \text{ eV} = (2.00 \times 1.609 \times 10^{-19}) \text{ J} \\ \text{or, } \phi &= 3.204 \times 10^{-19} \text{ J} = h v_0 = hc/\lambda_0 \\ \text{or, } 3.204 \times 10^{-19} &= [(6.626 \times 10^{-34})(3 \times 10^8)] / \lambda_0 \\ \text{or, } \lambda_0 &= 6.204 \times 10^{-7} \text{ m}\end{aligned}$$

Maximum energy of the liberated electron ,

$$\begin{aligned}\frac{1}{2}mv^2 &= hv - \phi \\ \text{or, } (\text{K.E.})_{\max} &= hc/\lambda - \phi \\ &= \{(6.626 \times 10^{-34})(3 \times 10^8) / 4.5 \times 10^{-7}\} - 3.204 \times 10^{-19} \\ \text{or, } (\text{K.E.})_{\max} &= 1.21 \times 10^{-19} \text{ J} = 0.755 \text{ eV}\end{aligned}$$

Stopping potential, V_s

$$\begin{aligned}\text{We know, } \frac{1}{2}mv^2 &= -eV_s = 0.755 \text{ electron-volt} = (1 \text{ e}) \times (0.755 \text{ volt}) \\ \text{So, } V_s &= 0.755 \text{ volt}\end{aligned}$$

PHOTOELECTRIC EFFECT

For the photoelectric effect in sodium metal, the following results were obtained:

$$\begin{array}{lll}10^{12} (\text{K.E.})_{\max} / \text{erg} : & 3.41 & 1.95 \\ \lambda / \text{\AA} : & 3125 & 4047\end{array}$$

where, $(\text{K.E.})_{\max}$ is the maximum kinetic energy of emitted electrons and λ is the wavelength of the incident radiation. Calculate Planck's constant and the work function for sodium. **[C.U. 2016]**

PHOTOELECTRIC EFFECT

Photoelectric effect gives strong evidence in favour of particle nature of light. Account for the statement.

[C.U. 2015]

Given that the work function of chromium is 4.40 eV. Calculate the kinetic energy of electrons emitted from a chromium surface that is irradiated with ultraviolet radiation of wavelength 200 nm.

[C.U. 2014]

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PHOTOELECTRIC EFFECT

Light of wavelength 552 nm or greater will not eject photoelectrons from a potassium surface. What is the work function (in eV) of potassium.

[C.U. 2012]

How can you use kinetic energy of photoelectron versus frequency plot in photoelectric experiments to distinguish between two metals.

[C.U. 2007]

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PHOTOELECTRIC EFFECT

What is photoelectric effect? How can the important features be explained?

[C.U. 2001]

Indicate and explain the salient features of the Photoelectric effect.

[C.U. 2005, 2003]

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Foundation of Quantum Mechanics

(Part - 4)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

COMPTON EFFECT

(*A confirmation of Photon model of light*)

According to *the quantum theory of light*, photon behaves like particle except for their mass.

Can we consider a collision between a photon and an electron as if both were billiard balls?

Arthur H. Compton (1923) provided the most conclusive confirmation of the particle aspect of radiation

COMPTON EFFECT

An X-ray photon strikes an electron which was initially at rest

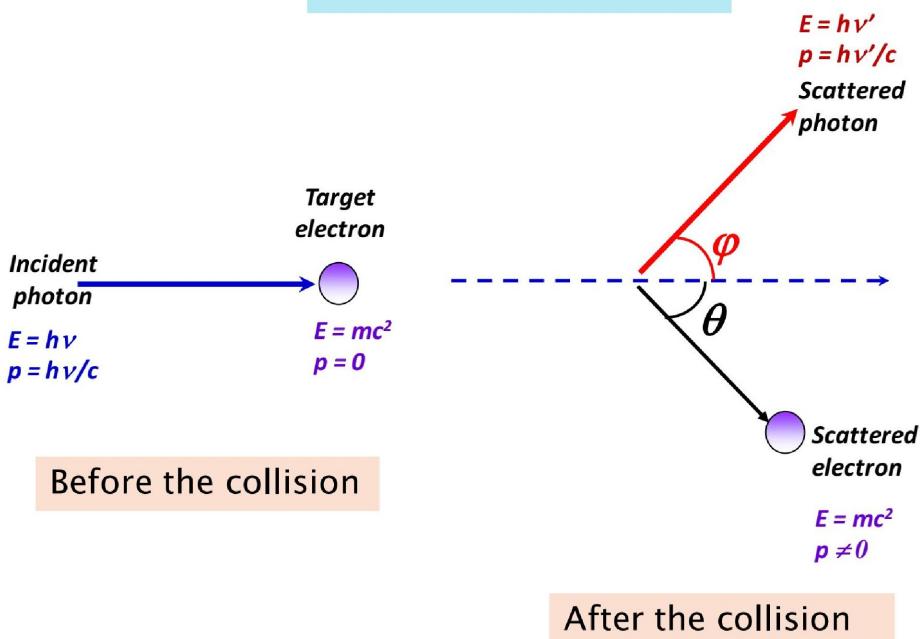
The electron begins to move making an angle with respect to the original direction of light, say, θ

The light is scattered through an angle, say, ϕ , with respect to the original direction of light

The wavelength of scattered radiation is longer than that of the incident radiation

The change in the wavelength of light is independent of θ but dependent on ϕ

COMPTON EFFECT



Arthur H. Compton (1923) provided the most conclusive confirmation of the particle aspect of radiation

COMPTON EFFECT

Consider this as a **collision** between a **photon** and an **electron** (like a collision between two billiard balls)

Energy and **momentum** is **conserved** in such a collision before and after the collision

Momentum is **conserved** in such a collision in each of the mutually perpendicular directions. (Here we will consider two directions – first, **along the original direction of photon**, and the second, **perpendicular to it** on the plane containing the photon and the electron)

loss in photon energy = gain in electron's energy

COMPTON EFFECT

Before the collision

Initial momentum of photon
(i.e. before collision) = $h\nu/c$
Initial momentum of electron
(i.e. before collision) = 0

After the collision

Momentum of the scattered
photon (i.e. after collision) =
 $h\nu'/c$
Momentum of electron after
collision = p

In the original photon direction

$$h\nu/c + 0 = (h\nu'/c) \cdot \cos \varphi + p \cdot \cos \theta$$

In the direction perpendicular to original photon direction

$$0 = (h\nu'/c) \cdot \sin \varphi - p \cdot \sin \theta$$



COMPTON EFFECT

Final result

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

The change in the wavelength of light is
independent of θ but dependent on φ

The equation gives the change in wavelength expected
for a photon that is scattered through an angle φ by a
particle of rest mass "m".



COMPTON EFFECT

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

$$\lambda' - \lambda = \Delta\lambda = \text{Compton Shift}$$

Change in wavelength i.e. $\Delta\lambda = (\lambda' - \lambda)$ is independent of the wavelength, λ of the incident photon.

Greatest wavelength change is possible, when,
 $\varphi = 180^\circ$, i.e. $\cos \varphi = -1$

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi) = \frac{h}{mc} (1 + 1) = 2 \frac{h}{mc} = 2\lambda_c$$

COMPTON EFFECT

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

$$\frac{h}{m_e c} = \lambda_c = \text{Compton Wavelength}$$

$$\frac{h}{m_e c} \quad \text{Has the dimension of length}$$

Planck constant, $h = 6.626 \times 10^{-34} \text{ Js}$
Speed of light in vacuum, $c = 3 \times 10^8 \text{ m.s}^{-1}$
Mass of electron, $m_e = 9.11 \times 10^{-31} \text{ kg}$

For the electron,

$$\begin{aligned}\lambda_c &= 2.426 \times 10^{-12} \text{ m} \\ &= 2.426 \text{ pm}\end{aligned}$$

COMPTON EFFECT

Why electron? Any other particle?

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

$$(\lambda' - \lambda) \alpha \frac{1}{m}$$

As the mass becomes smaller and smaller, the change in wavelength becomes greater. Since, electron has the least mass, the maximum wavelength change in Compton effect is
 $2\lambda_c = 4.852 \text{ pm}$



COMPTON EFFECT

Why X-ray? Any other radiation?

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

Magnitude of change of the wavelength of light, i.e. $\Delta\lambda = (\lambda' - \lambda)$ is quite small. Since, if $\Delta\lambda$ is independent of λ , so, smaller the value of λ , greater will be the value of $\Delta\lambda/\lambda$.

This magnitude of $\Delta\lambda$ or less are readily observable only in X-rays
(the shift in wavelength for visible light is less than 0.01% of the initial wavelength, whereas for X-rays of $\lambda = 0.1 \text{ nm}$, it is several percent.)



COMPTON EFFECT

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

Arthur Holly Compton (1892 – 1962) received Nobel Prize in 1927.



COMPTON EFFECT

Numerical Problem – 1: X-rays of 10.0 pm are scattered from a target. (a) Find the wavelength of the X-rays scattered through 45°. (b) Find the maximum wavelength present in the scattered X-rays. (c) Find the maximum Kinetic energy of the recoil electrons.

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

or, $\lambda' = \lambda + \lambda_c (1 - \cos 45)$

or, $\lambda' = 10.7 \text{ pm}$



COMPTON EFFECT

Numerical Problem - 1: X-rays of 10.0 pm are scattered from a target. (a) Find the wavelength of the X-rays scattered through 45° . (b) Find the maximum wavelength present in the scattered X-rays. (c) Find the maximum Kinetic energy of the recoil electrons.

$\Delta\lambda = (\lambda' - \lambda)$ is maximum, when $\varphi = 180^\circ$

$$\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi)$$

or, $\lambda' - \lambda = \frac{h}{mc} (1 - \cos \varphi) = \lambda_c (1 - \cos 180^\circ) = \lambda_c \{1 - (-1)\} = 2\lambda_c = 4.9$

or, $\lambda = 10 + 4.9 = 14.9 \text{ pm}$



COMPTON EFFECT

Numerical Problem - 1: X-rays of 10.0 pm are scattered from a target. (a) Find the wavelength of the X-rays scattered through 45° . (b) Find the maximum wavelength present in the scattered X-rays. (c) Find the maximum Kinetic energy of the recoil electrons.

loss in photon energy = gain in electron's energy

$$(K.E.)_{\max} = h(v - v')$$

$$= hc \left(\frac{1}{\lambda} - \frac{1}{\lambda'} \right) = hc \left(\frac{1}{10 \times 10^{-12}} - \frac{1}{14.9 \times 10^{-12}} \right)$$

$$= 6.54 \times 10^{-15} \text{ J}$$

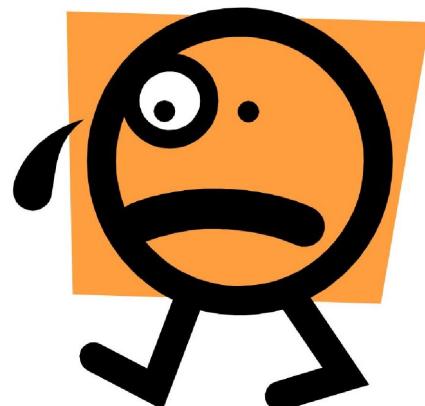


COMPTON EFFECT

What is Compton wavelength? State the significance of the Compton effect. [C.U. 2017]

Write down an expression for “Compton shift” and indicate therein the parameter “Compton wavelength”. What is the value of scattering angle for which the Compton shift becomes maximum? [C.U. 2015]

Explain what you understand by Compton effect. Determine the scattering angle for which the shift in wavelength would be maximum. ? [C.U. 2013]



Foundation of Quantum Mechanics

(Part – 5)

Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

What is Light?

Photoelectric Effect

Compton Effect

Black-body radiation

Confirmation of Photon model of light

Diffraction

Interference

Supports wave theory of light

What is Light?

We can think of light as having a dual character

Either theory by itself is only part of the story and can explain only certain effects

The “true nature” of light includes both wave and particle characters, even though there is nothing in everyday life to help us visualize that.



De Broglie's Hypothesis

If **light** can display **wave – particle duality**, then **matter** also might **display wave-like properties** under certain conditions

The de Broglie formula for wavelength

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

h = Planck constant

p = **mv** = momentum of the particle



De Broglie's Hypothesis

If we consider the *theory of relativity*

The de Broglie formula for wavelength

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

γ is the *relativistic factor*

$$\gamma = \frac{1}{\sqrt{1 - v^2/c^2}}$$

- When, $v \ll c$, $\gamma = 1$
- When velocity of particle (v) is comparable with velocity of light (c), $\gamma \neq 1$

De Broglie's Hypothesis

The de Broglie formula for wavelength

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

- Macroscopic bodies have high momenta, so their wavelengths are undetectably small and wave-like properties cannot be observed.
- Electromagnetic radiations in UV – vis region has long wavelengths, so momenta of individual photons are very small.

De Broglie's Hypothesis

The de Broglie formula for wavelength

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

The **wave** and **particle** aspects of moving bodies can never be observed at the same time.

De Broglie had no direct experimental evidence to support his conjecture

It was verified by experiments involving the *diffraction of electrons by crystals* by **Davisson** and **Germer** in 1927

In 1929, Louis de Broglie (1892 – 1987) received the Nobel Prize

De Broglie's Hypothesis

Both the wave and particle nature of radiations are associated with energy according to the following relations

Planck's:

$$E = h\nu = \frac{hc}{\lambda}$$

Einstein

$$E = mc^2$$

Combining,

$$\frac{hc}{\lambda} = mc^2$$

Or,

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

Or,

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

De Broglie's Hypothesis

Numerical problem – 1: Find the de Broglie wavelength of a **46 g** golf ball with a velocity of **30 m/s**

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} Js}{(0.046 kg)(30 ms^{-1})} = 4.8 \times 10^{-34} m$$

This wavelength of the golf ball is so small compared with its dimension that we should not expect to find any wave aspects in its behavior



De Broglie's Hypothesis

Numerical problem – 1: Find the de Broglie wavelength of an electron with a velocity of **10^7 m/s**

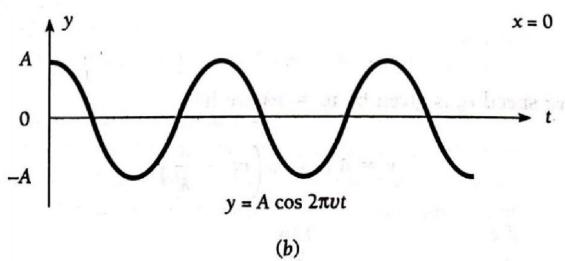
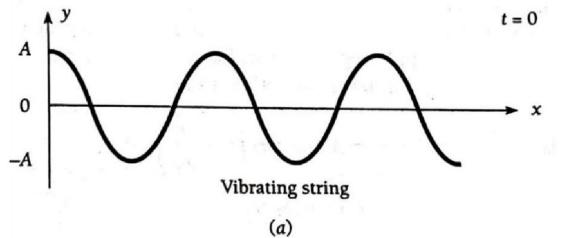
$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6.626 \times 10^{-34} Js}{(9.11 \times 10^{-31} kg)(10^7 ms^{-1})} = 7.3 \times 10^{-11} m$$

This dimension of atoms are comparable with this value (radius of the hydrogen atom is **5.3×10^{-11} m**)



Heisenberg's Uncertainty Principle

$$y = A \cos 2\pi\nu t$$



de Broglie waves cannot be represented by the formula resembling,

$$y = A \cdot \cos(\omega t - kx)$$

Heisenberg's Uncertainty Principle

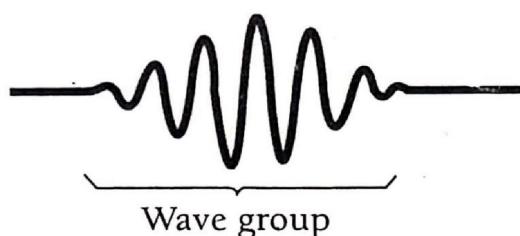


Figure 3.3 A wave group.

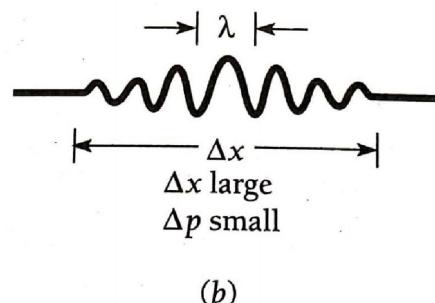
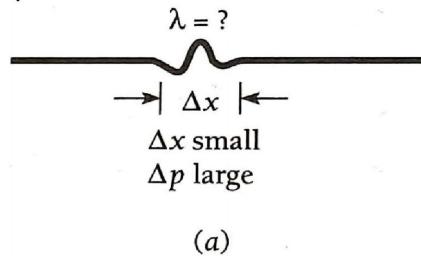
We expect the wave representation of a moving body to correspond to a **wave packet** or **wave group**, whose waves have **amplitudes** upon which the **probability of finding the body** depends

Heisenberg's Uncertainty Principle

To regard the moving particle as a wave group implies that there are fundamental limits to the accuracy with which we can measure position and momentum.

The narrower the wave group, the more precisely a particle's **position** can be **specified**. However, the **wavelength** of the waves in a narrow packet is **not well defined**

A wide wave group, has clearly **defined wavelength**. The momentum is a precise quantity. But **where is** the particle **located?**



Heisenberg's Uncertainty Principle

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

Uncertainty in momentum along X - coordinate = Δp_x

Uncertainty in position along X - coordinate = Δx .

$$\Delta x \Delta p_x \geq \frac{\hbar}{2}$$

$$\Delta y \Delta p_y \geq \frac{\hbar}{2}$$

$$\Delta z \Delta p_z \geq \frac{\hbar}{2}$$

Heisenberg's Uncertainty Principle

Heisenberg's uncertainty principle can be generalized to any pair of complementary or canonically conjugate, dynamic variables

Energy and time, form a pair of complementary variables

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

In the above equation, Δt is to be interpreted as the lifetime of the state whose energy is uncertain by ΔE

Heisenberg's Uncertainty Principle

Numerical problem – 2: What is the uncertainty in momentum and velocity (along X-coordinate) if we wish to locate an electron within an atom so that $\Delta x = 50 \text{ pm}$?

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

Or,
$$\Delta p_x = \frac{\hbar}{2\Delta x} = \frac{h}{(2\pi)2\Delta x} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 50 \times 10^{-12}} = 1.055 \times 10^{-24}$$

$$\Delta p_x = \Delta(mv_x) = m(\Delta v_x)$$

Or,
$$\Delta v_x = \frac{\Delta p_x}{m} = \frac{1.055 \times 10^{-24}}{9.11 \times 10^{-31}} = 1.16 \times 10^6 \text{ ms}^{-1}$$

This is a very large uncertainty in speed.

Heisenberg's Uncertainty Principle

Numerical problem - 3: Calculate the uncertainty in velocity of a cricket ball having mass 200g, if the uncertainty in its position is of the order of 5 pm.

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

$$\text{Or, } \Delta p_x = \frac{\hbar}{2\Delta x} = \frac{h}{(2\pi)2\Delta x} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 5 \times 10^{-12}} = 1.055 \times 10^{-24}$$

$$\Delta p_x = \Delta(mv_x) = m(\Delta v_x)$$

$$\text{Or, } \Delta v_x = \frac{\Delta p_x}{m} = \frac{1.055 \times 10^{-24}}{0.2} = 5.28 \times 10^{-23} \text{ ms}^{-1}$$

This uncertainty is negligible in comparison to the usual velocity of the cricket ball

Heisenberg's Uncertainty Principle

Numerical problem - 4: When an excited nucleus decays, it emits γ -rays. The life-time of an excited state of a nucleus is of the order of 10^{-12} s. What is the uncertainty in energy of the γ -ray produced?

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

$$\text{Or, } \Delta E = \frac{\hbar}{2\Delta t} = \frac{h}{(2\pi)2\Delta t} = \frac{6.626 \times 10^{-34}}{4 \times 3.14 \times 1 \times 10^{-12}} = 5.28 \times 10^{-23} \text{ J}$$

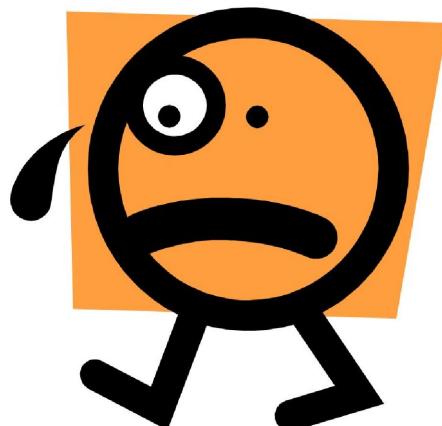
C. U. Questions

Show that a small change in the speed of a particle Δv causes a change in its de Broglie wavelength $|\Delta\lambda| = \frac{|\Delta v| \lambda_o}{v_o}$ where, v_o and λ_o are its initial speed and de Broglie wavelength respectively. (C.U. 2017)

Estimate the minimum uncertainty in the X-component of the velocity of an electron whose position is measured with an uncertainty 1.0×10^{-10} m. (C.U. 2016)

An electron is travelling at $1/4^{\text{th}}$ the speed of light. Calculate its de Broglie wavelength taking into account the relativistic change in mass. (C.U. 2014)

An excited atom gives up excess energy by emitting a photon of characteristic frequency. The average period that elapses between the excitation of the atom and the time it radiates is 1.0×10^{-8} s. Find the inherent uncertainty in the frequency of the photon. (C.U. 2014)



Foundation of Quantum Mechanics

(Part - 6)

Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

THE SCHRODINGER WAVE EQUATION

Schrodinger equation is a **fundamental postulate of quantum mechanics**, just as Newton's laws of motion are fundamental postulates of classical mechanics

We **cannot derive** the Schrodinger equation, but we can at least show that it is plausible and perhaps even trace Schrodinger's original line of thought.

The solutions to the Schrodinger equation are called "**wave functions**".

Wave functions give a complete description of any system

THE SCHRODINGER WAVE EQUATION

This equation can be
time-dependent
or
time-independent

For many applications in quantum mechanics to Chemistry, the simpler time-independent Schrodinger equation can be used.

Solutions to time-independent Schrodinger equation are called *Stationary State* wave functions

THE SCHRODINGER WAVE EQUATION

In 1926, the Austrian Physicist Erwin Schrodinger proposed an equation for finding the wave functions of any system.

For a one particle, one-dimensional system, the time-dependent Schrodinger equation is postulated to be,

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

$\hat{V}(x,t)$ is the potential energy operator of the particle at the point x;
“m” is mass of the particle

THE SCHRODINGER WAVE EQUATION

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + \hat{V}(x,t) \Psi(x,t) \quad (1)$$

Now let us restrict ourselves to the special case where the potential energy, V , is not a function of time (t), but depends only on position (x).

$\hat{V}(x,t)$ can be substituted by $\hat{V}(x)$

The time-dependent equation can be solved by the *method of separation of variables*

$$\Psi(x,t) = f(t) \cdot \psi(x) \quad (2)$$

THE SCHRODINGER WAVE EQUATION

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + \hat{V}(x,t) \Psi(x,t) \quad (1)$$

$$\Psi(x,t) = f(t) \cdot \psi(x) \quad (2)$$

Taking partial derivatives of equation – (2),

$$\frac{\partial \Psi(x,t)}{\partial t} = \frac{\partial f(t)}{\partial t} \psi(x) \quad (3)$$

$$\frac{\partial^2 \Psi(x,t)}{\partial x^2} = f(t) \frac{\partial^2 \psi(x)}{\partial x^2} \quad (4)$$

THE SCHRODINGER WAVE EQUATION

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + \hat{V}(x) \Psi(x,t) \quad (1)$$

$$\Psi(x,t) = f(t) \cdot \psi(x) \quad (2)$$

Equation – (1) becomes,

$$-\frac{\hbar}{i} \frac{\partial f(t)}{\partial t} \psi(x) = -\frac{\hbar^2}{2m} f(t) \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \Psi(x,t) \quad (3)$$

Dividing both sides by, $f(t) \cdot \psi(x)$,

$$-\frac{\hbar}{i} \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \quad (4a)$$

THE SCHRODINGER WAVE EQUATION

$$-\frac{\hbar}{i} \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \quad (4a)$$

Right hand side of the equation – (4a) is independent of t

Left hand side of the equation is independent of x

This is only possible when both sides are equal to a constant term, say, E

THE SCHRODINGER WAVE EQUATION

$$-\frac{\hbar}{i} \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \quad (4a)$$

Equating **left hand side** with E,

$$-\frac{\hbar}{i} \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = E \quad (5)$$

Equating **right hand side** with E,

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) = E \quad (6)$$



THE SCHRODINGER WAVE EQUATION

Equation – (5)

$$-\frac{\hbar}{i} \frac{1}{f(t)} \frac{\partial f(t)}{\partial t} = E \quad (5)$$

Or, $\frac{\partial f(t)}{f(t)} = -\frac{iE}{\hbar} \partial t$

Or, $\partial \ln f(t) = -\frac{iE}{\hbar} \partial t$

Or, $\ln f(t) = -\frac{iEt}{\hbar} + \text{const.}$

Or, $f(t) = A \exp\left(-\frac{iEt}{\hbar}\right)$



THE SCHRODINGER WAVE EQUATION

Equation - (6)

$$-\frac{\hbar^2}{2m} \frac{1}{\psi(x)} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \psi(x) = E \psi(x) \quad (6)$$

Or, $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \hat{V}(x) \psi(x) = E \psi(x)$

Or, $\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right] \psi(x) = E \psi(x)$

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

It is the *time-independent Schrodinger equation* for a single particle of mass "m" in one dimension

\hat{H} is called *Hamiltonian operator* or *total energy (kinetic plus potential) operator* of the system.

THE SCHRODINGER WAVE EQUATION

$$-\frac{\hbar}{i} \frac{\partial \Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + \hat{V}(x,t) \Psi(x,t) \quad (1)$$

$$\Psi(x,t) = f(t) \cdot \psi(x) \quad (2)$$

$$f(t) = A \exp\left(-\frac{iEt}{\hbar}\right)$$

So, equation - (2) becomes

$$\Psi(x,t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right)$$

The time-independent wave equation represents a **stationary state** i.e. a state in which the **expectation values** of properties do not change with time

THE SCHRODINGER WAVE EQUATION

Significance of E

E has the same dimension as V, so E has the **dimension of energy**. In fact, we postulate that E is the energy of the system

Ψ and Ψ^2

The wave function Ψ contains all information we can possibly know about the system it describes

Max Born, who postulated that, $|\Psi(x,t)|^2 dx$ gives the **probability** at time t of finding the particle in a region of the X-axis lying between x and x + dx. The function $|\Psi(x,t)|^2 dx$ is the probability density for finding the particle of various places on the X-axis

THE SCHRODINGER WAVE EQUATION

But what exactly is this "wave function", and what does it do for you once you've got it?

After all, a particle, by its nature, is localized at a point, whereas the wave function (as its name suggests) is spread out in space (it's a function of x, for any given time t).

How can such an object be said to describe the state of a particle?

The answer is provided by **Born's statistical interpretation of the wave function**

THE SCHRODINGER WAVE EQUATION

Although the wave function itself depends on time, t, the probability density is independent of t

The time-dependent Schrodinger equation is,

$$\Psi(x,t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right)$$

And

$$|\Psi(x,t)|^2 = \psi^* \psi = \psi^*(x) \exp\left(+\frac{iEt}{\hbar}\right) \psi(x) \exp\left(-\frac{iEt}{\hbar}\right) = |\psi(x)|^2$$

Foundation of Quantum Mechanics

(Part - 7)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

OPERATORS in QUANTUM MECHANICS

New Mathematical technique for the new Theory

An **operator** represents a mathematical instruction and it operates upon any function that occurs on the immediate right side of the concerned operators.

“**log**” means to change a function $f(x)$ into a new function, $g(x) = \log f(x)$

“**square root**” denotes the operation of taking the square root of the function that appears to the right side of it. $g(x) = \sqrt{f(x)}$.



OPERATORS in QUANTUM MECHANICS

Different types of operators

Differential & Integral Operators: $\frac{d}{dx}$, $\int(\)dx$, etc.

Arithmetic Operators : +, -, / (division), \times (multiplication), $\sqrt{\ }$ (square root), etc.

Trigonometric Operators: $\sin(\)$, $\cos(\)$, $\tan(\)$, $\sin^{-1}(\)$, etc.

Vector Operators: $\vec{\nabla} = \vec{i} \frac{\partial}{\partial x} + \vec{j} \frac{\partial}{\partial y} + \vec{k} \frac{\partial}{\partial z}$

$$\vec{\nabla}^2 = \vec{\nabla} \cdot \vec{\nabla} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$



OPERATORS in QUANTUM MECHANICS

Types of Operators

Linear Operator

An operator, \hat{P} , is said to be linear operator if the following two conditions are satisfied:

$$\hat{P}(\psi_i \pm \psi_j) = \hat{P}\psi_i \pm \hat{P}\psi_j$$

and

$$\hat{P}(c\psi_i) = c\hat{P}\psi_i$$



OPERATORS in QUANTUM MECHANICS

Linear Operator

$$\hat{P}(\psi_i \pm \psi_j) = \hat{P}\psi_i \pm \hat{P}\psi_j \quad \text{and} \quad \hat{P}(c\psi_i) = c\hat{P}\psi_i$$

Example - 1:SQRT

$$\sqrt{(\psi_i \pm \psi_j)} \neq \sqrt{\psi_i} \pm \sqrt{\psi_j}$$

$$\sqrt{c\psi} \neq c\sqrt{\psi}$$

So, SQRT is NOT a linear operator



OPERATORS in QUANTUM MECHANICS

Linear Operator

$$\hat{P}(\psi_i \pm \psi_j) = \hat{P}\psi_i \pm \hat{P}\psi_j \quad \text{and} \quad \hat{P}(c\psi_i) = c\hat{P}\psi_i$$

Example -2: $\frac{d}{dx}$

$$\frac{d}{dx}(\psi_i \pm \psi_j) = \frac{d\psi_i}{dx} \pm \frac{d\psi_j}{dx}$$

$$\frac{d}{dx}(c\psi) = c \frac{d\psi}{dx}$$

So, $\frac{d}{dx}$ is a linear operator



OPERATORS in QUANTUM MECHANICS

Linear Operator

$$\hat{P}(\psi_i \pm \psi_j) = \hat{P}\psi_i \pm \hat{P}\psi_j \quad \text{and} \quad \hat{P}(c\psi_i) = c\hat{P}\psi_i$$

Example -3: $\frac{d^2}{dx^2}$

$$\frac{d^2}{dx^2}(\psi_i \pm \psi_j) = \frac{d^2\psi_i}{dx^2} \pm \frac{d^2\psi_j}{dx^2}$$

$$\frac{d^2}{dx^2}(c\psi) = c \frac{d^2\psi}{dx^2}$$

So, $\frac{d^2}{dx^2}$ is a linear operator



OPERATORS in QUANTUM MECHANICS

Linear Operator

$$\hat{P}(\psi_i \pm \psi_j) = \hat{P}\psi_i \pm \hat{P}\psi_j \quad \text{and} \quad \hat{P}(c\psi_i) = c\hat{P}\psi_i$$

Example -4: $\sin(\psi)$

$$\sin(\psi_i \pm \psi_j) \neq \sin\psi_i \pm \sin\psi_j$$

$$\sin(c\psi) \neq c \sin\psi$$

So, $\sin(\psi)$ is NOT a linear operator

More example (DIY): exponential; log; $\tan^{-1}(\psi)$; $(\psi)^2$;

OPERATORS in QUANTUM MECHANICS

Types of Operators

Hermitian Operator (a special kind of linear operator)

An operator, \hat{P} is said to be Hermitian operator, if it satisfies the following relation for all well-behaved functions

$$\int_{config.\lim} \psi_i^* \hat{P} \psi_j d\tau = \int_{config.\lim} (\hat{P} \psi_i)^* \psi_j d\tau$$

For a special case, when, $\psi_i = \psi_j = \psi$,

$$\int_{config.\lim} \psi^* \hat{P} \psi d\tau = \int_{config.\lim} (\hat{P} \psi)^* \psi d\tau$$

OPERATORS in QUANTUM MECHANICS

Hermitian Operator

$$\int_{config.\lim} \psi_i^* \hat{P} \psi_j d\tau = \int_{config.\lim} (\hat{P} \psi_i)^* \psi_j d\tau$$

Using **braket** notation,

$$\langle \psi_i | \hat{P} \psi_j \rangle = \langle \hat{P} \psi_i | \psi_j \rangle$$

It implies that whatever occurs on the left hand side of the vertical line are **complex conjugate**, denoted by a superscript, *****.

OPERATORS in QUANTUM MECHANICS

Hermitian Operator

Example 1: $\frac{d}{dx}$

$$\begin{aligned} & \int_{config.\lim} \psi_i^* \frac{d}{dx} \psi_j dx \\ &= \psi_i^* \psi_j \Big|_{config.\lim} - \int_{config.\lim} \frac{d}{dx} \psi_i^* \psi_j dx \\ &= 0 - \int_{config.\lim} \frac{d}{dx} \psi_i^* \psi_j dx \\ &\neq \int_{config.\lim} \frac{d}{dx} \psi_i^* \psi_j dx \end{aligned}$$

(for a well-behaved function, ψ_i and ψ_j , $\psi_i^* \psi_j \Big|_{config.\lim} = 0$)

Hermitian Operator

Example 2: $i \frac{d}{dx}$

$$\begin{aligned}
 & \int_{config.\lim} \psi_i * \left(i \frac{d}{dx} \right) \psi_j dx \\
 &= i \psi_i * \psi_j \Big|_{config.\lim} - \int_{config.\lim} \left(i \frac{d}{dx} \right) \psi_i * \psi_j dx \\
 &= 0 - i \int_{config.\lim} \left(\frac{d}{dx} \right)^* \psi_i * \psi_j dx \\
 &= + \int_{config.\lim} (-i) \left(\frac{d}{dx} \right)^* \psi_i * \psi_j dx \\
 &= + \int_{config.\lim} (i) * \left(\frac{d}{dx} \right)^* \psi_i * \psi_j dx \\
 &= + \int_{config.\lim} \left(i \frac{d}{dx} \right)^* \psi_i * \psi_j dx
 \end{aligned}$$

(for a well-behaved function, ψ_i and ψ_j , $\psi_i * \psi_j \Big|_{config.\lim} = 0$)



Hermitian Operator

Example 3: $\frac{d^2}{dx^2}$

$$\begin{aligned}
 & \int_{config.\lim} \psi_i * \left(\frac{d^2}{dx^2} \right) \psi_j dx = \psi_i * \frac{d}{dx} \psi_j \Big|_{config.\lim} - \int_{config.\lim} \left(\frac{d}{dx} \right) \psi_i * \frac{d}{dx} \psi_j dx \\
 &= 0 - \int_{config.\lim} \left(\frac{d}{dx} \right) \psi_i * \frac{d}{dx} \psi_j dx \\
 &= - \int_{config.\lim} \left(\frac{d}{dx} \right) \psi_i * \frac{d}{dx} \psi_j dx \\
 &= - \left(\frac{d}{dx} \right) \psi_i * \psi_j \Big|_{config.\lim} + \int_{config.\lim} \left(\frac{d^2}{dx^2} \right) \psi_i * \psi_j dx \\
 &= 0 + \int_{config.\lim} \left(\frac{d^2}{dx^2} \right) \psi_i * \psi_j dx \\
 &= + \int_{config.\lim} \left(\frac{d}{dx} \right)^* \psi_i * \psi_j dx
 \end{aligned}$$

(for a well-behaved function, ψ_i and ψ_j , $\psi_i * \psi_j \Big|_{config.\lim} = 0$)



Hermitian Operator

Example 4: $\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

(Hint.

$\frac{\partial^2}{\partial x^2}$ is a Hermitian operator. Similarly, $\frac{\partial^2}{\partial y^2}$ and $\frac{\partial^2}{\partial z^2}$ are also

Hermitian operator. Linear combination of Hermitian operators is also a Hermitian).

Foundation of Quantum Mechanics

(Part - 8)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

COMMUTATION of two Operators

An operator, is said to commute with another operator if

$$\hat{P}\hat{Q}\psi = \hat{Q}\hat{P}\psi$$

We define the commutator of the two operators, and as

$$[\hat{P}, \hat{Q}] = \hat{P}\hat{Q}\psi - \hat{Q}\hat{P}\psi$$

If, $\hat{P}\hat{Q}\psi = \hat{Q}\hat{P}\psi$, then, $[\hat{P}, \hat{Q}] = 0$ and we say that, and commute



COMMUTATION of two Operators

Example – 1

$$\hat{P} = \frac{\partial}{\partial x} \quad \hat{Q} = \frac{\partial}{\partial y} \quad \psi = x^3y^2$$

$$\hat{P}\hat{Q}\psi = \frac{\partial}{\partial x} \frac{\partial}{\partial y} (x^3y^2) = \frac{\partial}{\partial x} (2x^3y) = 6x^2y$$

And,

$$\hat{Q}\hat{P}\psi = \frac{\partial}{\partial y} \frac{\partial}{\partial x} (x^3y^2) = \frac{\partial}{\partial y} (3x^2y^2) = 6x^2y$$

So, $[\hat{P}, \hat{Q}] = \hat{P}\hat{Q}\psi - \hat{Q}\hat{P}\psi = 0$



COMMUTATION of two Operators

Example - 2

$$\hat{P} = \frac{\partial}{\partial x}$$

$$\hat{Q} = x$$

$$\psi = Ax^n$$

$$\hat{P}\hat{Q}\psi = \frac{\partial}{\partial x}x(Ax^n) = \frac{\partial}{\partial x}(Ax^{n+1}) = (n+1)Ax^n$$

And,

$$\hat{Q}\hat{P}\psi = x\frac{\partial}{\partial x}(Ax^n) = x(nAx^{n-1}) = nAx^n$$

So,

$$[\hat{P}, \hat{Q}] = \hat{P}\hat{Q}\psi - \hat{Q}\hat{P}\psi = (n+1-n)Ax^n = 1.\psi \neq 0$$

The *anti-commutator* of \hat{P} and \hat{Q} is defined as,

$$\hat{P}\hat{Q}\psi + \hat{Q}\hat{P}\psi$$

COMMUTATION of two Operators

Example - 3

$$\hat{P} = x$$

$$\hat{Q} = \frac{\partial}{\partial x}$$

$$\psi = f(x)$$

Let us take a generalized function instead of a specific function

$$\left[x, \frac{d}{dx} \right] = x \frac{d}{dx} f(x) - \frac{d}{dx} xf(x) = x \frac{d}{dx} f(x) - f(x) - x \frac{df(x)}{dx} = -f(x) = (-1)f(x)$$

So, the two operators do not commute

And,

$$\left[x, \frac{d}{dx} \right] = -1$$

COMMUTATION of two Operators

Example -4

$$\hat{P} = x^2$$

$$\hat{Q} = \frac{\partial}{\partial x}$$

$$\psi = f(x)$$

Let us take a generalized function instead of a specific function

$$\left[x^2, \frac{d}{dx} \right] = x^2 \frac{d}{dx} f(x) - \frac{d}{dx} x^2 f(x) = x^2 \frac{d}{dx} f(x) - 2x f(x) - x^2 \frac{df(x)}{dx} = -2x f(x) = (-2x) f(x)$$

So, the two operators do not commute

And,

$$\left[x^2, \frac{d}{dx} \right] = -2x$$

COMMUTATION of two Operators

Example -5 (DIY)

Show that

$$\left[x^3, \frac{d}{dx} \right] = -3x^2$$

$$\left[x, \frac{d}{dx} \right] = -1$$

So, using the Method of Induction

$$\left[x^2, \frac{d}{dx} \right] = -2x$$

$$\left[x^n, \frac{d}{dx} \right] = -n \cdot x^{n-1}$$

$$\left[x^3, \frac{d}{dx} \right] = -3x^2$$

COMMUTATION of two Operators

Example - 6

Calculate $\left[\frac{d}{dx}, x \right]$

$$\left[\frac{d}{dx}, x \right] = \frac{d}{dx} xf(x) - x \frac{d}{dx} f(x) = f(x) + x \frac{df(x)}{dx} - x \frac{df(x)}{dx} = f(x) = (+1)f(x)$$

So, $\left[\frac{d}{dx}, x \right] = 1$

But we have shown $\left[x, \frac{d}{dx} \right] = -1$

$$\left. \begin{array}{l} \left[\frac{d}{dx}, x \right] = 1 \\ \left[x, \frac{d}{dx} \right] = -1 \end{array} \right\} \quad \left[\frac{d}{dx}, x \right] = -\left[x, \frac{d}{dx} \right]$$

$$[\hat{A}, \hat{B}] = -[\hat{B}, \hat{A}] \quad (\text{Anti-symmetry})$$



COMMUTATION of two Operators

Example - 7

Calculate $\left[x, \frac{d^2}{dx^2} \right]$

$$\left[x, \frac{d^2}{dx^2} \right] = x \frac{d^2}{dx^2} f(x) - \frac{d^2}{dx^2} \{xf(x)\} = x \frac{d^2 f(x)}{dx^2} - \frac{d}{dx} \left\{ f(x) + x \frac{df(x)}{dx} \right\}$$

$$= x \frac{d^2 f(x)}{dx^2} - \frac{df(x)}{dx} - \frac{df(x)}{dx} - x \frac{d^2 f(x)}{dx^2}$$

$$= \left(-2 \frac{d}{dx} \right) f(x)$$

So,

$$\left[x, \frac{d^2}{dx^2} \right] = -2 \frac{d}{dx}$$



COMMUTATION of two Operators

Example -8 (DIY)

Show that

$$\left[x, \frac{d^3}{dx^3} \right] = -3 \frac{d^2}{dx^2}$$

$$\left[x, \frac{d}{dx} \right] = -1$$

$$\left[x, \frac{d^2}{dx^2} \right] = -2 \frac{d}{dx}$$

$$\left[x, \frac{d^3}{dx^3} \right] = -3 \frac{d^2}{dx^2}$$

So, using the Method of Induction

$$\left[x, \frac{d^n}{dx^n} \right] = -n \frac{d^{n-1}}{dx^{n-1}}$$



COMMUTATION of two Operators

Example -9

Show that

$$[\hat{P}\hat{Q}, \hat{R}] = \hat{P}[\hat{Q}, \hat{R}] + [\hat{P}, \hat{R}]\hat{Q}$$

$$\begin{aligned} [\hat{P}\hat{Q}, \hat{R}] &= \hat{P}\hat{Q}\hat{R} - \hat{R}\hat{P}\hat{Q} \\ &= \hat{P}\hat{Q}\hat{R} - \hat{P}\hat{R}\hat{Q} + \hat{P}\hat{R}\hat{Q} - \hat{R}\hat{P}\hat{Q} \\ &= \hat{P}(\hat{Q}\hat{R} - \hat{R}\hat{Q}) + (\hat{P}\hat{R} - \hat{R}\hat{P})\hat{Q} \\ &= \hat{P}[\hat{Q}, \hat{R}] + [\hat{P}, \hat{R}]\hat{Q} \end{aligned}$$

(Distributivity)



COMMUTATION of two Operators

Example -10

Calculate

$$\left[x^2, \frac{d}{dx} \right]$$

Given: $\left[x, \frac{d}{dx} \right] = -1$

$$[\hat{P}\hat{Q}, \hat{R}] = \hat{P}[\hat{Q}, \hat{R}] + [\hat{P}, \hat{R}]\hat{Q}$$

Using **distributivity** property of Commutator,

$$\left[x^2, \frac{d}{dx} \right] = \left[x \cdot x, \frac{d}{dx} \right] = x \left[x, \frac{d}{dx} \right] + \left[x, \frac{d}{dx} \right] x = x(-1) + (-1)x = -2x$$

Foundation of Quantum Mechanics

(Part – 9)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

The BORN Interpretation of the Wavefunction

Wave function contains all the dynamical information about the system it describes

But what exactly is this "wave function"?

The answer is provided by *Born's statistical interpretation* of the wave function,

$|\psi(x, t)|^2$ gives the probability of finding the particle at point x , at time t



The BORN Interpretation of the Wavefunction

He made use of an analogy with the **wave theory of light**, in which the square of the amplitude of an electromagnetic wave in a region is interpreted as its intensity and therefore (in quantum terms) as a measure of the probability of finding a photon in the region

If the wave function of a particle has the value ψ at some point x , the **probability of finding the particle** between x and $x + dx$ is proportional to $|\psi|^2 dx$ or $\psi^* \psi dx$ (if ψ is complex).

ψ itself has no physical interpretation

The wave function, ψ itself is called the **probability amplitude**



The BORN Interpretation of the Wavefunction

the probability of finding the particle between x and $x + dx$ is proportional to $|\psi|^2 dx$ or $\psi^* \psi dx$ (if ψ is complex).

Every complex function, ψ can be written as,

$$\begin{aligned}\psi &= A + iB \\ \text{So, } \psi^* &= A - iB\end{aligned}$$

Hence,

$$\begin{aligned}|\psi|^2 &= \psi^* \psi = (A + iB)(A - iB) \\ &= A^2 - i^2 B^2 \\ &= A^2 + B^2\end{aligned}$$

So, $|\psi|^2 = \psi^* \psi$ is always a positive, real quantity.

$|\psi|^2 = \psi^* \psi$ cannot be negative or complex because of the way it is defined.



The BORN Interpretation of the Wavefunction

NORMALIZATION

The total probability of finding the particle somewhere (i.e. within the configurational limit) must be unity.

$$\int_{config.\lim.} \psi^*(x) \psi(x) dx = 1$$

A wave function that obeys this equation is said to be **NORMALIZED**



The BORN Interpretation of the Wavefunction

NORMALIZATION

Some acceptable or well-behaved wave functions are not normalized. So, to meet the statistical requirement, it has to be normalized. The process of transforming a **normalizable wave function** into **normalized wave function** is called **NORMALIZATION**

Suppose, $\psi(x)$ is an acceptable wave function, but it is not normalized

$$\int_{\text{config. lim.}} \psi^*(x)\psi(x)dx \neq 1$$

But

$$\int_{\text{config. lim.}} \psi^*(x)\psi(x)dx = \text{constant}$$



The BORN Interpretation of the Wavefunction

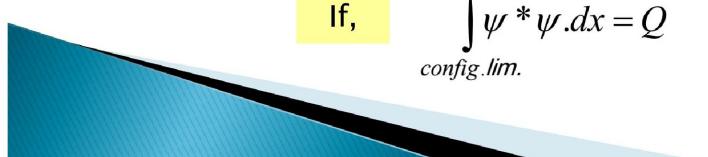
NORMALIZATION

To normalize it, $\psi(x)$ is multiplied by a term, say **N**, so that the new wave function, $\psi_1(x) = N\psi(x)$ becomes a normalized wave function. Here **N** is a constant and is called the **normalization constant**

$$\int_{\text{config. lim.}} \psi_1^* \psi_1 dx = 1 \quad \text{Or,} \quad \int_{\text{config. lim.}} N^* \psi^* N \psi dx = 1$$

$$\text{Or,} \quad |N|^2 \int_{\text{config. lim.}} \psi^* \psi dx = 1$$

$$\text{If,} \quad \int_{\text{config. lim.}} \psi^* \psi dx = Q \quad \text{Then,} \quad |N| = \frac{1}{\sqrt{Q}}$$



NORMALIZATION

Example – 1

The wave function of a particle of mass “m” which moves in one dimension between $x = a$ and $x = b$, is,

$$\psi = \frac{A}{x}$$

 where, A is a normalization constant. Calculate A.

$$\int_a^b \psi * \psi .dx = 1$$

Or, $|A|^2 \int_a^b \frac{1}{x^2} dx = 1$

Or, $|A|^2 \left[-\frac{1}{x} \right]_a^b = 1$

Or, $|A|^2 \left[-\frac{1}{b} + \frac{1}{a} \right] = 1$

Or, $|A|^2 \left[\frac{b-a}{ab} \right] = 1$ Or, $|A| = \sqrt{\frac{ab}{b-a}}$



NORMALIZATION

*Example – 2

The wave function of a particle of mass “m” which moves in one dimension between $x = 0$ and $x = L$, is, ,

$$\psi = A \cdot \sin \frac{n\pi x}{L}$$

 where, A is a normalization constant. Calculate A.

$$\int_a^b \psi * \psi .dx = 1$$

Or, $|A|^2 \int_0^L \sin^2 \frac{n\pi x}{L} .dx = 1$ Or, $|A|^2 \frac{1}{2} \int_0^L 2 \cdot \sin^2 \frac{n\pi x}{L} .dx = 1$

If $\frac{n\pi x}{L} = z$, $dx = \frac{L}{n\pi} dz$

Or, $|A|^2 \frac{1}{2} \frac{L}{n\pi} \int_0^{n\pi} 2 \cdot \sin^2 z .dz = 1$

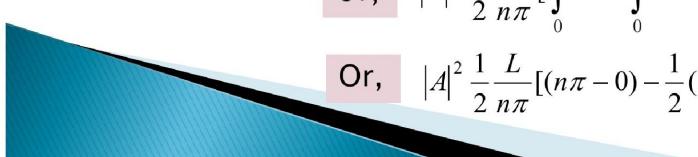
When, $x = 0$, $z = 0$;
 when, $x = L$, $z = n\pi$

Or, $|A|^2 \frac{1}{2} \frac{L}{n\pi} \int_0^{n\pi} [1 - \cos 2z] dz = 1$

Or, $|A|^2 \frac{1}{2} \frac{L}{n\pi} [\int_0^{n\pi} dz - \int_0^{n\pi} \cos 2z .dz] = 1$

Or, $|A|^2 \frac{1}{2} \frac{L}{n\pi} [(n\pi - 0) - \frac{1}{2}(0 - 0)] = 1$

Or, $|A| = \sqrt{\frac{2}{L}}$



NORMALIZATION

*Example – 3

Calculate the normalization constant for the wave function $\psi = \exp(i\theta)$ between 0 and 2π .

$$|A|^2 \int_0^{2\pi} \psi^* \psi d\theta = 1$$

Or, $|A|^2 \int_0^{2\pi} \exp(-i\theta) \exp(i\theta) d\theta = 1$

Or, $|A|^2 \int_0^{2\pi} d\theta = 1$

Or, $|A|^2 (2\pi - 0) = 1$

Or, $|A| = \frac{1}{\sqrt{2\pi}}$

Foundation of Quantum Mechanics

(Part – 10)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara

EIGENVALUE and EIGENFUNCTION

“Eigen” is a German word meaning
“characteristic”

Generally, an operator, \hat{A} , when it operates on a function, say, ψ_i , gives a new function, ψ_j

But under some special circumstances, where the operator and the function has matching properties such that \hat{A} operating on a function ψ_i gives back the original function multiplied by a constant, say, a_i

$$\hat{A}\psi_i = a_i\psi_i$$

EIGENVALUE and EIGENFUNCTION

$$\hat{A}\psi_i = a_i\psi_i$$

We then say that, ψ_i is an eigenfunction of and have the eigenvalue, a_i

The problem of determining ψ_i and a_i for a given \hat{A} is called an eigenvalue problem

EIGENVALUE and EIGENFUNCTION

$$\hat{A}\psi_i = a_i\psi_i$$

Example - 1

$$\hat{A} = \frac{d}{dx} \quad \text{and} \quad \psi = \exp(2x)$$

$$\hat{A}\psi = \frac{d}{dx} [\exp(2x)] = 2 \cdot \exp(2x) = 2\psi$$

Hence, $\psi = \exp(2x)$ is an eigenfunction of the operator $\hat{A} = \frac{d}{dx}$ with eigenvalue, 2



EIGENVALUE and EIGENFUNCTION

Example - 2

$$\hat{A} = \frac{d^2}{dx^2} \quad \text{and} \quad \psi = \exp(mx)$$

$$\hat{A}\psi = \frac{d^2}{dx^2} [\exp(mx)] = m^2 \cdot \exp(mx) = m^2 \cdot \psi$$

Hence, $\psi = \exp(mx)$ is an eigenfunction of the operator $\hat{A} = \frac{d^2}{dx^2}$ with eigenvalue, m^2



EIGENVALUE and EIGENFUNCTION

Let us go back to the time-independent form of the Schrodinger equation

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

Or, $\left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right] \psi(x) = E \psi(x)$

Or, $\hat{H} \psi(x) = E \psi(x)$ where $\hat{H} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right]$

We can see that we have formulated the Schrodinger equation as an eigenvalue problem



EIGENVALUE and EIGENFUNCTION

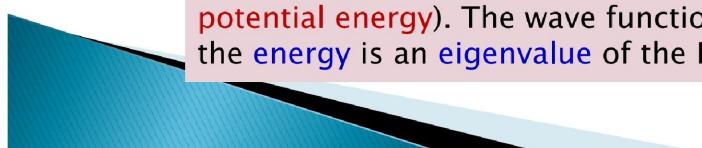
$$\hat{H} \psi(x) = E \psi(x) \quad \text{where} \quad \hat{H} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right]$$

\hat{H} is called the **Hamiltonian operator**. The wave function is an eigenfunction and the **energy** is an **eigenvalue** of the Hamiltonian operator

This suggests that a correspondence between the Hamiltonian operator and the energy

Hamiltonian operator after the nineteenth century mathematician, **Sir William Rowan Hamilton**

The **Hamiltonian operator** is the operator corresponding to the total energy of the system (i.e. the sum of **kinetic energy** and **potential energy**). The wave function is an **eigenfunction** and the **energy** is an **eigenvalue** of the Hamiltonian operator.



EIGENVALUE and EIGENFUNCTION

$$\hat{H}\psi(x) = E\psi(x) \quad \text{where} \quad \hat{H} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right]$$

Schrodinger equation is basically of the form:

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

The importance of the eigenvalue equation is the pattern

(Energy operator) ψ = (energy) ψ

This pattern is repeated for other observables, or measurable properties of a system, such as the momentum or the electric dipole moment

(Operator corresponding to an observable) ψ = (Value of the observable) ψ

EIGENVALUE and EIGENFUNCTION

Example – 3

Find the eigenfunction and eigenvalue of the operator, $\hat{A} = \frac{d}{dx}$

Let the function be $f(x)$

$$\frac{df(x)}{dx} = kf(x) \quad \text{Or,} \quad \frac{df(x)}{f(x)} = k \cdot dx$$

Integrating both sides, $\ln f(x) = kx + z$

$$\text{Or, } f(x) = \exp(kx) \cdot \exp(z)$$

$$\text{Or, } f(x) = c \cdot \exp(kx)$$

[where, $c = \exp(z)$]

EIGENVALUE and EIGENFUNCTION

Example – 4

A state, $\psi = N \exp(-ax^2)$ satisfies an eigenvalue equation, $H\Psi = E\Psi$ with, $\hat{H} = -\frac{d^2}{dx^2} + x^2$

Find the possible value of “a” and eigenvalue, E.

[C.U. 2006]

$$\begin{aligned}
 \hat{H}\psi &= E\psi \\
 \text{So } &\left(-\frac{d^2}{dx^2} + x^2 \right) N \exp(-ax^2) \\
 &= -\frac{d^2}{dx^2} N \exp(-ax^2) + x^2 N \exp(-ax^2) \\
 &= 2aN \frac{d}{dx} [x \exp(-ax^2)] + x^2 N \exp(-ax^2) \\
 &= N \exp(-ax^2) [2a - 4a^2 x^2] + x^2 N \exp(-ax^2) \\
 &= N \exp(-ax^2) [2a - 4a^2 x^2 + x^2]
 \end{aligned}$$

For the function to be an eigenfunction

$$-4a^2 x^2 + x^2 = 0$$

$$E = 2 \left(\pm \frac{1}{2} \right) = \pm 1$$

$$\text{Or, } a^2 = \frac{1}{4} \quad \text{Or, } a = \pm \frac{1}{2}$$

Foundation of Quantum Mechanics

(Part – 11)

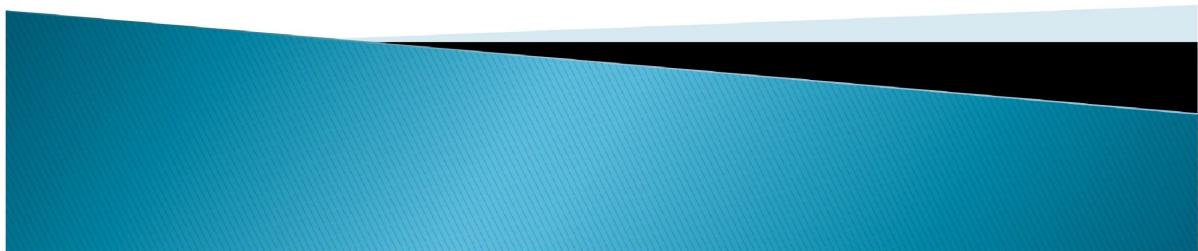
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



EIGENVALUE and EIGENFUNCTION

Let us go back to the time-independent form of the Schrodinger equation

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

Or,

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

Or,

$$\hat{H} \psi(x) = E \psi(x) \quad \text{where} \quad \hat{H} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right]$$

We can see that we have formulated the Schrodinger equation as an eigenvalue problem



EIGENVALUE and EIGENFUNCTION

$$\hat{H}\psi(x) = E\psi(x) \quad \text{where} \quad \hat{H} = \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V}(x) \right]$$

\hat{H} is called the **Hamiltonian operator**. The wave function is an eigenfunction and the **energy** is an **eigenvalue** of the Hamiltonian operator

This suggests that a correspondence between the Hamiltonian operator and the energy

The **Hamiltonian operator** is the operator corresponding to the total energy of the system (i.e. the sum of **kinetic energy** and **potential energy**). The wave function is an **eigenfunction** and the **energy** is an **eigenvalue** of the Hamiltonian operator.

OPERATORS

Observables are represented by **operators**, built from the following position and momentum operators

$$\hat{x} = x$$

$$\hat{p}_x = -i\hbar \frac{d}{dx} = \frac{\hbar}{i} \frac{d}{dx}$$

$$\text{translational kinetic energy} = \frac{1}{2}mv^2 = \frac{(mv)^2}{2m} = \frac{p^2}{2m}$$

$$\text{kinetic energy operator} \quad \hat{T} = \frac{\hat{p}_x^2}{2m} = \frac{1}{2m} \left(-i\hbar \frac{d}{dx} \right)^2 = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

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

OPERATORS

potential energy for a Harmonic oscillator

$$V(x) = \frac{1}{2} kx^2$$

potential energy operator

$$\hat{V} = \frac{1}{2} kx^2$$

Each observable (i.e. physically measurable property of a system) has a corresponding Hermitian Operator

$$\hat{x} = x$$

$$\hat{p}_x = -i\hbar \frac{d}{dx} = \frac{\hbar}{i} \frac{d}{dx}$$

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

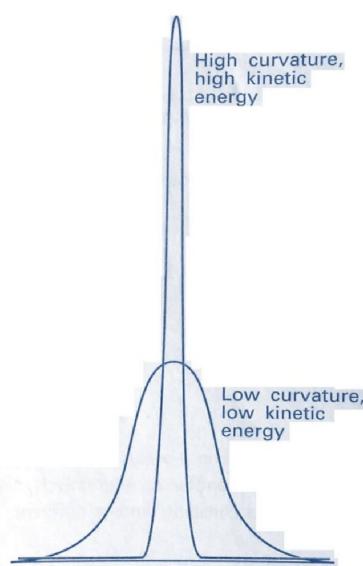
Etc.

OPERATORS

In mathematics, second derivative of a function is a measure of its curvature. A large second derivative indicates a sharply curved function.

It follows that a **sharply curved wavefunction** is associated with a **high kinetic energy** and one with a **low curvature** is associated with a **low kinetic energy**.

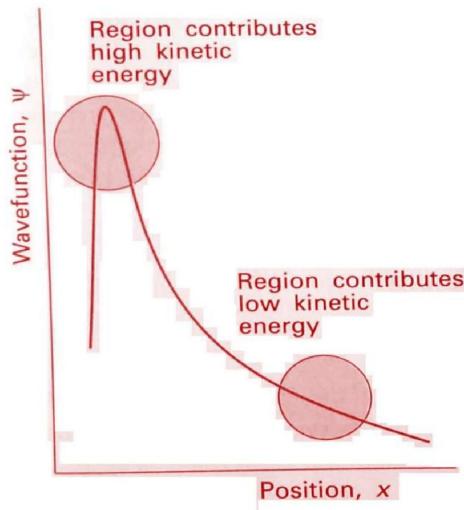
This interpretation is consistent with **de Broglie's relation**, which predicts a short wavelength (a sharply curved wavefunction) when the linear momentum (and hence kinetic energy) is high.



OPERATORS

The curvature of a wavefunction, in general, varies from place to place. Wherever a wavefunction is sharply curved, its contribution to the total energy (i.e. kinetic energy) is low

The observed kinetic energy of the particle is an integral of all the contributions of the kinetic energy from each region.



Superposition and Expectation Values

What is the linear momentum of the particle with $\psi = 2A \cos kx$

Using operator technique,

$$-i\hbar \frac{d}{dx} \psi = -i\hbar \frac{d(\cos kx)}{dx} = -i\hbar 2A(-k)\sin kx = +k\hbar i(2A \sin kx) = -\frac{2k\hbar}{i} A \sin kx$$

this expression is NOT an eigenvalue problem

However, this cosine wavefunction is a linear combination of $\exp(ikx)$ and $\exp(-ikx)$

$$\psi = \psi_1 + \psi_2$$

$$\psi = A[\exp(ikx) + \exp(-ikx)] = 2A \cos(kx)$$

the total wavefunction is a superposition of more than one wavefunction

Superposition and Expectation Values

$$\psi = \psi_1 + \psi_2$$

$$\psi = A. [\exp(ikx) + \exp(-ikx)] = 2A \cos(kx)$$

Using operator technique,

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

and

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

If the momentum of the particle is repeatedly measured in a long series of observations, then its magnitude will be found to $k\hbar$



Superposition and Expectation Values

Suppose the wavefunction is known to be a superposition of many different linear momentum eigenfunctions

$$\psi = c_1 \psi_1 + c_2 \psi_2 + \dots = \sum c_k \psi_k$$

c_k are numerical coefficients and ψ_k corresponds to different momentum state

When the momentum is measured, in a **single observation**, one of the eigenvalues corresponding to the ψ_k that contribute to the superposition will be found

The average value of a **large number of observations** is given by the **expectation value**, say, $\langle a \rangle$ of the operator, \hat{A} corresponding to the observable of interest



Superposition and Expectation Values

The average value of a large number of observations is given by the expectation value, say, $\langle a \rangle$ of the operator, \hat{A} corresponding to the observable of interest

$$\langle a \rangle = \int_{\text{config. lim.}} \psi^* \hat{A} \psi d\tau \quad (\text{for normalized wavefunctions})$$

$$\langle a \rangle = \frac{\int_{\text{config. lim.}} \psi^* \hat{A} \psi d\tau}{\int_{\text{config. lim.}} \psi^* \psi d\tau} \quad (\text{If the wavefunction is not normalized})$$

Expectation value is the weighted average of a large number of observations of a property



Superposition and Expectation Values

$$\langle a \rangle = \int_{\text{config. lim.}} \psi^* \hat{A} \psi d\tau \quad (\text{for normalized wavefunctions})$$

$$\langle A \rangle = \int_{\text{config. lim.}} \psi^* \hat{A} \psi d\tau = \int_{\text{config. lim.}} \psi^* a \psi d\tau = a \int_{\text{config. lim.}} \psi^* \psi d\tau = a$$

every observation of the property, A , results in the value, a , the mean value of all the observations is also, a



Superposition and Expectation Values

A **wavefunction** that is not an eigenfunction of the operator of interest can be written as a **linear combination** of eigenfunctions

$$\psi = c_1\psi_1 + c_2\psi_2$$

Hence,

$$\begin{aligned}\langle A \rangle &= \int_{config.\lim.} \psi * \hat{A} \psi .d\tau = \int_{config.\lim.} (c_1\psi_1 + c_2\psi_2) * \hat{A}(c_1\psi_1 + c_2\psi_2) .d\tau \\ &= \int_{config.\lim.} (c_1\psi_1 + c_2\psi_2) * (c_1a_1\psi_1 + c_2a_2\psi_2) .d\tau \\ &= c_1 * c_1 a_1 \int \psi_1 * \psi_1 .d\tau + c_2 * c_2 a_2 \int \psi_2 * \psi_2 .d\tau + c_1 * c_2 a_2 \int \psi_1 * \psi_2 .d\tau + c_2 * c_1 a_1 \int \psi_2 * \psi_1 .d\tau\end{aligned}$$

i.e. $\langle A \rangle = |c_1|^2 a_1 + |c_2|^2 a_2$ because $\int_{config.\lim.} \psi_i \psi_j .d\tau = 0$

Expectation value is the weighted average of a large number of observations of a property

ORTHOGONALITY

$$\int_{config.\lim.} \psi_i * \psi_j .d\tau = 0$$

A very general rule in quantum mechanics is that eigenfunctions corresponding to different eigenvalues of the same operator are **orthogonal**

Condition of Normalization

$$\int_{config.\lim.} \psi_i * \psi_i .d\tau = 1$$

$$\int_{config.\lim.} \psi_i * \psi_j .d\tau = \delta_{ij}$$

When, $i = j$, $\delta_{ij} = 1$

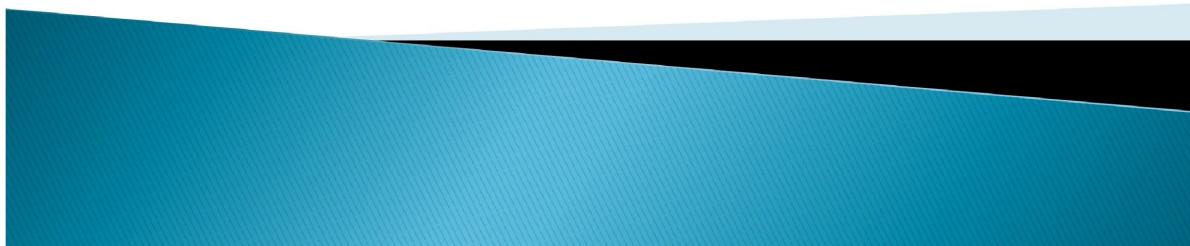
When, $i \neq j$, $\delta_{ij} = 0$



Foundation of Quantum Mechanics

(Part – 12)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara



POSTULATES of QUANTUM MECHANICS

POSTULATE 1

The state of a quantum mechanical system is completely specified by a function $\psi(x)$ that depends upon the coordinate of the particle. All possible information about the system can be derived from $\psi(x)$. This function, called wave function or the state function, has the important property that, $\psi(x)^*\psi(x)dx$ is the probability that the particle lies in the interval dx , located at the position x .

We can see that we have formulated the Schrodinger equation as an eigenvalue problem

POSTULATES of QUANTUM MECHANICS

Acceptability of wave function

The wave function $\psi(x)$ must be normalized

$$\int_{all.space} \psi(x)^* \psi(x).dx = 1 \quad \text{for one-dimensional system}$$

$$\iint_{all.space} \psi(x)^* \psi(x).dxdy = 1 \quad \text{for two-dimensional system}$$

$$\iiint_{all.space} \psi(x)^* \psi(x).dxdydz = 1 \quad \text{for three-dimensional system}$$

POSTULATES of QUANTUM MECHANICS

Acceptability of wave function

For $\psi(x)$ to be a physically acceptable wave function, it and its first derivative must be single-valued, continuous, and finite

These requirements can be summarized by saying that $\psi(x)$ must be well-behaved.



POSTULATES of QUANTUM MECHANICS

Acceptability of wave function

ψ must not be infinite anywhere

If it were, the integral in the above equation(s) would be infinite.
The normalization constant would be zero.
The normalized wave function would then be zero everywhere, except where it is infinite, which would be unacceptable.

The requirement that ψ is finite everywhere rules out many possible solutions of the Schrodinger equation



POSTULATES of QUANTUM MECHANICS

Acceptability of wave function

ψ must be single-valued

We can imagine a solution of the Schrodinger equation that gives rise to more than one values of $|\psi|^2$ at a single point.

The Born interpretation implies that such solutions are unacceptable, because it would be absurd to have more than one probability that a particle is at some point.

ψ must have only one value at each point of space



POSTULATES of QUANTUM MECHANICS

Acceptability of wave function

The Schrodinger equation itself is a second-order differential equation,

The second derivative of ψ must be well-defined if the equation is to be applicable everywhere.

We can take the second derivative of a function only if it is a **continuous** (so there are no sharp steps in it) and **its first derivative, its slope, is continuous** (so there are no kinks).



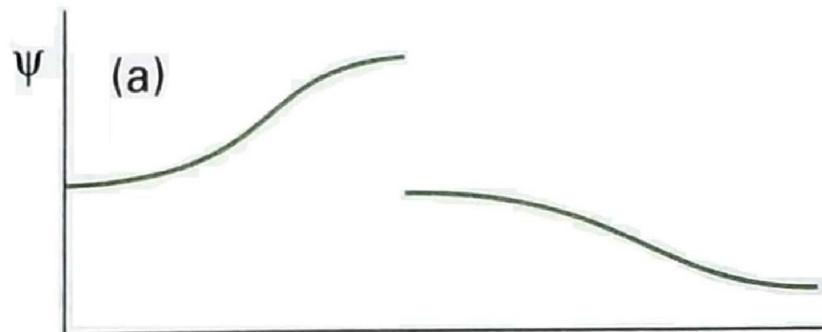
POSTULATES of QUANTUM MECHANICS

Acceptability of wave function

The restrictions are so severe that acceptable solutions of the Schrodinger equation do not, in general, exist for arbitrary values of the energy, E.

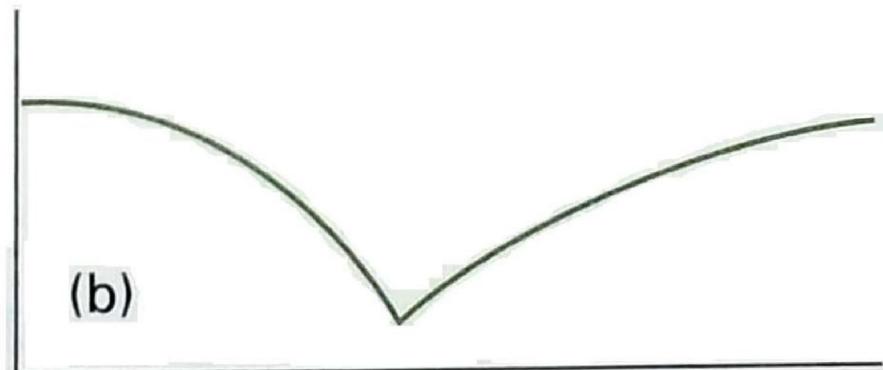
In other words, a particle may possess only certain energies, for otherwise its wave function would be physically unacceptable

POSTULATES of QUANTUM MECHANICS



unacceptable because it is not continuous

POSTULATES of QUANTUM MECHANICS

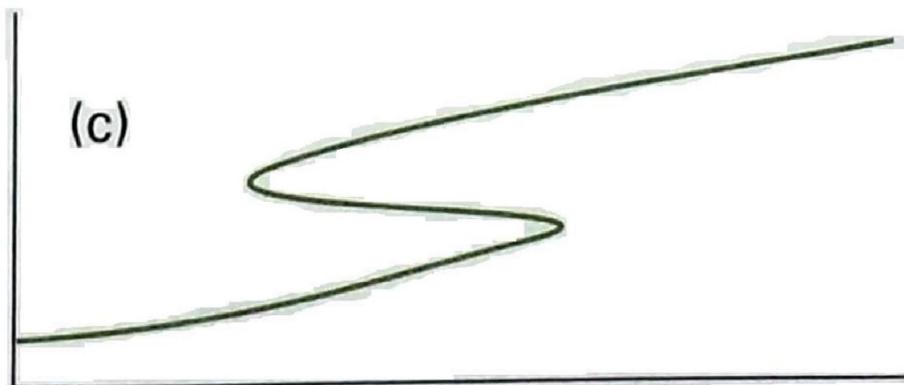


(b)

unacceptable because its slope is discontinuous



POSTULATES of QUANTUM MECHANICS

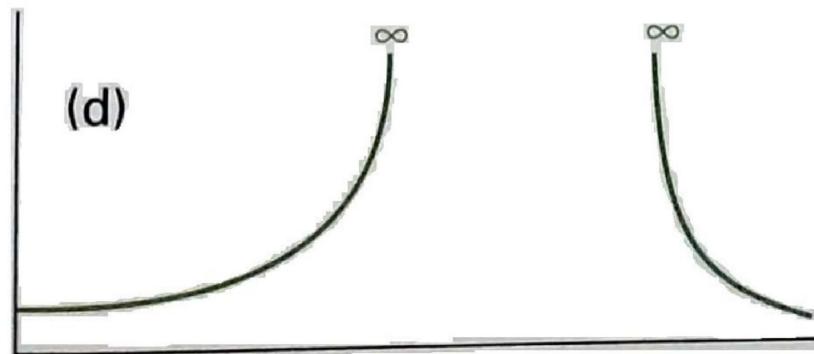


(c)

unacceptable because it is not single-valued



POSTULATES of QUANTUM MECHANICS



unacceptable because it is infinite over a finite region

POSTULATES of QUANTUM MECHANICS

Example – 1: Determine whether each of the following functions is acceptable or not as a state function over the indicated intervals:

- (a) $\exp(-x)$ $[0, \infty]$
- (b) $\exp(-x)$ $[-\infty, +\infty]$
- (c) $\sin^{-1} x$ $[-1, 1]$
- (d) $(\sin x)/x$ $[0, \infty]$
- (e) $\exp(-|x|)$ $[-\infty, +\infty]$

POSTULATES of QUANTUM MECHANICS

- (a) **Acceptable**; the function is single-valued, continuous, finite and quadratically integrable over the indicated interval.
- (b) **Not acceptable**; the function cannot be normalized over the indicated interval because, at $x \rightarrow \infty$, $\exp(-x) \rightarrow \infty$.
- (c) **Not acceptable**; because $\sin^{-1} x$ is a multi-valued function.
- (d) **Acceptable**; realize that $(\sin x)/x$ is finite at $x = 0$
- (e) **Not acceptable**; the first derivative of $\exp(-|x|)$ is not continuous at $x = 0$.

Foundation of Quantum Mechanics

(Part – 13)

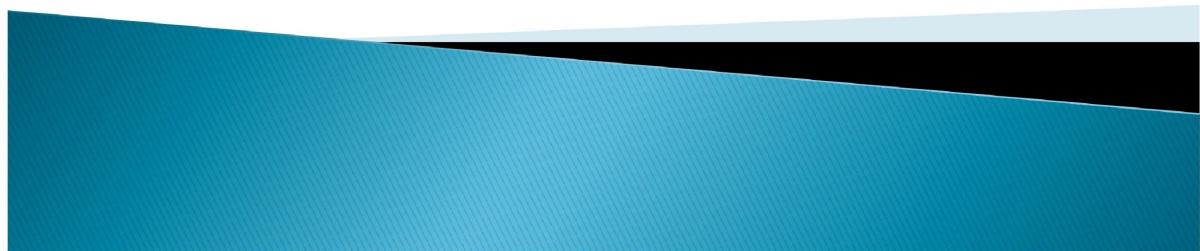
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



POSTULATES of QUANTUM MECHANICS

POSTULATE 2

To every observable in classical mechanics, there corresponds an operator in quantum mechanics

Any quantum mechanical operator must be a Hermitian operator



POSTULATES of QUANTUM MECHANICS

Observable		Operator	
Name	Symbol	Symbol	Operation
Position	x	\hat{x}	Multiply by x
	r	\hat{R}	Multiply by r
Momentum	P_x	\hat{p}_x	$-i\hbar \frac{\partial}{\partial x}$
	P	\hat{p}	$-i\hbar \left(\vec{i} \frac{\partial}{\partial x} + \vec{j} \frac{\partial}{\partial y} + \vec{k} \frac{\partial}{\partial z} \right)$
Kinetic energy	T_x	\hat{T}_x	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$
	T	\hat{T}	$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$

POSTULATES of QUANTUM MECHANICS

Observable		Operator	
Name	Symbol	Symbol	Operation
Potential energy	$V(x)$	$\hat{V}(x)$	Multiply by $V(x)$
	In gravitational field, $V = mgx$		$\hat{V}(x) = mgx$
	Harmonic oscillator, $V = \frac{1}{2}kx^2$		$\hat{V}(x) = \frac{1}{2}kx^2$
	In electro-static field, $V = (q_1 q_2)/x$		

POSTULATES of QUANTUM MECHANICS

Observable		Operator	
Name	Symbol	Symbol	Operation
Total energy	E	\hat{H}	
		$\hat{H} = \hat{T} + \hat{V}$	$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$ (for one-dimensional SHO)
Angular momentum	$\vec{L} = \vec{r} \times \vec{p}$	$\hat{L} = \hat{r} \times \hat{p}$	$\hat{L} = \hat{r} \times (-i\hbar \nabla)$
	$I_x = y p_z - z p_y$		$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$
	$I_y = z p_x - x p_z$		$\hat{L}_y = -i\hbar \left(z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$
	$I_z = x p_y - y p_x$		$\hat{L}_z = -i\hbar \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$

POSTULATES of QUANTUM MECHANICS

POSTULATE 3

In any measurement of the observable associated with the operator A , the only values that will ever be observed are the eigenvalues, a , which satisfy the eigenvalue equation

$$\hat{A}\psi = a\psi$$

POSTULATES of QUANTUM MECHANICS

POSTULATE 4

If a system is in a state described by a normalized wave function, ψ , then the average value of the observable corresponding to \hat{A} is given by

$$\langle a \rangle = \int_{-\infty}^{+\infty} \psi * \hat{A} \psi d\tau$$

POSTULATES of QUANTUM MECHANICS

Example: Calculate the average value (or expectation value) of energy for the particle in a one-dimensional box with length L.

Given: $\psi = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ and $0 \leq x \leq L$.

The particle in a one-dimensional box only has kinetic energy

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

Expectation value of energy

$$\langle E \rangle = \int_0^L \psi * \hat{H} \psi dx = \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} dx$$

POSTULATES of QUANTUM MECHANICS

$$\begin{aligned}
 \langle E \rangle &= \int_0^L \psi * \hat{H} \psi dx = \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} dx \\
 &= \frac{2}{L} \left(-\frac{\hbar^2}{2m} \right) \int_0^L \sin \frac{n\pi x}{L} \left(\frac{d^2}{dx^2} \right) \sin \frac{n\pi x}{L} dx = \frac{2}{L} \left(-\frac{\hbar^2}{2m} \right) (-1) \left(\frac{n\pi}{L} \right)^2 \int_0^L \sin \frac{n\pi x}{L} \sin \frac{n\pi x}{L} dx \\
 &= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{\hbar^2}{2m} \right) \int_0^L 2 \sin^2 \frac{n\pi x}{L} dx \\
 \langle E \rangle &= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{n\pi} \right) \left(\frac{\hbar^2}{2m} \right) \int_0^{n\pi} 2 \sin^2 z dz \\
 &= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{n\pi} \right) \left(\frac{\hbar^2}{2m} \right) \int_0^{n\pi} (1 - \cos 2z) dz \\
 &= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{n\pi} \right) \left(\frac{\hbar^2}{2m} \right) \left[(n\pi - 0) - \frac{1}{2}(0 - 0) \right] = \frac{n^2 \hbar^2}{8mL^2}
 \end{aligned}$$

Let $\frac{n\pi x}{L} = z$ So, $dx = \frac{L}{n\pi} dz$

When, $x = 0, z = 0$ and
when, $x = L, z = n\pi$



POSTULATES of QUANTUM MECHANICS

Example: Calculate $\langle E^2 \rangle$ for the particle in a one-dimensional box with length L. Given: and $0 \leq x \leq L$.

$$\psi = \sqrt{\frac{2}{L}} \sin \left(\frac{n\pi x}{L} \right)$$

Hint $\hat{H}^2 = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) = \left(\frac{\hbar^2}{2m} \right)^2 \frac{d^4}{dx^4}$



Answer: $\langle E^2 \rangle = \left(\frac{n^2 \hbar^2}{8mL^2} \right)^2$

POSTULATES of QUANTUM MECHANICS

Example: Suppose a particle is in the state, $\psi(x) = \sqrt{\frac{30}{L^5}}x(L-x)$ within the limit $0 \leq x \leq L$. (a) Show that the function is normalized. (b) Calculate the average energy associated with this state. Given, $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$.

Hint

$$\int_0^L \psi * \psi dx = \int_0^L \sqrt{\frac{30}{L^5}}x(L-x) \sqrt{\frac{30}{L^5}}x(L-x) dx = 1$$

$$\langle E \rangle = \int_0^L \psi * \hat{H} \psi dx = \int_0^L \sqrt{\frac{30}{L^5}}x(L-x) \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sqrt{\frac{30}{L^5}}x(L-x) dx$$

Answer: $\langle E \rangle = \frac{5\hbar^2}{4\pi^2 m L^2}$

POSTULATES of QUANTUM MECHANICS

POSTULATE 5

The wave function or state function of a system evolves in time according to the time - dependent Schrodinger equation

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

Any quantum mechanical operator must be a Hermitian operator

Wave functions and operators generally are complex quantities, but certainly the eigenvalues must be real

$$\hat{A}\psi = a\psi \quad (1)$$

We multiply equation – (1) from the left by ψ^* and integrate to obtain

$$\int_{all.space} \psi^* \hat{A}\psi .dx = a \int_{all.space} \psi^* \psi .dx = a \quad (2)$$

Now, we take the complex conjugate of equation – (1)

$$\hat{A}^* \psi^* = a^* \psi^* = a \psi^* \quad (3)$$

Now, we multiply equation – (3) from left by ψ and integrate to obtain

$$\int_{all.space} \psi \hat{A}^* \psi^* .dx = a \int_{all.space} \psi \psi^* .dx = a \quad (4)$$

Comparing equation – (2) and (4), we get,

$$\int_{all.space} \psi^* \hat{A}\psi .dx = \int_{all.space} \psi \hat{A}^* \psi^* .dx \quad (5)$$

Foundation of Quantum Mechanics

(Part – 14)

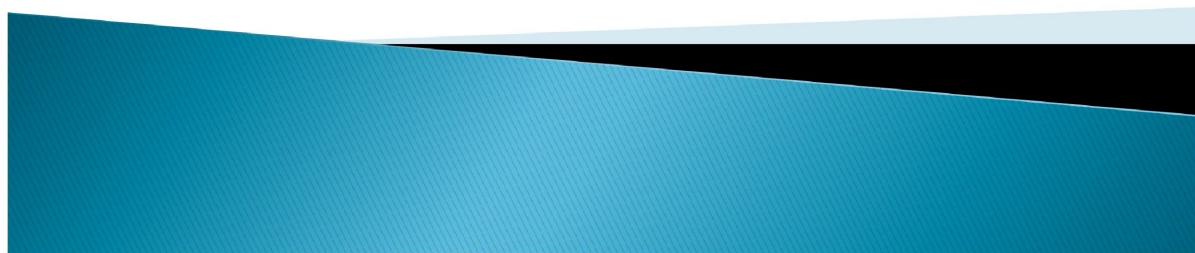
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



POSTULATES of QUANTUM MECHANICS

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POSTULATES of QUANTUM MECHANICS

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

The above equation is same as what we had mentioned earlier

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

Using method of separation of variables,

$$\Psi(x,t) = f(t).\psi(x)$$

$$\text{Here, } f(t) = A \exp\left(-\frac{iEt}{\hbar}\right)$$

$$\text{So, } \Psi(x,t) = \psi(x) \exp\left(-\frac{iEt}{\hbar}\right)$$



POSTULATES of QUANTUM MECHANICS

What's so great about separable solutions?

Solutions to the (time-dependent) Schrodinger equation are
stationary states

Although the wave function itself does (obviously) depend on t, the probability density does not—the time dependence cancels out

$$|\Psi(x,t)|^2 = \Psi * \Psi = \psi * \psi(x) \exp\left(+\frac{iEt}{\hbar}\right) \psi(x) \exp\left(-\frac{iEt}{\hbar}\right) = |\psi(x)|^2$$



POSTULATES of QUANTUM MECHANICS

What's so great about separable solutions?

Same thing happens in calculating the expectation value of any dynamical variable.

$$\langle a \rangle = \int_{-\infty}^{+\infty} \Psi^* \hat{A} \Psi d\tau = \int_{-\infty}^{+\infty} \{\psi(x)f(t)\}^* \hat{A}\{\psi(x)f(t)\} d\tau = \int_{-\infty}^{+\infty} \psi^* \hat{A} \psi d\tau$$

Every expectation value is constant in time.

So, we might as well drop the factor $\mathcal{A}(t)$ altogether, and simply use ψ (i.e. psi in lower case) in place of Ψ (i.e. psi in upper case)



POSTULATES of QUANTUM MECHANICS

What's so great about separable solutions?

Solutions to the (time-dependent) Schrodinger equation are *states of definite total energy*.

Time-independent Schrodinger equation

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

The expectation value of the total energy is

$$\langle H \rangle = \int_{-\infty}^{+\infty} \psi^* \hat{H} \psi d\tau = E \int_{-\infty}^{+\infty} \psi^* \psi d\tau = E$$



Any quantum mechanical operator must be a Hermitian operator

Wave functions and operators generally are complex quantities, but certainly the eigenvalues must be real

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We multiply equation – (1) from the left by ψ^* and integrate to obtain

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$$\hat{A}^* \psi^* = a^* \psi^* = a \psi^* \quad (3)$$

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$$\int_{all.space} \psi^* \hat{A}\psi .dx = \int_{all.space} \psi \hat{A}^* \psi^* .dx \quad (5)$$

The commutator of two operators plays a central role in the Uncertainty Principle

If operators do not commute, then their corresponding observable quantities do not have simultaneously well-defined values

Operator of momentum

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

Operator of position

$$\hat{x}$$

It can be easily shown

$$[x, \hat{p}_x] = \left[x, -i\hbar \frac{\partial}{\partial x} \right] \neq 0$$

It can be also shown

$$[x, \hat{p}_y] = \left[x, -i\hbar \frac{\partial}{\partial y} \right] = 0$$

This means that **position along X-axis** and **momentum along Y-axis** can be simultaneously and accurately measured.

The commutator of two operators plays a central role in the Uncertainty Principle

If operators do not commute, then their corresponding observable quantities do not have simultaneously well-defined values

$$[\hat{L}_x, \hat{L}_y] \neq 0$$

$$[\hat{L}_y, \hat{L}_z] \neq 0$$

$$[\hat{L}_z, \hat{L}_x] \neq 0$$

$$[\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$$



BRAKET notation

$$\int_{-\infty}^{+\infty} \psi_i * \psi_i d\tau = 1 \quad \longrightarrow \quad \langle \psi_i | \psi_i \rangle = 1$$

$$\int_{-\infty}^{+\infty} \psi_i * \psi_j d\tau = 0 \quad \longrightarrow \quad \langle \psi_i | \psi_j \rangle = 0$$

$$\langle a \rangle = \int_{-\infty}^{+\infty} \psi * \hat{A} \psi d\tau \quad \longrightarrow \quad \langle a \rangle = \langle \psi | \hat{A} \psi \rangle$$

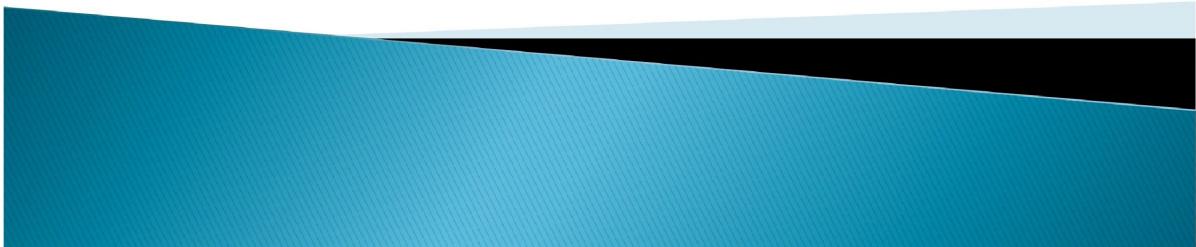




Foundation of Quantum Mechanics

(Part – 15)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara



To find the properties of system according to quantum mechanics, we need to solve the appropriate Schrodinger equation.

We will deal with the essentials of three basic types of motion:

translation, vibration and rotation.

These motions play important role in chemistry because they are the ways in which molecules store energy.

Translational motion → Particle in a box

Vibrational motion → Simple Harmonic Oscillator

Rotational motion → Rigid rotor



Translational motion → Particle in a box

A free particle

Particle in a one-dimensional box

Particle in a two-dimensional box

Particle in a three-dimensional box



THE FREE PARTICLE

Let us consider a particle of mass "m" which moves in the absence of any external forces along the X-axis only.

The absence of forces implies that the potential energy is constant, so for convenience we may choose $V = 0$.

The components of momentum along the Y- and Z- axis are zero; that along X-axis is p_x

$$\text{Total energy} = \text{K.E.} + \text{P.E.} = \text{K.E.}$$

$$E = \frac{1}{2} m v_x^2 = \frac{p_x^2}{2m}$$



THE FREE PARTICLE

The Schrodinger equation of the system

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

Or, $(\hat{T} + \hat{V})\psi = E\psi$

Or, $\hat{T}\psi = E\psi$

Or, $-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = E\psi$

Or, $\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0$



THE FREE PARTICLE

The Schrodinger equation of the system

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0$$

This differential equation has two solutions

$$\psi_1 = A \exp\left(+\frac{i\sqrt{2mE}}{\hbar}x\right)$$

&

$$\psi_2 = B \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right)$$

(A,B are constants)

THE FREE PARTICLE

If we operate on ψ_1 with the momentum operator

$$\hat{p}_x \psi_1 = -i\hbar \frac{\partial \psi_1}{\partial x} = -i\hbar \left(\frac{i\sqrt{2mE}}{\hbar} \right) \psi_1 = +\sqrt{2mE} \cdot \psi_1$$

&

$$\hat{p}_x \psi_2 = -i\hbar \frac{\partial \psi_2}{\partial x} = +i\hbar \left(\frac{i\sqrt{2mE}}{\hbar} \right) \psi_2 = -\sqrt{2mE} \cdot \psi_2$$

ψ_1 describes a particle moving in $+x$ direction with the classical momentum. On the other hand ψ_2 describes the particle moving in the $-x$ direction with the classical momentum.

Since no other conditions are specified, the energy may have any value, and so may the momentum. The spectrum of energy eigen values is continuous, as is that of the momentum eigen values.

THE FREE PARTICLE

Using ψ_1 , let us calculate the probability $\psi_1^* \psi_1$

$$\psi_1 = A \exp\left(+\frac{i\sqrt{2mE}}{\hbar}x\right) \quad \& \quad \psi_1^* = A^* \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right)$$

$$|\psi_1|^2 = \psi_1^* \psi_1 = A^* A = |A|^2$$

But **A** is constant. So $|A|^2$ is a constant and is independent of the value of x . This means that the probability of finding the particle is the same everywhere along its path.

ψ_1 describes a particle moving in $+x$ direction with momentum $\sqrt{2mE}$.
So its momentum is precise.

In other words, if momentum is specified precisely, it is impossible to predict the location of the particle.

THE FREE PARTICLE

Similar results will be obtained using ψ_2

$$\psi_2 = B \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right) \quad \& \quad \psi_2^* = B^* \exp\left(+\frac{i\sqrt{2mE}}{\hbar}x\right)$$

$$|\psi_2|^2 = \psi_2^* \psi_2 = B^* B = |B|^2$$

But **B** is constant. So $|B|^2$ is a constant and is independent of the value of x . This means that the probability of finding the particle is the same everywhere along its path.

ψ_2 describes a particle moving in $-x$ direction with momentum $-\sqrt{2mE}$.
So its momentum is precise.

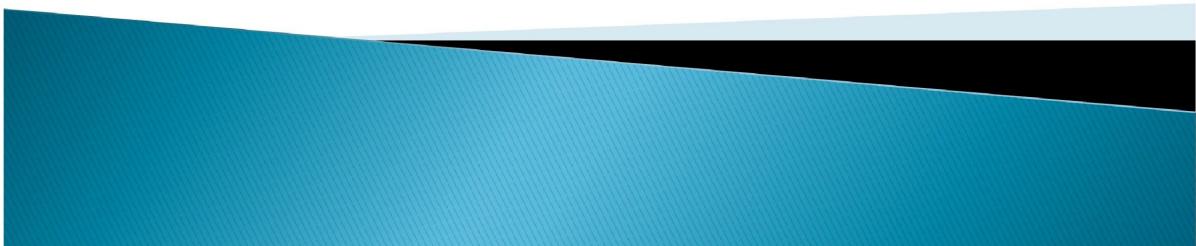
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Foundation of Quantum Mechanics

(Part – 16)

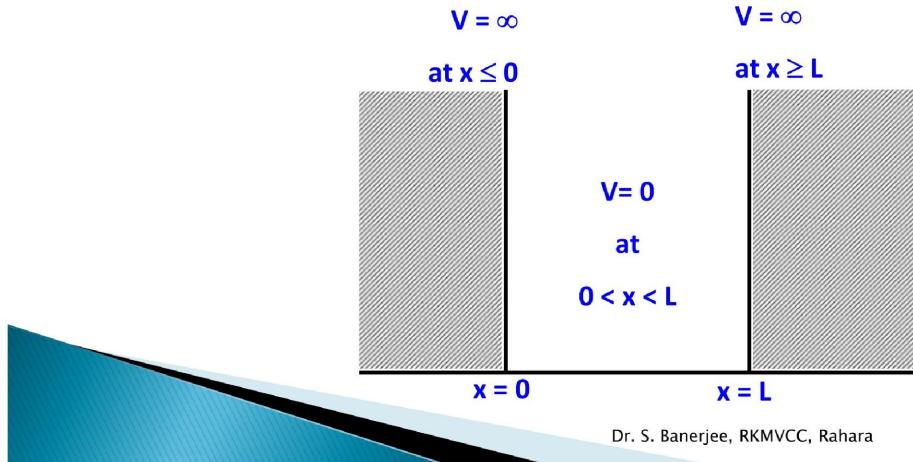
Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara



Particle in a one-dimensional box

Let us consider a particle confined in a one-dimensional box of length "L". The particle is confined within an infinite square well potential i.e. potential energy, $V = \infty$ at $x \geq L$ and $x \leq 0$; $V = 0$ at $0 < x < L$

The absence of forces implies that the potential energy is constant, so for convenience we may choose $V = 0$.



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Particle in a one-dimensional box

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

Or,

$$(\hat{T} + \hat{V})\psi = E\psi$$

Or,

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

Or,

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

Or,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0$$

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Particle in a one-dimensional box

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$$\frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0$$

This differential equation has two solutions

$$\psi_1 = A \exp\left(+\frac{i\sqrt{2mE}}{\hbar}x\right) \quad \& \quad \psi_2 = B \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right)$$

(A,B are constants)

A more general solution is, $\psi = \psi_1 + \psi_2$

$$\psi = A \exp\left(\frac{i\sqrt{2mE}}{\hbar}x\right) + B \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right) \quad (1)$$

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Particle in a one-dimensional box

Two boundary conditions are,

$$\psi = 0 \text{ when } x \leq 0$$

and

$$\psi = 0 \text{ when } x \geq L$$

Boundary condition - 1

$$\psi = 0 \text{ when } x = 0$$

So equation (1) becomes, $A + B = 0$ or $B = -A$

So, equation (1) can be written as,

$$\psi = A \left[\exp\left(\frac{i\sqrt{2mE}}{\hbar}x\right) - \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right) \right] \quad (2)$$

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Particle in a one-dimensional box

$$\psi = A \left[\exp\left(\frac{i\sqrt{2mE}}{\hbar}x\right) - \exp\left(-\frac{i\sqrt{2mE}}{\hbar}x\right) \right] \quad (2)$$

But from Euler's equation,

$$\exp(iy) - \exp(-iy) = 2i \sin y$$

So equation (2) becomes,

$$\psi = 2Ai \sin\left(\sqrt{2mE} \frac{x}{\hbar}\right)$$

Or,

$$\psi = C \sin\left(\sqrt{2mE} \frac{x}{\hbar}\right) \quad (3)$$



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Particle in a one-dimensional box

$$\psi = C \sin\left(\sqrt{2mE} \frac{x}{\hbar}\right) \quad (3)$$

Boundary condition – 2

$$\psi = 0 \text{ when } x = L$$

So equation (3) becomes, $\psi = C \sin\left(\sqrt{2mE} \frac{L}{\hbar}\right) = 0$

But $C \neq 0$, otherwise particle would be nowhere.

Hence, $\sin\left(\sqrt{2mE} \frac{L}{\hbar}\right) = 0 = \sin(n\pi)$

Or, $\left(\sqrt{2mE} \frac{L}{\hbar}\right) = (n\pi) \quad \text{Or, } \left(\sqrt{2mE} \frac{1}{\hbar}\right) = \frac{n\pi}{L} \quad (4)$

where, $n = 1, 2, 3, \dots$

$n = 0$ not acceptable, otherwise particle would be nowhere



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Particle in a one-dimensional box

$$\psi = C \sin\left(\sqrt{2mE} \frac{x}{\hbar}\right) \quad (3)$$

where, $n = 1, 2, 3, \dots$

So equation (4) becomes, $\psi_n = C \sin\left(\frac{n\pi x}{L}\right)$

Let us find the value of "C"

This can be done by using the condition of NORMALIZATION

$$\int_0^L \psi_n^* \psi_n dx = 1$$

Substituting the value of ψ_n in this equation, we get, $|C|^2 = \frac{2}{L}$

Choosing C as real number,

$$C = \sqrt{\frac{2}{L}}$$

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Particle in a one-dimensional box

$$\psi = C \sin\left(\sqrt{2mE} \frac{x}{\hbar}\right) \quad (3)$$

So equation (3) becomes, $\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ where, $n = 1, 2, 3, \dots$

In equation (4), it was shown, $\left(\sqrt{2mE_n} \frac{L}{\hbar}\right) = (n\pi)$

Or, $2mE_n = \frac{(n\pi\hbar)^2}{L^2}$

Or, $E_n = \frac{(n\pi\hbar)^2}{2mL^2} = \frac{n^2\pi^2}{2mL^2} \left(\frac{h}{2\pi}\right)^2 = \frac{n^2h^2}{8mL^2}$

Or, $E_n = \frac{n^2h^2}{8mL^2}$ where, $n = 1, 2, 3, \dots$

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Particle in a one-dimensional box

$$\psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{where, } n = 1, 2, 3, \dots$$

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{where, } n = 1, 2, 3, \dots$$

Since n may have only integral values, E_n may have only the special value given by the above equation.

The energy in this system is quantized and “ n ” is called a quantum number.

It is evident that quantization is introduced when the particle is restricted to interior of the box.

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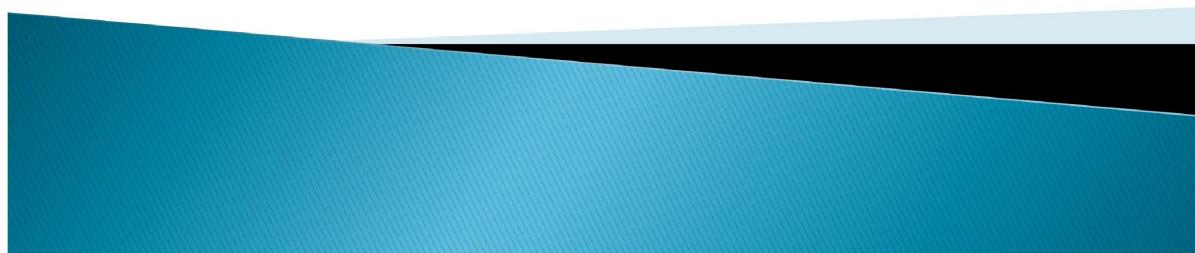
Foundation of Quantum Mechanics

(Part – 17)

Dr. Subhabrata Banerjee

Associate Professor

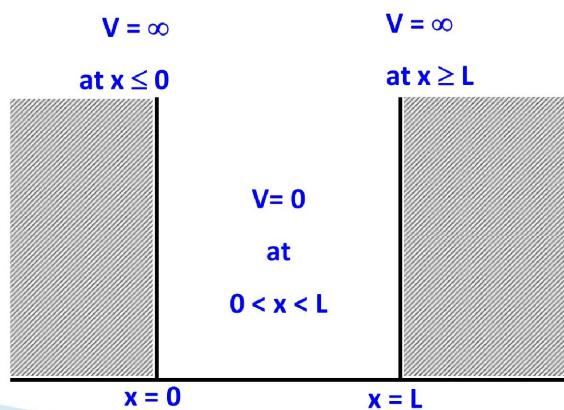
Department of Chemistry
Ramakrishna Mission V. C. College
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$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{where, } n = 1, 2, 3, \dots$$

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Particle in a one-dimensional box

$$E_n = \frac{n^2 h^2}{8mL^2} \quad \text{where, } n = 1, 2, 3, \dots$$

E_n proportional to n^2

$$\text{When, } n = 3 \quad E_3 = \frac{3^2 h^2}{8mL^2} = \frac{9h^2}{8mL^2}$$

$$E_n \propto n^2$$

$$\text{When, } n = 2 \quad E_2 = \frac{2^2 h^2}{8mL^2} = \frac{4h^2}{8mL^2}$$

$$\text{When, } n = 1 \quad E_1 = \frac{h^2}{8mL^2}$$

Energy corresponding to $n = 1$ is the lowest possible energy of this system. It is called zero-point energy (E_0).

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Particle in a one-dimensional box

n = 4

$$E_n = \frac{16h^2}{8mL^2}$$

$$E_n = \frac{n^2 h^2}{8mL^2}$$

where, n = 1,2,3,.....

n = 3

$$E_n = \frac{9h^2}{8mL^2}$$

n = 2

$$E_2 = \frac{4h^2}{8mL^2}$$

n = 1

$$E_1 = \frac{h^2}{8mL^2}$$

Gap between successive energy levels increases as "n" increases



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Particle in a one-dimensional box

n = 4

$$E_n = \frac{16h^2}{8mL^2}$$

$$E_n = \frac{n^2 h^2}{8mL^2} = n^2 E_0$$

Gap between successive energy levels

n = 3

$$E_n = \frac{9h^2}{8mL^2}$$

$$\Delta E = E_{n+1} - E_n$$

Or, $\Delta E = (2n+1)E_0$

n = 2

$$E_2 = \frac{4h^2}{8mL^2}$$

Or, $\Delta E = (2n+1) \frac{h^2}{8mL^2}$

$$\Delta E \propto (2n+1)$$

n = 1

$$E_1 = \frac{h^2}{8mL^2}$$

Gap between successive energy levels increases as "n" increases



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Particle in a one-dimensional box

Gap between successive energy levels

$$\Delta E = (2n+1) \frac{h^2}{8mL^2}$$

i.e.

$$\Delta E \propto \frac{1}{L^2}$$

This separation decreases as the length of the container increases, and is very small when the container has macroscopic dimensions. The separation of adjacent levels becomes zero when the length of the container is very long.

Atoms and molecules free to move in normal laboratory-sized vessels may therefore be treated as though their translational energy is **NOT quantized**.

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Particle in a one-dimensional box

Consider an electron, $m \approx 10^{-30} \text{ kg}$ within a box the size of an atom ($L \approx 10^{-10} \text{ m}$)

The zero-point energy,

$$E_O = E_1 = \frac{h^2}{8mL^2} = 5.5 \times 10^{-18} \text{ J} \approx 34 \text{ eV}$$

Spacing between first two energy levels is,

$$\Delta E = E_2 - E_1 = \frac{3h^2}{8mL^2} = 3E_O = 3 \times 34 \text{ eV} = 102 \text{ eV}$$

The energy quantization is readily observed here

What about a Macroscopic System?

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Particle in a one-dimensional box

Energy of n^{th} level

$$E_n = \frac{n^2 h^2}{8mL^2} = n^2 E_0$$

Gap between successive energy levels is,

$$\Delta E = (2n+1) \frac{h^2}{8mL^2}$$

Now

$$\frac{\Delta E}{E_n} = \frac{(2n+1)E_0}{n^2 E_0} = \frac{(2n+1)}{n^2}$$

In the classical limit, $n \rightarrow \infty$,

$$\frac{\Delta E}{E_n} = \frac{(2n+1)}{n^2} = 0$$

At higher values of “n”, the levels become so close together as to be practically indistinguishable.

The energy quantization is NOT detected here

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Particle in a one-dimensional box

Consider a ball bearing of mass, $m = 1 \text{ g}$ within a box 10 cm in length, having a velocity 1 cm/s

Zero point energy,

$$E_0 = \frac{h^2}{8mL^2} = 5.49 \times 10^{-63} \text{ J}$$

The kinetic energy of the ball bearing

$$= [0.5 \times (0.001\text{kg}) \times (0.01\text{m/s})^2] = 5 \times 10^{-8} \text{ J} = E_n$$

Let's find out the “n” corresponding to this energy

We know

$$E_n = n^2 E_0$$

Or,

$$\frac{E_n}{E_0} = n^2$$

Or,

$$n^2 = (5 \times 10^{-8}) / (5.49 \times 10^{-63}) \approx 10^{55}$$

Or,

$$n = 3 \times 10^{27}$$

The gap between “n” and “(n + 1)”

$$\Delta E = (2n+1)E_0 = [2(3 \times 10^{27}) + 1][5.49 \times 10^{-63}] \text{ J} \approx 3 \times 10^{-35} \text{ J}$$

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Particle in a one-dimensional box

Consider a ball bearing of mass, $m = 1 \text{ g}$ within a box 10 cm in length, having a velocity 1 cm/s

Zero point energy,

$$E_O = \frac{\hbar^2}{8mL^2} = 5.49 \times 10^{-63} \text{ J}$$

Value of "n" corresponding to this energy $n = 3 \times 10^{27}$

The gap between "n" and "(n + 1)" $\Delta E = (2n+1)E_O \approx 3 \times 10^{-35} \text{ J}$

Thus to observe the quantization in this system would require us to distinguish between an energy of $5 \times 10^{-8} \pm 3 \times 10^{-35} \text{ J}$

This type of precision is impossible, so we do not observe the quantization in the kinetic energy of the ball bearing

In the limit of high quantum numbers, the results of quantum mechanics approach those of classical mechanics.

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Foundation of Quantum Mechanics

(Part – 18)

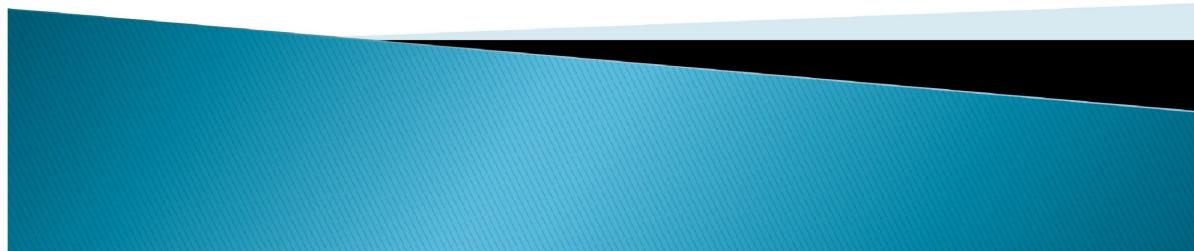
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



Particle in a one-dimensional box

For a particle in one-dimensional box, its kinetic energy,

$$E_n = \frac{n^2 h^2}{8mL^2} = \frac{p_x^2}{2m}$$

$$\text{Or, } p_x = \pm \frac{nh}{2L}$$

Again from de Broglie relation, $\lambda = h/p_x$ Or,

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

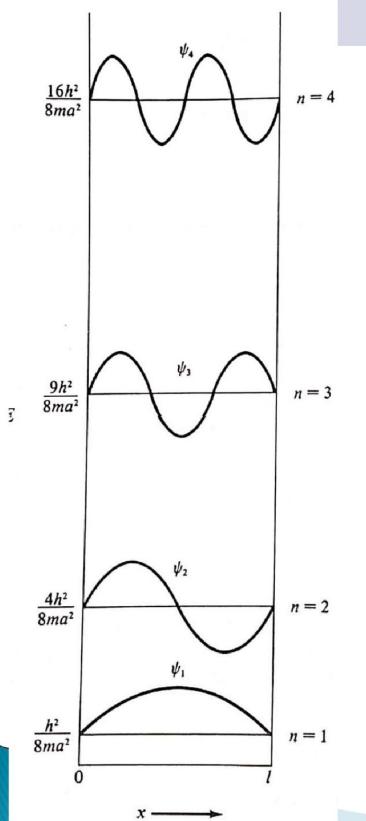
Comparing the two equations, $\frac{h}{\lambda} = \frac{nh}{2L}$ Or,

$$L = n \left(\frac{\lambda}{2} \right)$$

This requires that an integral number of half wavelengths fit exactly in the length “L”.



Particle in a one-dimensional box



$$L = n \left(\frac{\lambda}{2} \right)$$

This requires that an integral number of half wavelengths fit exactly in the length "L".

where, $n = 1, 2, 3, \dots$

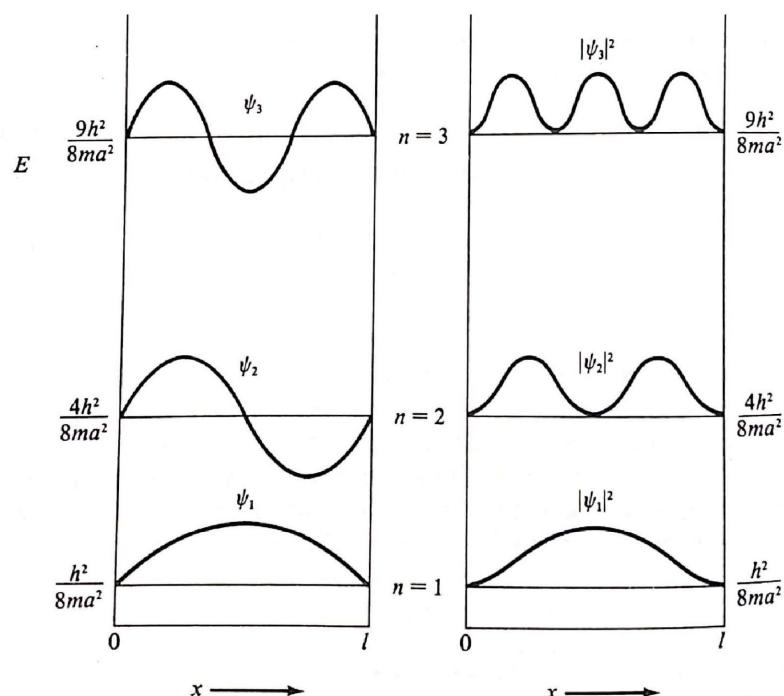
Or,

Comparing the two equations,

Or,

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Particle in a one-dimensional box



Energy
levels, wave
functions
and
probability
density

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Particle in a one-dimensional box

Energy of a particle of mass "m" in a one-dimensional box of length "L" can also be calculated using the classical expression of kinetic energy of the particle and the *de Broglie relation*

its kinetic energy

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

from de Broglie relation

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

Again,

$$L = n\left(\frac{\lambda}{2}\right) \quad \text{Or,} \quad \lambda = \left(\frac{2L}{n}\right)$$

substituting the values of "p" and "λ",

$$E = \frac{p^2}{2m} = \frac{1}{2m} \left(\frac{h}{\lambda} \right)^2 = \frac{1}{2m} \left(\frac{nh}{2L} \right)^2 = \frac{n^2 h^2}{8mL^2}$$

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Particle in a one-dimensional box

Expectation value of Position

$$\langle x \rangle = \int_0^L \psi_n^* x \psi_n dx$$

$$\text{Or, } \langle x \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) x \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

Standard Integral

$$\text{Or, } \langle x \rangle = \frac{2}{L} \int_0^L x \sin^2\left(\frac{n\pi x}{L}\right) dx \quad \int_0^L x \sin^2(\alpha x) dx = \left[\frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2} \right]$$

$$\text{Or, } \langle x \rangle = \left[\frac{x^2}{4} - \frac{x \sin 2\alpha x}{4\alpha} - \frac{\cos 2\alpha x}{8\alpha^2} \right] \quad \text{where, } \alpha = n\pi/L$$

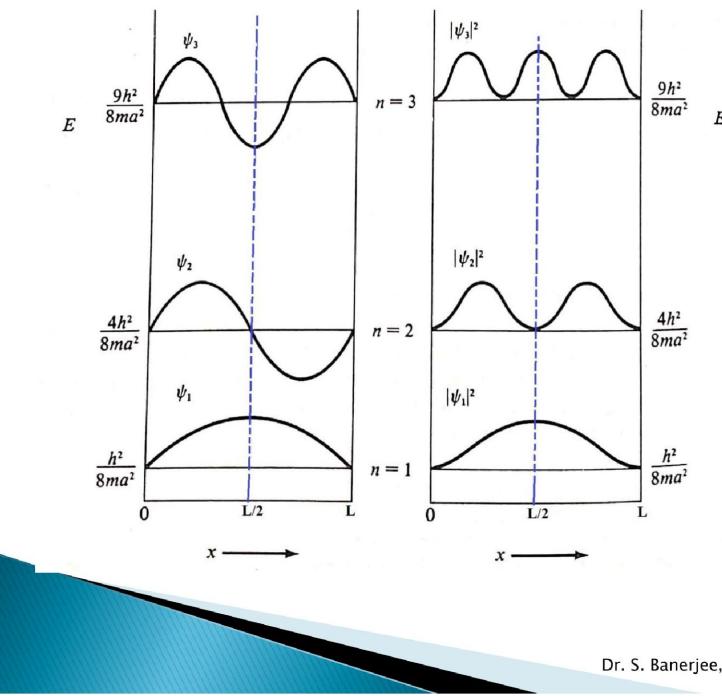
$$\text{Or, } \langle x \rangle = \frac{L}{2}$$

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Particle in a one-dimensional box

Expectation value of Position

$$\langle x \rangle = \frac{L}{2}$$



The result means that the average position of the particle is the middle of the box in all quantum states.

There is no conflict with the fact that at $L/2$ in the $n = 2, 4, 6, \dots$ states, because $\langle x \rangle$ is an average and not a probability.

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Particle in a one-dimensional box

Expectation value of p_x

$$\langle p_x \rangle = \int_0^L \psi_n^* p_x \psi_n dx$$

Or,
$$\langle p_x \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \left(-i\hbar \frac{\partial}{\partial x}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

Or,
$$\langle p_x \rangle = -i\hbar \frac{n\pi}{L^2} \int_0^L 2 \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx$$

Or,
$$\langle p_x \rangle = -i\hbar \frac{n\pi}{L^2} \int_0^L \sin\left(\frac{2n\pi x}{L}\right) dx$$

Or,
$$\langle p_x \rangle = 0$$

This value implies that the particle in the box is equally likely to move in either direction. The particle is moving back and forth, and so its average momentum for any value of "n" is zero

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Particle in a one-dimensional box

Expectation value of x^2

$$\langle x^2 \rangle = \int_0^L \psi_n^* x^2 \psi_n dx$$

Or, $\langle x^2 \rangle = \frac{2}{L} \int_0^L x^2 \sin^2\left(\frac{n\pi x}{L}\right) dx$

Or, $\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$

Using Standard Integral

(where, $\alpha = n\pi/L$)

Standard Integral

$$\int_0^L x^2 \sin^2(\alpha x) dx = \left[\frac{x^3}{6} - \left(\frac{x^2}{4\alpha} - \frac{1}{8\alpha^2} \right) \sin 2\alpha x - \frac{x \cos 2\alpha x}{4\alpha^2} \right]$$

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Particle in a one-dimensional box

Expectation value of x^2

$$\langle x^2 \rangle = \frac{L^2}{3} - \frac{L^2}{2n^2\pi^2}$$

Expectation value of x

$$\langle x \rangle = \frac{L}{2}$$

Uncertainty in measurement of Position, Δx

$$\Delta x = (\langle x^2 \rangle - \langle x \rangle^2)^{1/2}$$

Or, $\Delta x = \left(\frac{L^2}{3} - \frac{L^2}{2n^2\pi^2} - \frac{L^2}{4} \right)^{1/2}$

Or, $\Delta x = \frac{L}{2\pi n} \left(\frac{n^2\pi^2}{3} - 2 \right)^{1/2}$

It is found that Δx is directly proportional to L . This simply means that the larger the region over which the particle can be found, the greater is the uncertainty in position.

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Particle in a one-dimensional box

Expectation value of p_x^2

$$\langle p_x^2 \rangle = \int_0^L \psi_n^* p_x^2 \psi_n dx$$

Or,

$$\langle p_x^2 \rangle = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \left(-\hbar^2 \frac{\partial^2}{\partial x^2}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx$$

Or,

$$\langle p_x^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{L^2} \frac{2}{L} \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx$$

Or,

$$\langle p_x^2 \rangle = \frac{2n^2 \pi^2 \hbar^2}{L^3} \cdot \frac{L}{2}$$

Or,

$$\langle p_x^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{L^2}$$

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Particle in a one-dimensional box

Expectation value of p_x^2

$$\langle p_x^2 \rangle = \frac{n^2 \pi^2 \hbar^2}{L^2}$$

Expectation value of p_x

$$\langle p_x \rangle = 0$$

Uncertainty in measurement of momentum, Δp_x

$$\Delta p_x = \left(\langle p_x^2 \rangle - \langle p_x \rangle^2 \right)^{1/2}$$

Or,

$$\Delta p_x = \left(\frac{n^2 \pi^2 \hbar^2}{L^2} - 0 \right)^{1/2}$$

Or,

$$\Delta p_x = \frac{n\pi\hbar}{L}$$

It is evident that Δp_x is inversely proportional to length of the box L. Thus, the more we try to localize the particle, the greater is the uncertainty in momentum.

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Particle in a one-dimensional box

Uncertainty in measurement of momentum, Δp_x

$$\Delta p_x = \frac{n\pi\hbar}{L}$$

Uncertainty in measurement of Position, Δx

$$\Delta x = \frac{L}{2\pi n} \left(\frac{n^2 \pi^2}{3} - 2 \right)^{1/2}$$

$$\Delta x \Delta p_x = \frac{L}{2\pi n} \left(\frac{n^2 \pi^2}{3} - 2 \right)^{1/2} \frac{n\pi\hbar}{L}$$

Or, $\Delta x \Delta p_x = \frac{\hbar}{2} \left(\frac{n^2 \pi^2}{3} - 2 \right)^{1/2}$

Or, $\Delta x \Delta p_x = 0.568\hbar$ (for $n = 1$)

Or, $\Delta x \Delta p_x > \frac{\hbar}{2}$

This inequality is the statement of the Heisenberg's Uncertainty Principle for the particle in a box.

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Foundation of Quantum Mechanics

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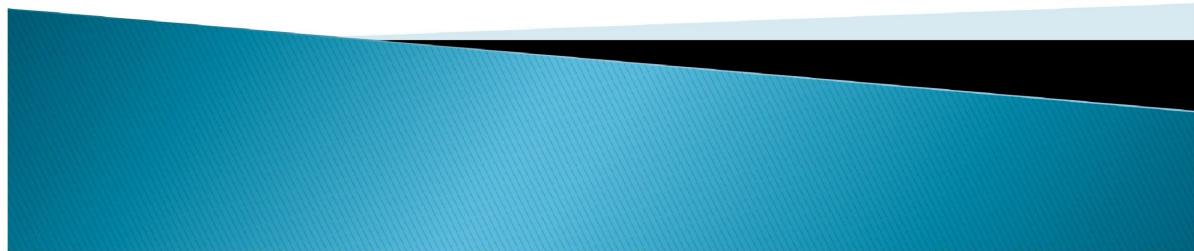
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



Particle in a one-dimensional box

Average value (or expectation value) of energy for the particle in a one-dimensional box with length L

The particle in a one-dimensional box only has kinetic energy $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$

$$\langle E \rangle = \int_0^L \psi^* \hat{H} \psi dx = \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} dx$$

$$= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{\hbar^2}{2m} \right) \int_0^L 2 \sin^2 \frac{n\pi x}{L} dx$$

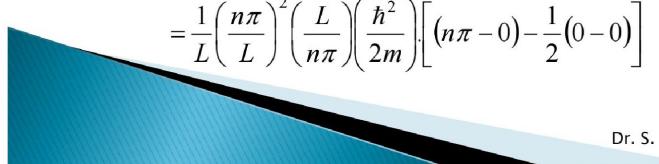
$$\langle E \rangle = \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{n\pi} \right) \left(\frac{\hbar^2}{2m} \right) \int_0^{n\pi} 2 \sin^2 z dz$$

$$= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{n\pi} \right) \left(\frac{\hbar^2}{2m} \right) \int_0^{n\pi} (1 - \cos 2z) dz$$

$$= \frac{1}{L} \left(\frac{n\pi}{L} \right)^2 \left(\frac{L}{n\pi} \right) \left(\frac{\hbar^2}{2m} \right) \left[(n\pi - 0) - \frac{1}{2}(0 - 0) \right] \quad \text{Or,} \quad \langle E \rangle = \frac{n^2 \hbar^2}{8mL^2}$$

Let, $\frac{n\pi x}{L} = z$; hence, $dx = \frac{L}{n\pi} dz$

When, $x = 0$, $z = 0$ and when, $x = L$, $z = n\pi$



Particle in a one-dimensional box

Average value (or expectation value) of $\langle E^2 \rangle$

operator corresponding to E^2 is

$$\hat{H}^2 = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right)^2 = \left(\frac{\hbar^2}{2m} \right)^2 \frac{d^4}{dx^4}$$

$$\langle E^2 \rangle = \int_0^L \psi * \hat{H}^2 \psi dx = \int_0^L \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right)^2 \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} dx$$

$$= \frac{1}{L} \left(\frac{\hbar^4}{4m^2} \right) \left(\frac{n\pi}{L} \right)^4 \cdot \int_0^L 2 \sin^2 \frac{n\pi x}{L} dx$$

$$\langle E^2 \rangle = \frac{1}{L} \left(\frac{\hbar^4}{4m^2} \right) \left(\frac{n\pi}{L} \right)^4 \left(\frac{L}{n\pi} \right) \cdot \int_0^{n\pi} 2 \sin^2 z dz$$

$$= \frac{1}{L} \left(\frac{\hbar^4}{4m^2} \right) \left(\frac{n\pi}{L} \right)^4 \left(\frac{L}{n\pi} \right) \cdot \int_0^{n\pi} (1 - \cos 2z) dz$$

$$= \frac{1}{L} \left(\frac{\hbar^4}{4m^2} \right) \left(\frac{n\pi}{L} \right)^4 \left(\frac{L}{n\pi} \right) \cdot \left[(n\pi - 0) - \frac{1}{2}(0 - 0) \right]$$

$$= \frac{1}{L} \left(\frac{\hbar^4}{4m^2} \right) \left(\frac{n\pi}{L} \right)^4 \left(\frac{L}{n\pi} \right) \cdot n\pi = \frac{n^4 \pi^4}{4m^2 L^4} \hbar^4 = \frac{n^4 \pi^4}{4m^2 L^4} \left(\frac{h}{2\pi} \right)^4 = \frac{n^4 h^4}{64m^2 L^4} = \left(\frac{n^2 h^2}{8mL^2} \right)^2 = \langle E \rangle^2$$

Let, $\frac{n\pi x}{L} = z$; hence, $dx = \frac{L}{n\pi} dz$

When, $x = 0$, $z = 0$ and when, $x = L$, $z = n\pi$

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Particle in a one-dimensional box

Average value (or expectation value) of $\langle E^2 \rangle$

$$\langle E^2 \rangle = \left(\frac{n^2 h^2}{8mL^2} \right)^2$$

Average value (or expectation value) of $\langle E \rangle$

$$\langle E \rangle = \frac{n^2 h^2}{8mL^2}$$

So, $\langle E^2 \rangle - \langle E \rangle^2 = 0$

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Particle in a one-dimensional box

Wave functions of a particle in a one-dimensional box forms a **orthonormal** set

To be a orthonormal set,
each of the wave function must be **normalized**, and
any two wavefunction must be **orthogonal**

$$\int_0^L \psi_n^* \psi_n dx = 1$$

and

$$\int_0^L \psi_n^* \psi_m dx = 0 \quad \text{where, } m \neq n$$

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Particle in a one-dimensional box

Wave functions of a particle in a 1-D box forms a **orthonormal** set

Each of the wave function must be **normalized**

$$\begin{aligned} \int_0^L \psi_n^* \psi_n dx &= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{1}{L} \int_0^L 2 \sin^2\left(\frac{n\pi x}{L}\right) dx \\ &= \frac{1}{L} \int_0^L \left[1 - \cos\left(\frac{2n\pi x}{L}\right)\right] dx \\ &= 1 \end{aligned}$$

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Particle in a one-dimensional box

Wave functions of a particle in a 1-D box forms a **orthonormal set**

Any two wave function must be **orthogonal**

$$\begin{aligned}\int_0^L \psi_n^* \psi_m dx &= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \sqrt{\frac{2}{L}} \sin\left(\frac{m\pi x}{L}\right) dx \quad \text{where, } m \neq n \\ &= \frac{1}{L} \int_0^L 2 \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{m\pi x}{L}\right) dx \\ &= \frac{1}{L} \int_0^L \left[\cos(n-m)\frac{\pi x}{L} - \cos(n+m)\frac{\pi x}{L} \right] dx \\ &= 0\end{aligned}$$

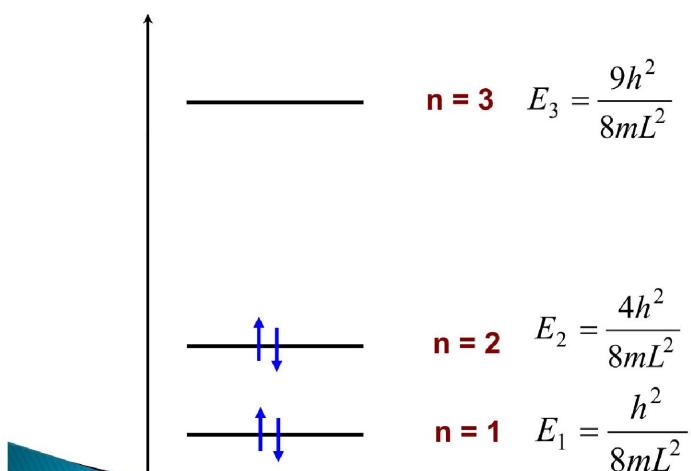
Note: $2\sin A \sin B = \cos(A-B) - \cos(A+B)$

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Particle in a one-dimensional box

The model of a particle in a one-dimensional box has been applied to the π electrons in linear conjugated hydrocarbons.

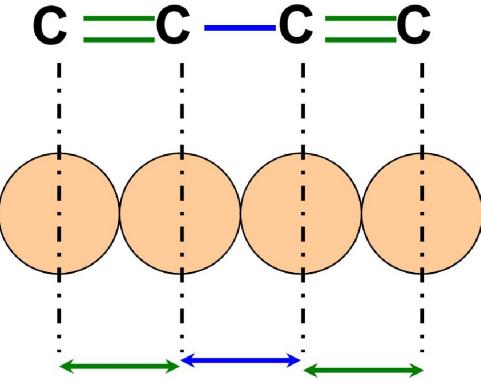
Consider butadiene, which has **four π electrons**



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Particle in a one-dimensional box

Consider butadiene, which has four π electrons



L = two C=C bond lengths ($2 \times 135 \text{ pm}$)

+

one C – C bond (154 pm)

+

the distance of a carbon atom radius at each end ($2 \times 77 \text{ pm} = 154 \text{ pm}$)*

or,

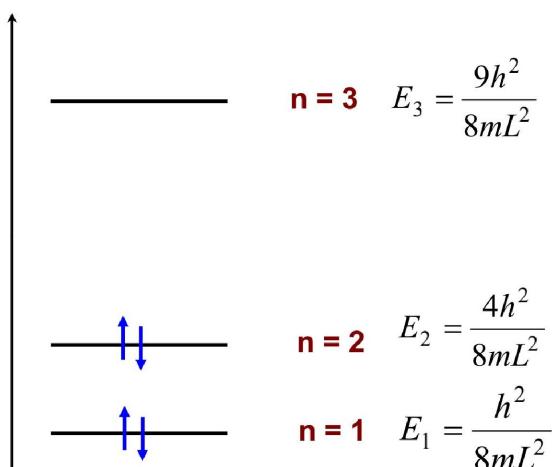
L = 578 pm

Although butadiene, like all polyenes, is not a linear molecule, it may be assumed that the π electrons in butadiene move along a straight line whose length, **L**

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Particle in a one-dimensional box

Consider butadiene, which has four π electrons



Butadiene has an absorption band at $4.61 \times 10^4 \text{ cm}^{-1}$

$$\Delta E = (3^2 - 2^2)E_O = \frac{5h^2}{8mL^2}$$

or, $\Delta E = \frac{5(6.626 \times 10^{-34})^2}{8(9.109 \times 10^{-31})(578 \times 10^{-12})^2}$

or, $\Delta E = 9.02 \times 10^{-19} \text{ J}$

or, $\bar{v} = \frac{\Delta E}{hc} = 4.54 \times 10^4 \text{ cm}^{-1}$

So this simple model, called **free-electron model**, can somewhat successfully explain the absorption spectrum of butadiene

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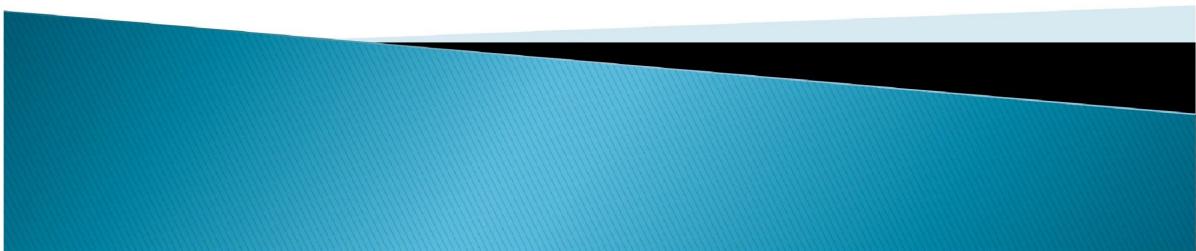


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Foundation of Quantum Mechanics

(Part – 20)

Dr. Subhabrata Banerjee
Associate Professor
Department of Chemistry
Ramakrishna Mission V. C. College
Rahara



Particle in a three-dimensional box

Let us consider a particle confined in a three – dimensional box

We also assume that the potential energy (V) is defined as follows

$$V = 0 \quad \text{at} \quad 0 < x < 0; \quad 0 < y < 0; \quad 0 < z < 0$$

$$V = \infty \quad \text{at} \quad x \leq 0, x \geq a; \quad y \leq 0, y \geq b; \quad z \leq 0, z \geq c$$

The Schrodinger equation

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

$$\text{Or,} \quad -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = E\Psi$$

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Let us assume now that ψ is a product of functions of individual coordinates

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

$$\text{Then,} \quad \frac{\partial^2 \Psi}{\partial x^2} = Y(y)Z(z) \frac{d^2 X(x)}{dx^2}$$

$$\frac{\partial^2 \Psi}{\partial y^2} = X(x)Z(z) \frac{d^2 Y(y)}{dy^2}$$

$$\frac{\partial^2 \Psi}{\partial z^2} = X(x)Y(y) \frac{d^2 Z(z)}{dz^2}$$

Let us insert these values in equation

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = E\Psi$$

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$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \Psi = E\Psi$$

Or, $-\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) X(x)Y(y)Z(z) = EX(x)Y(y)Z(z)$

Or, $-\frac{\hbar^2}{2m} \left[Y(y)Z(z) \frac{d^2X(x)}{dx^2} + X(x)Z(z) \frac{d^2Y(y)}{dy^2} + X(x)Y(y) \frac{d^2Z(z)}{dz^2} \right] = EX(x)Y(y)Z(z)$

dividing both sides by $X(x)Y(y)Z(z)$,

$$-\frac{\hbar^2}{2m} \left[\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} + \frac{1}{Z(z)} \frac{d^2Z(z)}{dz^2} \right] = E$$

Or, $-\frac{\hbar^2}{2m} \left[\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} + \frac{1}{Z(z)} \frac{d^2Z(z)}{dz^2} \right] = E_x + E_y + E_z$

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$$-\frac{\hbar^2}{2m} \left[\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} + \frac{1}{Z(z)} \frac{d^2Z(z)}{dz^2} \right] = E_x + E_y + E_z$$

$$-\frac{\hbar^2}{2m} \left[\frac{1}{X(x)} \frac{d^2X(x)}{dx^2} \right] = E_x \quad \text{Or, } \frac{d^2X(x)}{dx^2} + \frac{2mE_x}{\hbar^2} X(x) = 0 \quad \text{Or, } X(x) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a}$$

$$-\frac{\hbar^2}{2m} \left[\frac{1}{Y(y)} \frac{d^2Y(y)}{dy^2} \right] = E_y \quad \text{Or, } \frac{d^2Y(y)}{dy^2} + \frac{2mE_y}{\hbar^2} Y(y) = 0 \quad \text{Or, } Y(y) = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b}$$

$$-\frac{\hbar^2}{2m} \left[\frac{1}{Z(z)} \frac{d^2Z(z)}{dz^2} \right] = E_z \quad \text{Or, } \frac{d^2Z(z)}{dz^2} + \frac{2mE_z}{\hbar^2} Z(z) = 0 \quad \text{Or, } Z(z) = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}$$

$$\Psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

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Particle in a three-dimensional box

$$-\frac{\hbar^2}{2m} \left[\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} + \frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2} + \frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} \right] = E_x + E_y + E_z$$

$$\Psi(x, y, z) = X(x)Y(y)Z(z)$$

Or, $\Psi(x, y, z) = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}$

Or, $\Psi(x, y, z) = \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$

$$E = E_x + E_y + E_z$$

Or, $E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$

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Particle in a three-dimensional box

DEGENERACY

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

When, $a = b = c = L$, (i.e. the box is cubic)

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2}$$

So, $E \propto (n_x^2 + n_y^2 + n_z^2)$

This creates the interesting case of **degeneracy**

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Particle in a three-dimensional box

DEGENERACY

For a CUBIC box

$$E = \left(n_x^2 + n_y^2 + n_z^2 \right) \frac{h^2}{8mL^2}$$

n_x	n_y	n_z	$n_x^2 + n_y^2 + n_z^2$	$E = \left(n_x^2 + n_y^2 + n_z^2 \right) \frac{h^2}{8mL^2}$
1	1	1	3	$E = \frac{3h^2}{8mL^2}$
2	1	1	6	$E = \frac{6h^2}{8mL^2}$
1	2	1	6	
1	1	2	6	
2	2	1	9	$E = \frac{9h^2}{8mL^2}$
2	1	2	9	
1	2	2	9	
3	1	1	11	$E = \frac{11h^2}{8mL^2}$
1	3	1	11	
1	1	3	11	

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Particle in a three-dimensional box : Degeneracy

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = \frac{6h^2}{8mL^2}$$

So, the energy states are different, but the energy eigen value is same for all the three states. This energy level is **three – fold degenerate**

$$E_{2,2,1} = E_{2,1,2} = E_{1,2,2} = \frac{9h^2}{8mL^2}$$

This energy level is **three – fold degenerate**

This is to be noted that the degeneracy occurs because the symmetry is introduced when the general rectangular box becomes a cube and that the degeneracy is “lifted” when the symmetry is destroyed by making the sides of different lengths.

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Particle in a three-dimensional box

What is the degree of degeneracy of the energy level for a particle in a cubic box with $E = \frac{51h^2}{8mL^2}$?

$$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2}$$

and $E = 51 \frac{h^2}{8mL^2}$

Comparing, $(n_x^2 + n_y^2 + n_z^2) = 51$

n_x	n_y	n_z	$n_x^2 + n_y^2 + n_z^2$	$E = (n_x^2 + n_y^2 + n_z^2) \frac{h^2}{8mL^2}$
7	1	1	51	
1	7	1	51	
1	1	7	51	
5	1	1	51	
1	5	1	51	
1	1	5	51	

This energy level is 6 - fold degenerate

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Particle in a two-dimensional box

For a two - dimensional rectangular box

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2}$$

When, $a = b = L$, (i.e. the box is square)

$$E = (n_x^2 + n_y^2) \frac{h^2}{8mL^2}$$

So,

DEGENERACY may appear
in at least one of the
energy levels

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Particle in a three-dimensional box

Let us consider a particle in a three – dimensional box, where, $a = b = 1.5 c$.

Calculate the degree of degeneracy of the first four energy levels.

DIY



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Foundation of Quantum Mechanics

(Part – 21)

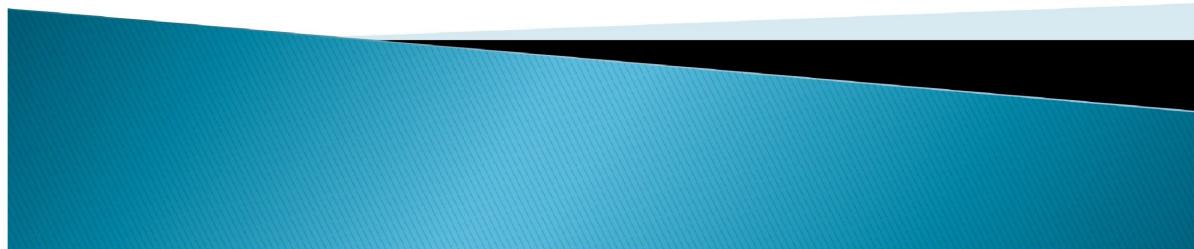
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



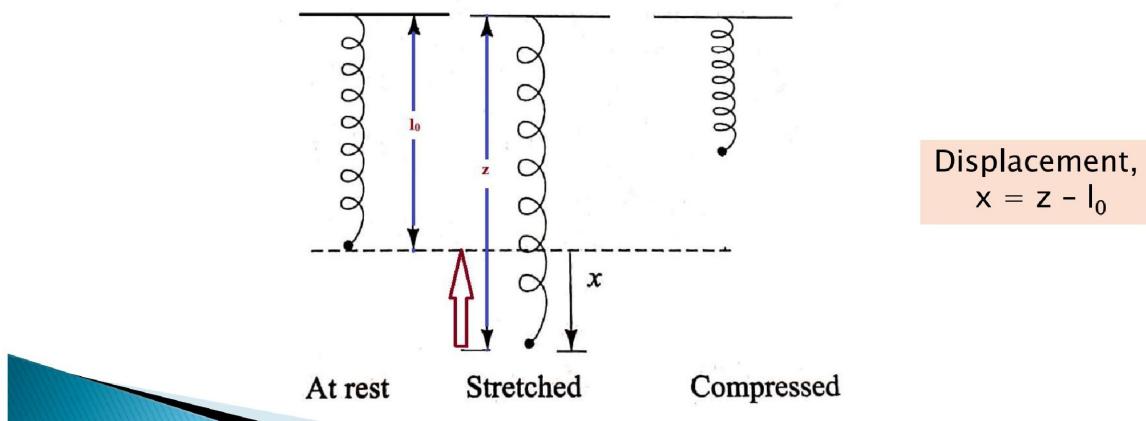
THE HARMONIC OSCILLATOR

The vibration of a diatomic molecule can be described by a Harmonic Oscillator

CLASSICAL MECHANICS

A harmonic oscillator obeys **Hooke's Law**

Let us consider a mass "m" connected to a wall by a spring
the equilibrium (or undisturbed) length of the spring = l_0



THE HARMONIC OSCILLATOR

A harmonic oscillator obeys **Hooke's Law**

force is directly proportional to the displacement

$$f = -k(z - l_0)$$

From **Newton's law**,

force = mass × acceleration

Or, $f = m \times a$

Or, $-k(z - l_0) = m \frac{d^2 z}{dt^2}$

Now, $\frac{d^2 x}{dt^2} = \frac{d^2 z}{dt^2}$

Displacement, $x = z - l_0$



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$$-k(z - l_0) = m \frac{d^2 z}{dt^2}$$

Or, $-k(z - l_0) = m \frac{d^2 z}{dt^2}$

Or, $-kx = m \frac{d^2 x}{dt^2}$

Or, $m \frac{d^2 x}{dt^2} + kx = 0$

Or, $\frac{d^2 x}{dt^2} + \left(\frac{k}{m}\right)x = 0$

“ k ” is called the force constant of the spring

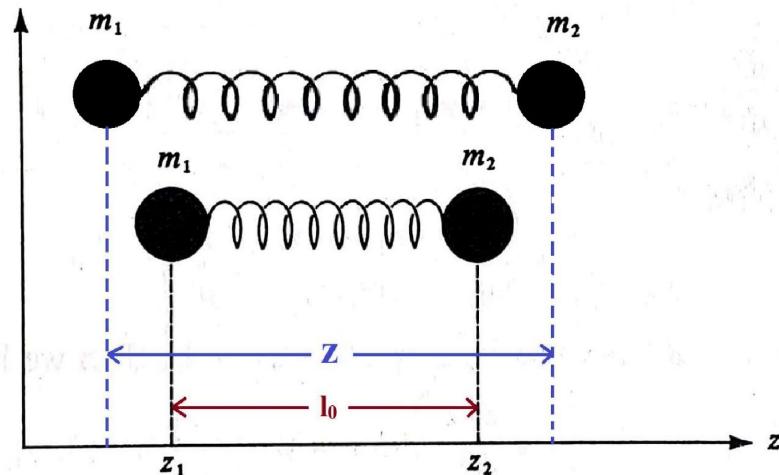
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$



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But a diatomic molecule has two masses, say m_1 and m_2 , as shown in the figure. Two masses are connected by a spring



Let us consider
the stretching of
the spring,
i.e. $Z_2 - Z_1 > l_0$

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Two masses are connected by a spring
For the two masses, we have **two equations**:

$$m_1 \frac{d^2 Z_1}{dt^2} = k(Z_2 - Z_1 - l_0) \quad \text{Or,} \quad \frac{d^2 Z_1}{dt^2} = \frac{k}{m_1}(Z_2 - Z_1 - l_0)$$

$$m_2 \frac{d^2 Z_2}{dt^2} = -k(Z_2 - Z_1 - l_0) \quad \text{Or,} \quad \frac{d^2 Z_2}{dt^2} = -\frac{k}{m_2}(Z_2 - Z_1 - l_0)$$

Subtracting one Equation from the other

$$\frac{d^2 Z_2}{dt^2} - \frac{d^2 Z_1}{dt^2} = -\frac{k}{m_2}(Z_2 - Z_1 - l_0) - \frac{k}{m_1}(Z_2 - Z_1 - l_0)$$

Or, $\frac{d^2}{dt^2}(Z_2 - Z_1) = -k\left(\frac{1}{m_2} + \frac{1}{m_1}\right)(Z_2 - Z_1 - l_0)$

Or, $\frac{d^2 x}{dt^2} = -\frac{k}{\mu}x$ Or, $\frac{d^2 x}{dt^2} + \frac{k}{\mu}x = 0$

$$\left(\frac{1}{m_2} + \frac{1}{m_1} \right) = \frac{1}{\mu}$$

and

$$x = (Z_2 - Z_1 - l_0)$$

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A single mass "m" connected to a wall by a spring

$$\frac{d^2x}{dt^2} + \left(\frac{k}{m}\right)x = 0$$

For two masses are connected by a spring

$$\frac{d^2x}{dt^2} + \frac{k}{\mu}x = 0$$

The motion of the two-body system must depend only on the relative separation of the two masses



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Potential energy, V, of a harmonic oscillator

$$f = -\frac{dV}{dx}$$

Or, $-kx = -\frac{dV}{dx}$

Or, $dV = kx \cdot dx$

Integrating both sides, $V = \frac{1}{2}kx^2 + \text{constant}$

at $x = 0, V = 0$ So, constant = 0

expression for the potential energy

$$V = \frac{1}{2}kx^2$$



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QUANTUM MECHANICS

We know that classical energy of a Harmonic Oscillator

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2$$

So, the Hamiltonian operator

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2$$

The Schrodinger equation for a Harmonic Oscillator

$$\hat{H}\psi = E\psi \quad \text{Or,} \quad \left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \right] \psi = E\psi$$

$$\text{Or,} \quad \frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2}kx^2 \right] \psi = 0$$

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QUANTUM MECHANICS

The Schrodinger equation for a Harmonic Oscillator

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2}kx^2 \right] \psi = 0$$

The Schrodinger equation for a Harmonic oscillator can be solved exactly

$$E_n = \left(n + \frac{1}{2} \right) h\nu \quad \text{where, } n = 0, 1, 2, \dots$$

And,

$$\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$$

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$$E_n = \left(n + \frac{1}{2} \right) h\nu \quad \text{where, } n = 0, 1, 2, \dots$$

Energy levels of a harmonic oscillator is quantized

When, $n = 0 \rightarrow E_0 = \frac{1}{2} h\nu$

$n = 1 \rightarrow E_1 = \frac{3}{2} h\nu$

$n = 2 \rightarrow E_2 = \frac{5}{2} h\nu$

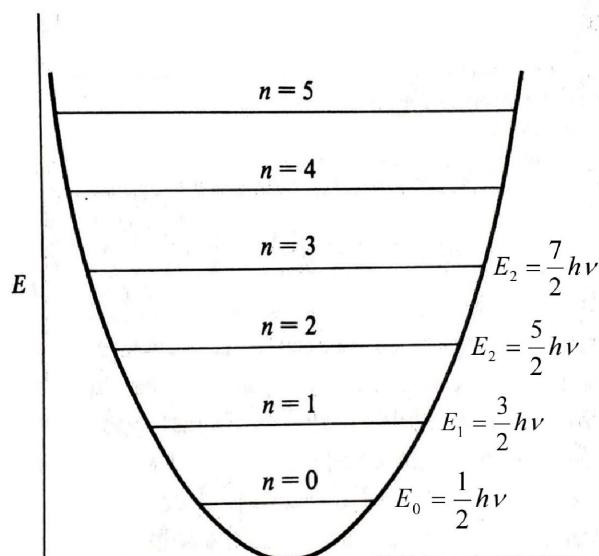
Etc.



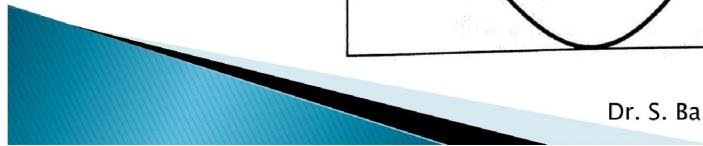
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$$E_n = \left(n + \frac{1}{2} \right) h\nu \quad \text{where, } n = 0, 1, 2, \dots$$



The lowest possible value of the energy, Zero - point energy, corresponds to, $n = 0$



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QUANTUM MECHANICS

The gap between two adjacent allowed energy levels

$$\Delta E = E_{n+1} - E_n$$

Or,

$$\Delta E = \left(n + 1 + \frac{1}{2} \right) h\nu - \left(n + \frac{1}{2} \right) h\nu$$

Or,

$$\Delta E = h\nu$$

ΔE is independent of "n".

So energy levels are equispaced

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It can be shown that for a harmonic oscillator, the allowed transition between energy levels occur only if $\Delta n = \pm 1$. Such a condition is called **SELECTION RULE**

$$\Delta E = h\nu_{obs}$$

Or,

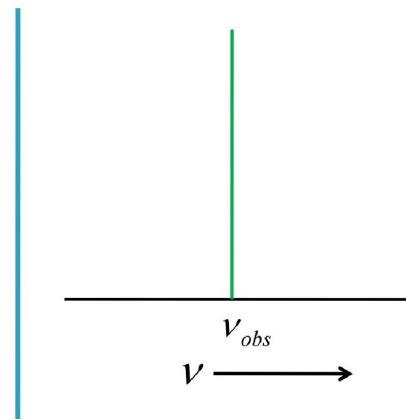
$$E_{n+1} - E_n = h\nu_{obs}$$

Or,

$$h\nu = h\nu_{obs}$$

Or,

$$\nu = \nu_{obs}$$



So spectrum associated with a harmonic oscillator consists of just one line

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Zero – point energy is NOT zero

This is in accordance with the **Uncertainty Principle**

Energy of a Harmonic Oscillator = K.E. + P.E.

If it were zero !!!

K.E. = 0 and P.E. = 0

$$\text{Or, } \frac{p^2}{2m} = 0$$
$$\text{Or, } p = 0$$
$$\text{Or, } V = \frac{1}{2}kx^2$$
$$\text{Or, } x = 0$$

Value of momentum exactly known

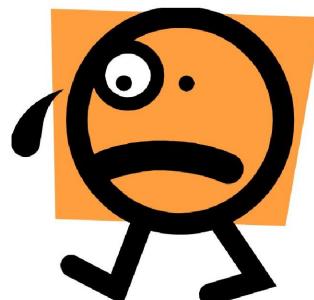
Value of position exactly known



So, no uncertainty in both position and momentum

This is against Uncertainty Principle !!!

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Foundation of Quantum Mechanics

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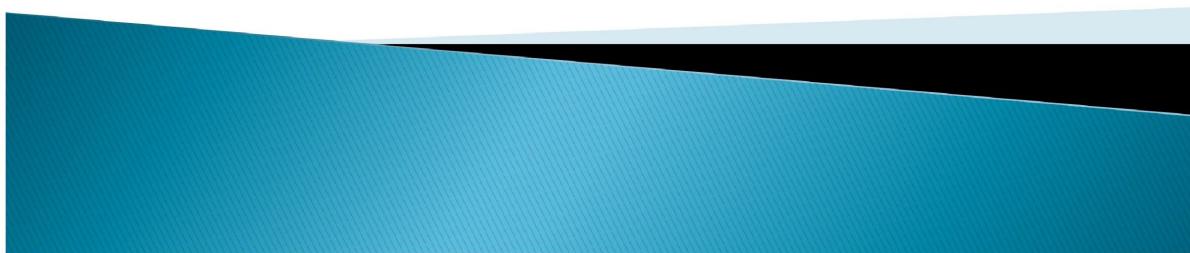
Dr. Subhabrata Banerjee

Associate Professor

Department of Chemistry

Ramakrishna Mission V. C. College

Rahara



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The Schrodinger equation for a Harmonic Oscillator

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

Or, $\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 \right] \psi = E\psi$

Or, $\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2} kx^2 \right] \psi = 0$

$$H = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$$

$$E_n = \left(n + \frac{1}{2} \right) h\nu \quad \text{where, } n = 0, 1, 2, \dots$$



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The Schrodinger equation for a Harmonic Oscillator

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2} kx^2 \right] \psi = 0$$

The general formula for the n^{th} wave function is as follows

$$\psi_n = \left(\frac{2m\nu}{\hbar} \right)^{1/4} (2^n n!)^{-1/2} H_n(y) \exp\left(-\frac{y^2}{2}\right)$$

Each function consists of a polynomial, called a Hermite Polynomial

The first six *Hermite polynomials* are listed in the table

n	$H_n(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
4	$16y^4 - 48y^2 + 12$
5	$32y^5 - 160y^3 + 120y$

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The Schrodinger equation for a Harmonic Oscillator

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left[E - \frac{1}{2} kx^2 \right] \psi = 0$$

The first four wave functions of harmonic oscillator are as follows

$$\psi_0 = \left(\frac{\alpha}{\pi} \right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\psi_1 = \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x \exp\left(-\frac{\alpha x^2}{2}\right)$$

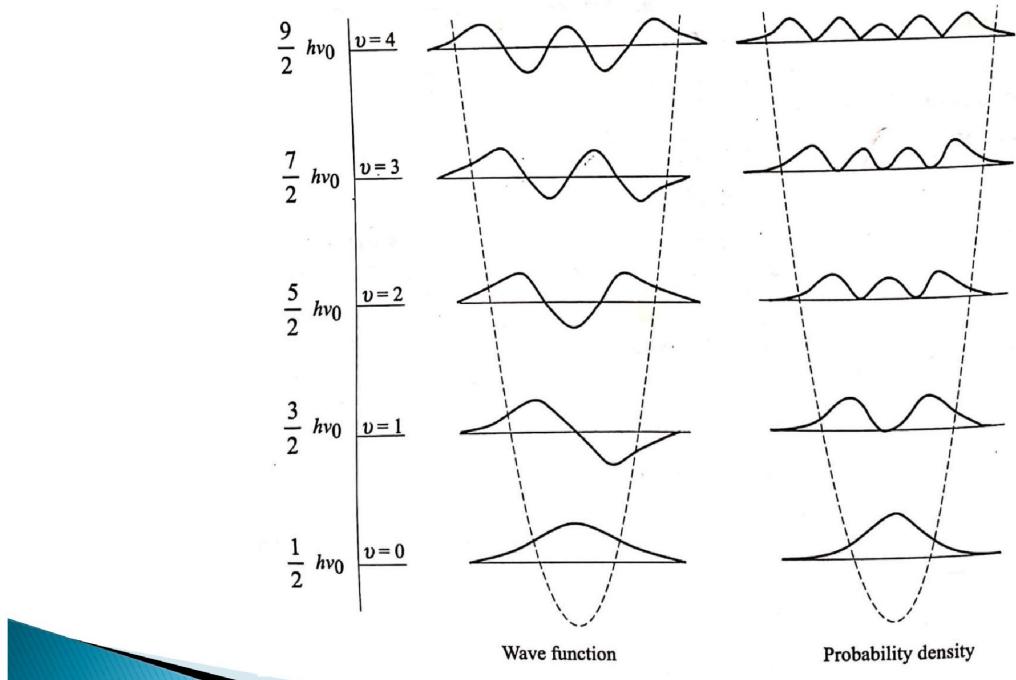
$$\psi_2 = \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\psi_3 = \left(\frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\alpha = \frac{(k\mu)^{1/2}}{\hbar}$$

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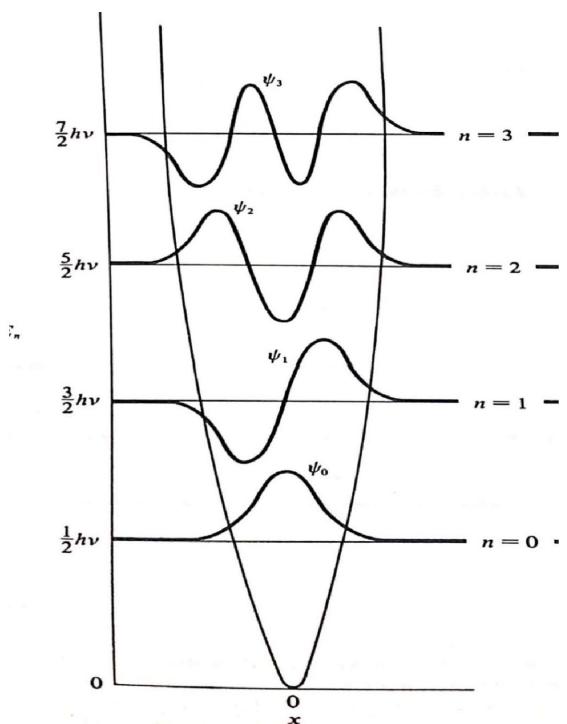
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$$\psi_3 = \left(\frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\psi_2 = \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\psi_1 = \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x \exp\left(-\frac{\alpha x^2}{2}\right)$$

$$\psi_0 = \left(\frac{\alpha}{\pi} \right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right)$$



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$$\psi_3 = \left(\frac{\alpha^3}{9\pi} \right)^{1/4} (2\alpha x^3 - 3x) \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{odd function}$$

$$\psi_2 = \left(\frac{\alpha}{4\pi} \right)^{1/4} (2\alpha x^2 - 1) \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{even function}$$

$$\psi_1 = \left(\frac{4\alpha^3}{\pi} \right)^{1/4} x \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{odd function}$$

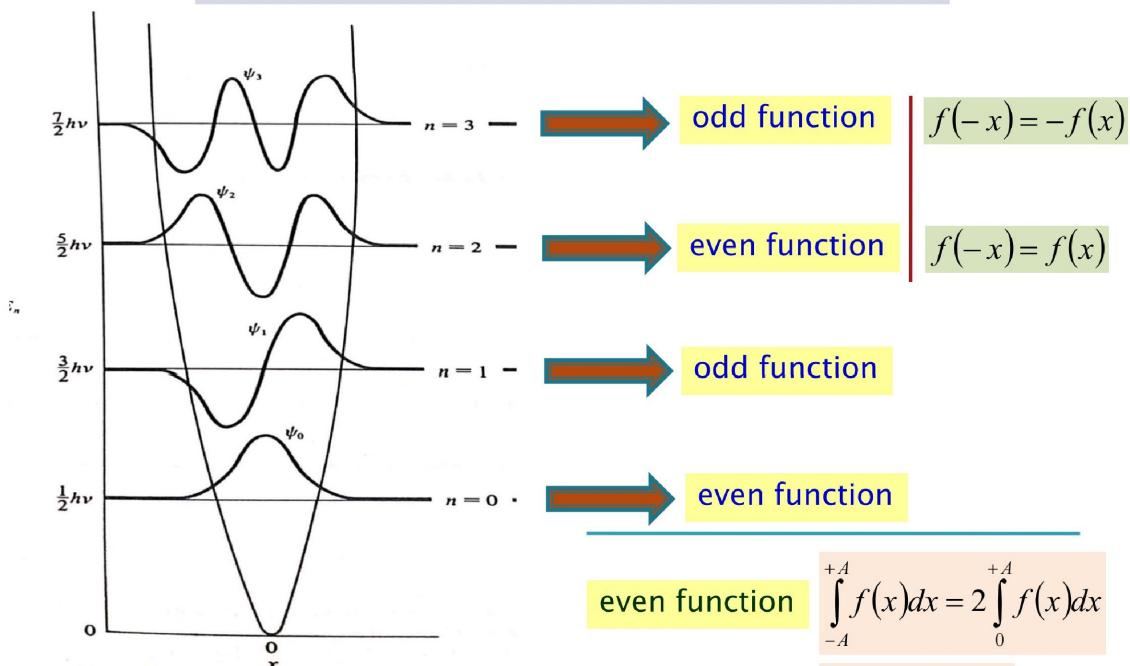
$$\psi_0 = \left(\frac{\alpha}{\pi} \right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{even function}$$

$$f(-x) = f(x) \quad \leftrightarrow \quad \text{even function}$$

$$f(-x) = -f(x) \quad \leftrightarrow \quad \text{odd function}$$

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$$\int_{-A}^{+A} f(x) dx = 2 \int_0^{+A} f(x) dx$$

$$\int_{-A}^{+A} f(x) dx = 0$$

Dr. S. Banerjee, RKMVCC, Rahara

THE HARMONIC OSCILLATOR

Show that ψ_0 is normalized

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{even function} \quad f(-x) = f(x)$$

$$\int_{-\infty}^{+\infty} \psi_0 * \psi_0 dx = \int_{-\infty}^{+\infty} \psi_0^2 dx$$

$$= \left(\frac{\alpha}{\pi}\right)^{1/2} 2 \int_0^{+\infty} \exp(-\alpha x^2) dx$$

$$= 2\left(\frac{\alpha}{\pi}\right)^{1/2} \frac{1}{2} \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$= 1$$

For even function

$$\int_{-A}^{+A} f(x) dx = 2 \int_0^{+A} f(x) dx$$

Standard integral

$$\int_0^{+\infty} \exp(-bx^2) dx = \frac{1}{2} \sqrt{\frac{\pi}{b}}$$

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THE HARMONIC OSCILLATOR

Show that ψ_0 and ψ_1 are orthogonal

$$\psi_0 = \left(\frac{\alpha}{\pi}\right)^{1/4} \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{even function} \quad f(-x) = f(x)$$

$$\psi_1 = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} x \cdot \exp\left(-\frac{\alpha x^2}{2}\right) \quad \rightarrow \quad \text{odd function} \quad f(-x) = -f(x)$$

$$\int_{-\infty}^{+\infty} \psi_0 * \psi_1 dx = \left(\frac{4\alpha^3}{\pi}\right)^{1/4} \left(\frac{\alpha}{\pi}\right)^{1/4} \int_{-\infty}^{+\infty} x \cdot \exp(-\alpha x^2) dx$$

$$= 0$$

since, the integrand is an ODD function

For odd function

$$\int_{-A}^{+A} f(x) dx = 0$$

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THE HARMONIC OSCILLATOR

Show that average displacement of a harmonic oscillator is zero for all the quantum states of a harmonic oscillator

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi_n(x) \cdot x \cdot \psi_n(x) dx = \int_{-\infty}^{+\infty} x \cdot \psi_n^2(x) dx = 0$$

since, the integrand is an ODD function

$\psi_n(x)$ is an even function when "n" is an even integer and $\psi_n(x)$ is an odd function when "n" is an odd integer.

But $\psi_n^2(x)$ is an even function for any value of "n".

Therefore, $x \cdot \psi_n^2(x)$ is an ODD function

For odd function

$$\int_{-A}^{+A} f(x) dx = 0$$

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THE HARMONIC OSCILLATOR

Show that for a harmonic oscillator, average momentum is zero

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \psi_n(x) \cdot \hat{p}_x \cdot \psi_n(x) dx = \int_{-\infty}^{+\infty} \psi_n(x) \left(-i\hbar \frac{d}{dx} \right) \psi_n(x) dx = 0$$

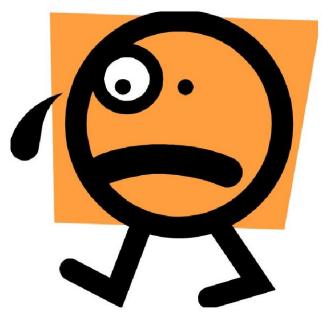
since, the integrand is an ODD function

The derivative of an ODD (EVEN) function is EVEN (ODD). So this integral vanishes because the integrand is the product of an ODD and EVEN function and hence is overall ODD.

For odd function

$$\int_{-A}^{+A} f(x) dx = 0$$

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