CHEM F111 : General Chemistry

Semester I: AY 2017-18

Lecture-05, 17-01-2018

Summary: Lecture - 04

General form of the wavefunctions:

$$\Psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a} \quad 0 \le x \le a, \; \text{n = 1, 2, 3 …..}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{8mb^2} = \frac{n^2h^2}{8mL^2}$$ Energy eigenvalues,

***L* = 2*b* – length of box.**

- Zero point energy – state represented by n=1
- Energy levels are not continuous

Work out: Determine the energy of a particle confined to move in one dimension of length l using the general form of the wavefunction:

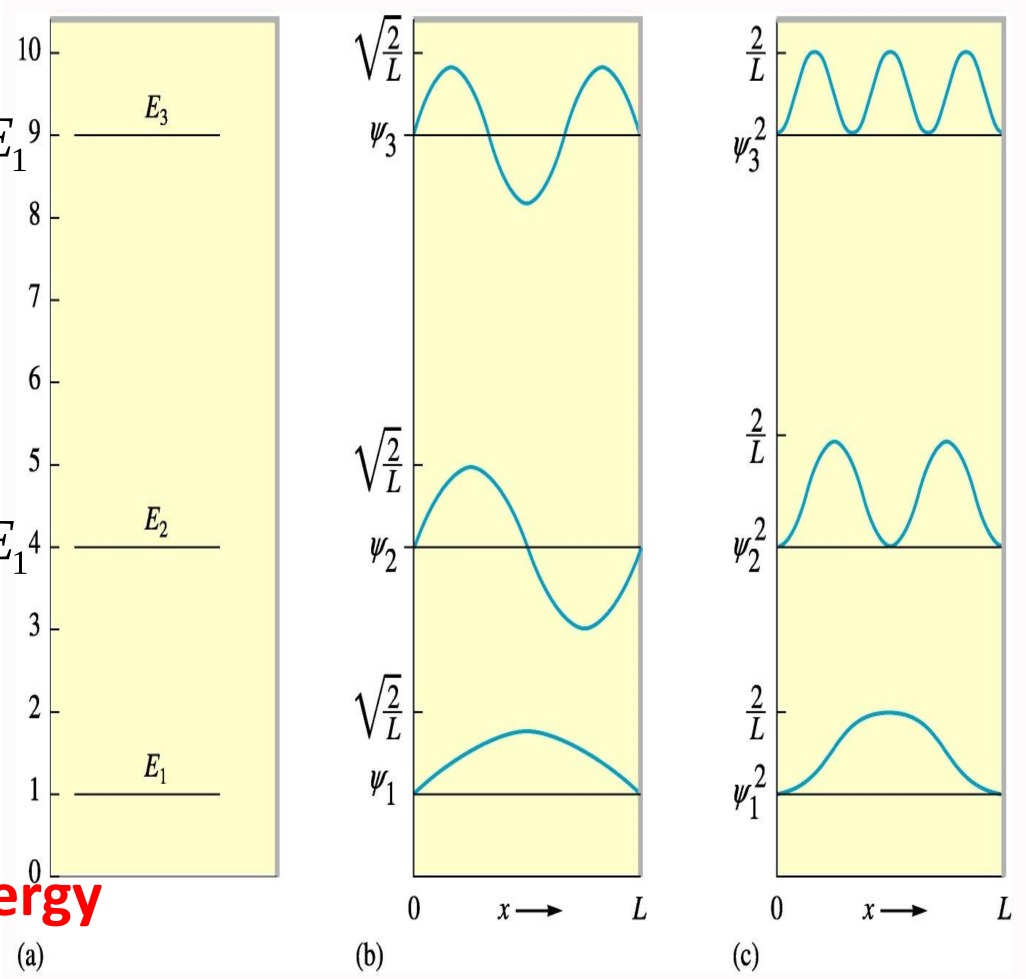
Wave functions & probability

$$E_3 = \frac{3^2 h^2}{8mL^2} = 9E_1$$

$$E_2 = \frac{2^2 h^2}{8mL^2} = 4E_1$$

$$E_1 = \frac{1^2 h^2}{8mL^2}$$

Zero point energy



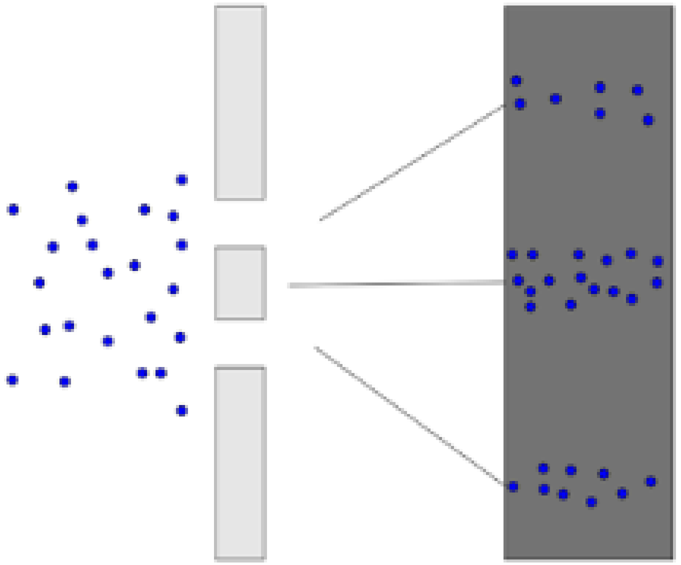
Observation: For n=2 state, there is zero probability of finding the particle at x = L/2.

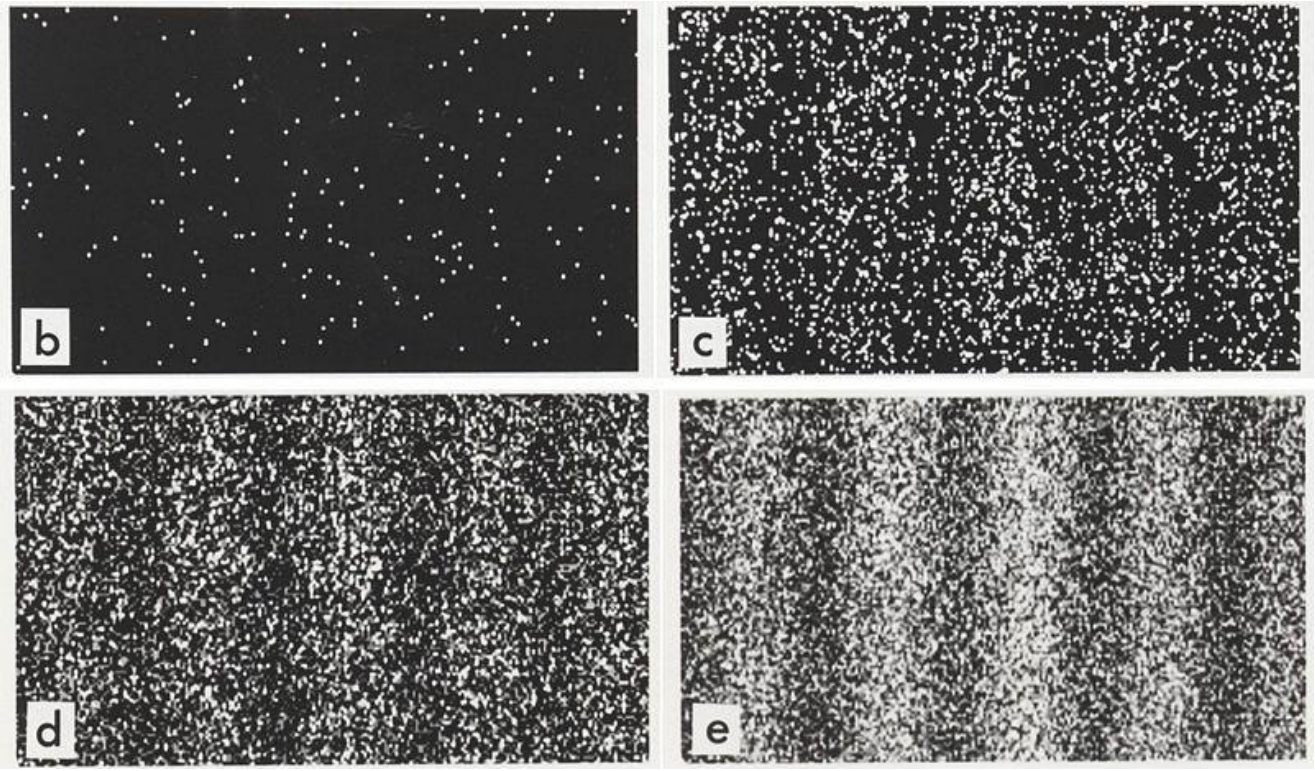
Question: How can the particle move from one side of the box to the other? As the particle is not found at the center.

 # Is this a valid question??

Microscopic particles can not fully and precisely be described by concept in classical physics.

Wave functions & probability

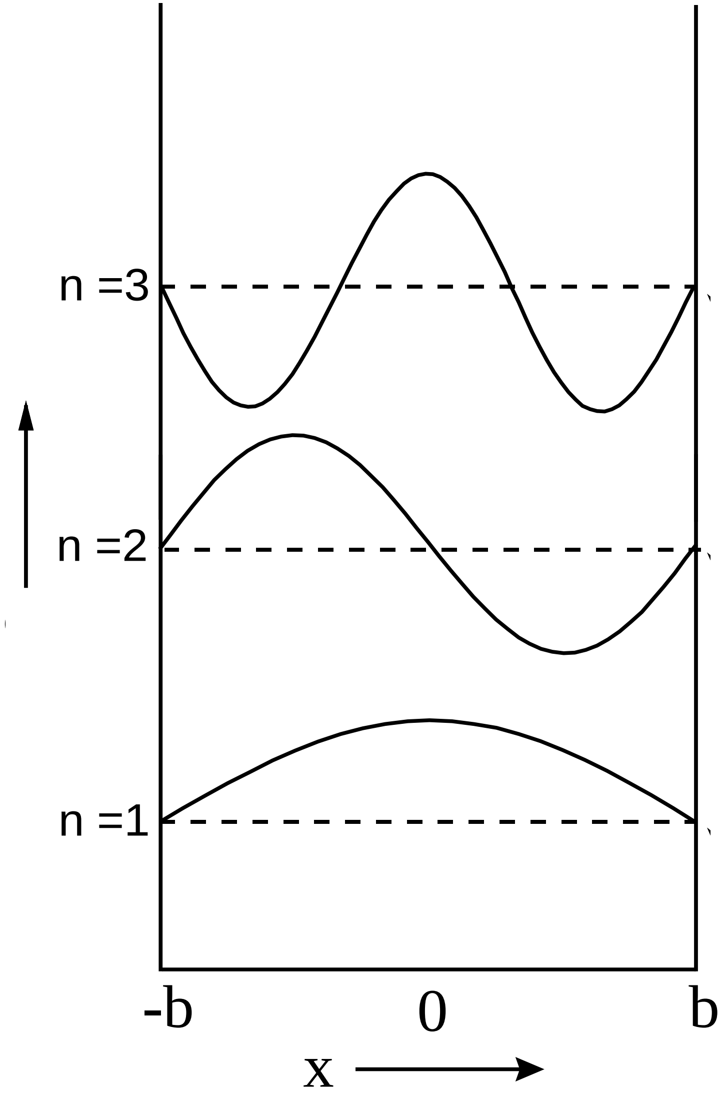




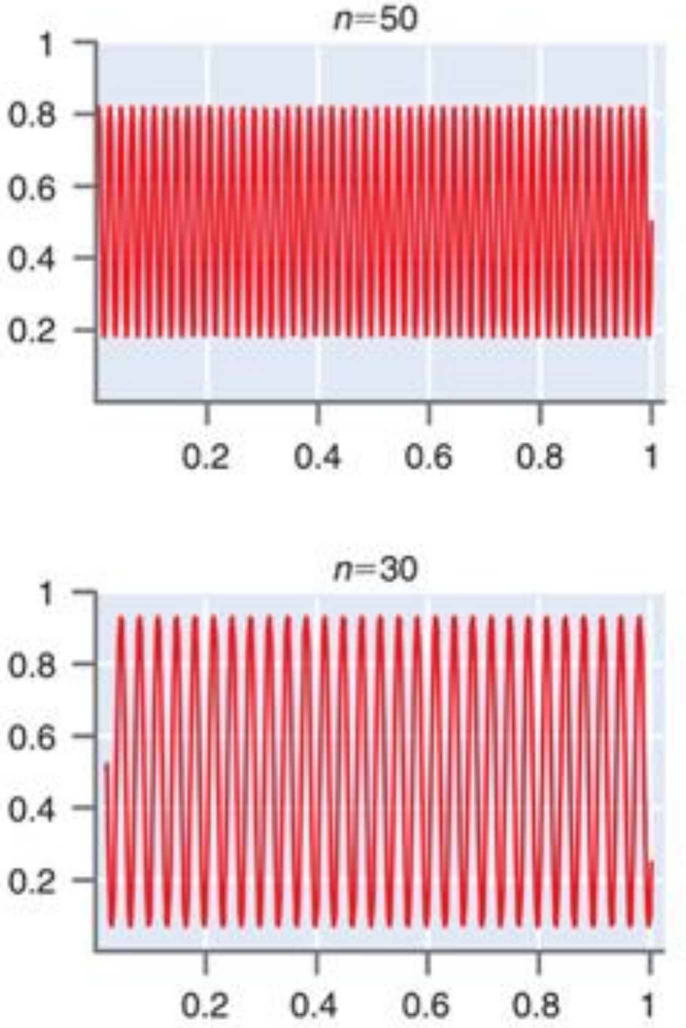
No. of e$^-$ is increasing (b) > (c) > (d) > (e)

Work out: Calculate the probability that a particle in a one-dimensional box of length a is found to be between 0 and a/2

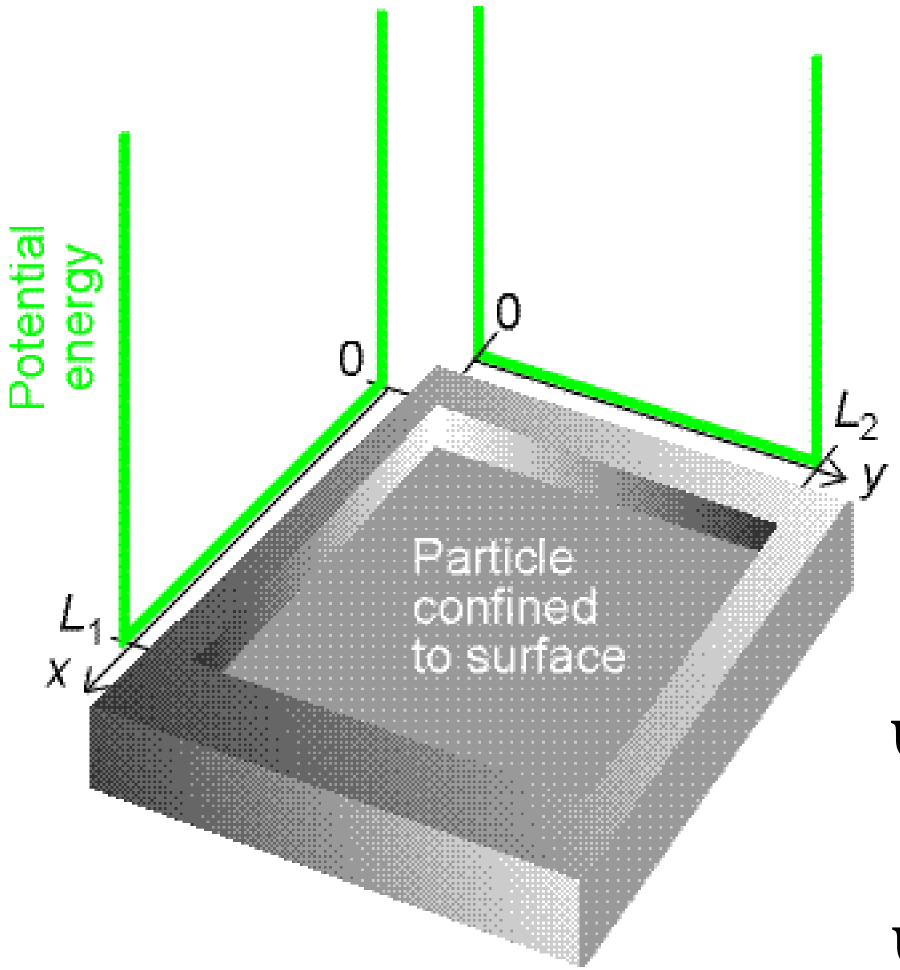
PIB: Comparison with classical results



- Probability of finding the particle.
- For high quantum number we approach classical limit – uniform probability density.
- Bohr correspondence principle.



PIB – Two dimensional



Within the box, V(x) = c; We may consider c = 0 [PIB – 1D]

V (x, y) = 0 in the region $0 \leq x \leq L_1$

$0 \leq y \leq L_2$

$$\Psi_{n_x}(x) = \left(\frac{2}{L_1}\right)^{1/2} \sin\frac{n\pi x}{a} \quad n_x = 1, 2, 3 \ldots..$$

$$\Psi_{n_y}(y) = \left(\frac{2}{L_2}\right)^{1/2} \sin\frac{n\pi y}{a} \quad n_y = 1, 2, 3 \ldots..$$

PIB – Two dimensional

$$\psi(x,y) = \sqrt{\frac{2}{L_1}}\sqrt{\frac{2}{L_2}}\sin\left(\frac{n_x \pi x}{L_1}\right)\sin\left(\frac{n_y \pi y}{L_2}\right)$$

$$E = \frac{n_x{}^2 h^2}{8mL_1{}^2} + \frac{n_y{}^2 h^2}{8mL_2{}^2}$$

Where n_x= 1, 2, 3….

n_y= 1, 2, 3…

PIB – Two dimensional, Square

For square box: $L_1 = L_2 = L$

Ground state: n_x= 1 & n_y=1

Ground state energy:

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

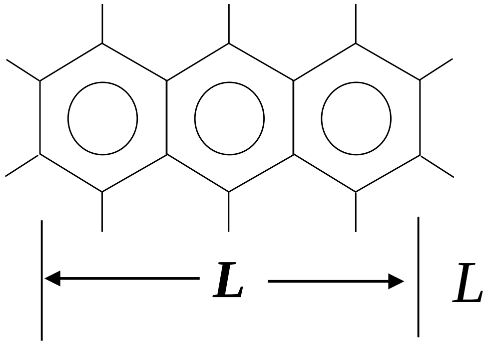
First excited state is **degenerate**:

$n_x = 2$ and $n_y = 1$ or $n_x = 1$ and $n_y = 2$

$$E = \frac{5h^2}{8mL^2}$$

PIB – Application

PIB: Simple model of molecular energy levels



$L \approx 6\ \text{Å}$

Anthracene

π electrons – consider "free" in box of length *L*.

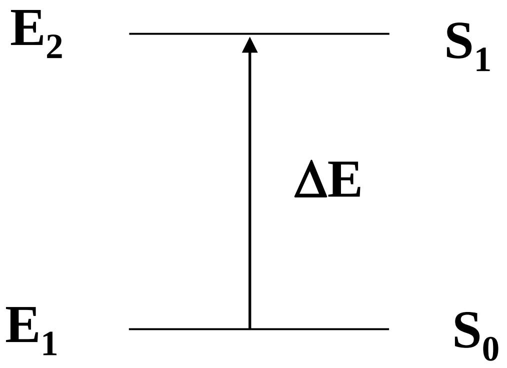
Ignore all coulomb interactions.

$$m = m_e = 9\times10^{-31}\ \text{kg}$$

$$L = 6\ \text{Å} = 6\times10^{-10}\ \text{m}$$

$$\text{h} = 6.6\times10^{-34}\ \text{Js}$$

$$\Delta\text{E} = 5.04\times10^{-19}\ \text{J}$$



Calculate wavelength of absorption of light.

Form particle in box energy level formula

$$\Delta E = E_2 - E_1 = \frac{3h^2}{8mL^2}$$

$$\Delta\text{E} = \text{h}\nu$$

$$\nu = \Delta\text{E}/\text{h} = 7.64\times10^{14}\ \text{Hz}$$

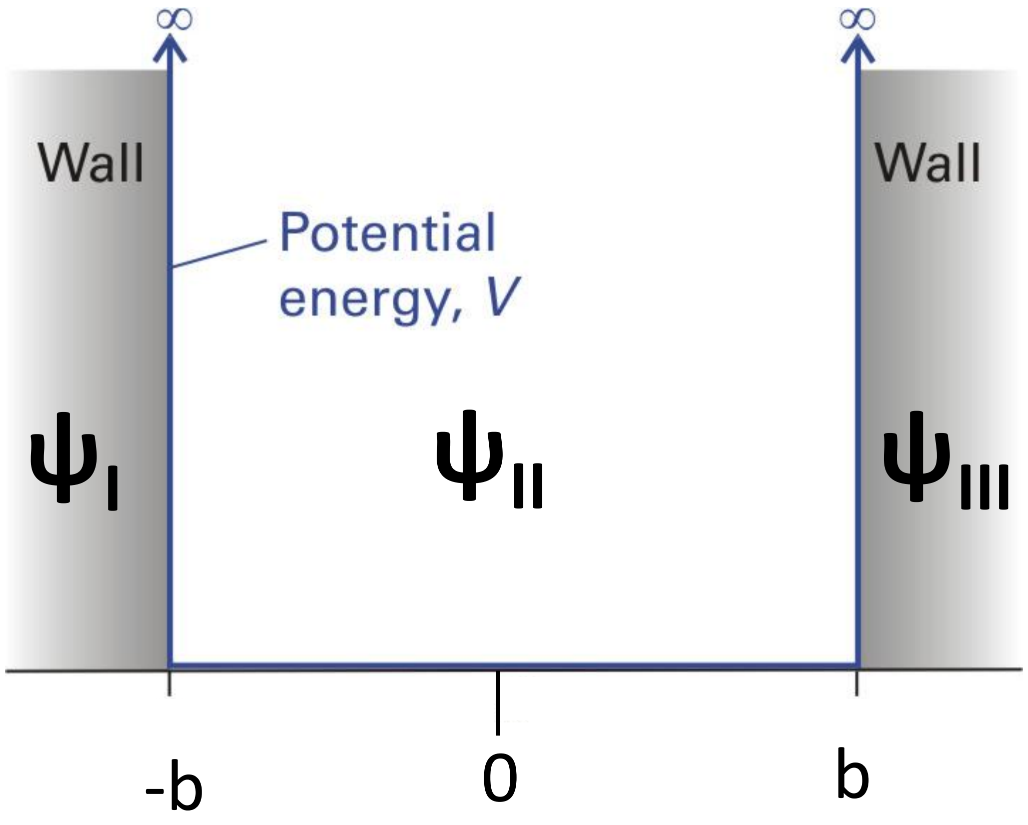
$$\lambda = \text{c}/\nu = 393\ \text{nm} \quad \text{blue-violet}$$

$$\text{Experiment} \Rightarrow 400\ \text{nm}$$

Big molecules ⟶ absorb in red.

Small molecules ⟶ absorb in UV.

Summary: PIB



$$U(x) = 0\ for\ -b < x < b$$

$$\Psi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\frac{n\pi x}{a}$$

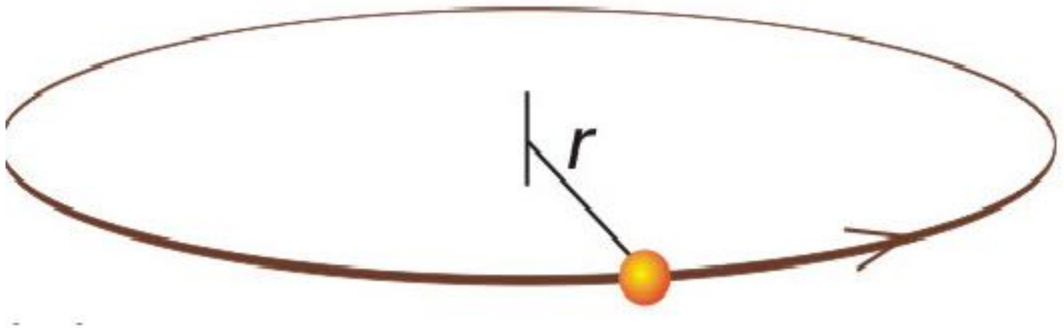
$$E_n = \frac{n^2\pi^2\hbar^2}{8mb^2} = \frac{n^2h^2}{8mL^2}$$ **Energy eigenvalues,**

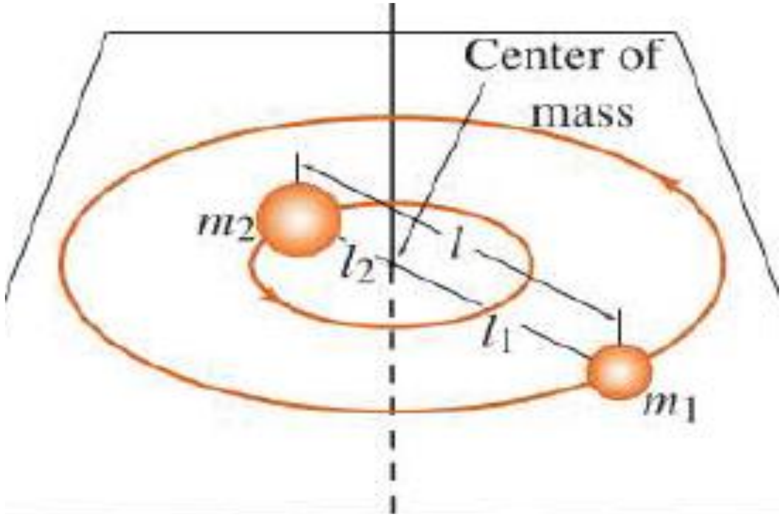
L = $2b$ – length of box.

- Zero point energy
- Degenerate states

Particle on a ring

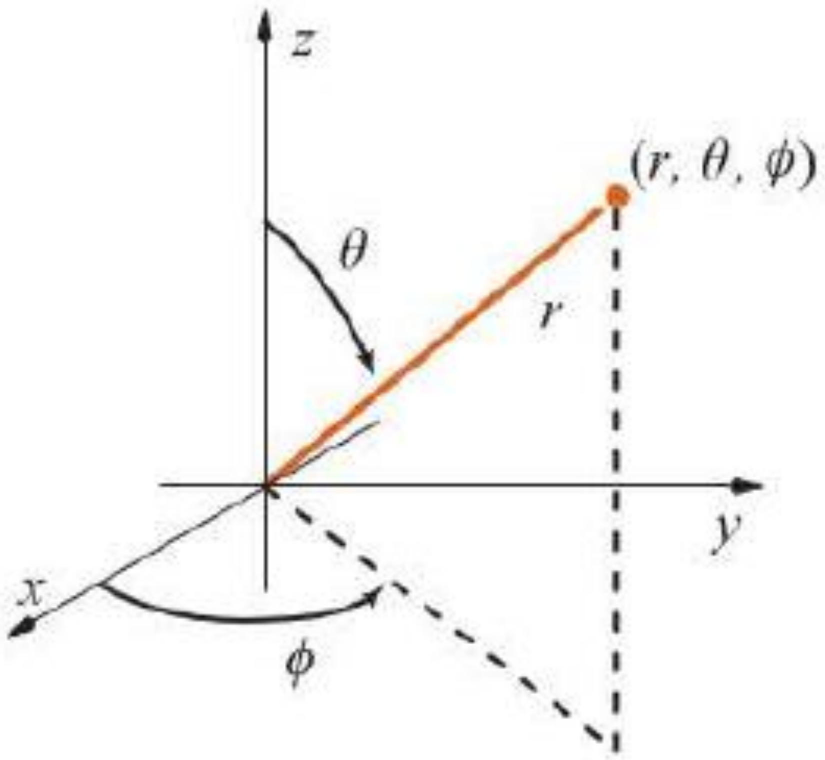
A simplified rotational problem: Rigid plane rotor





- For a diatomic molecule – bond length is fixed.
- The molecule is constrained to rotate in a plane – assume the surface is frictionless.
- Rigid plane rotor is a one-dimensional angular momentum problem.
- Angular momentum: $L = I\omega$ (I = moment of inertia = μr^2)

Particle on a ring



r and θ are fixed

Cartesian to polar coordinates:

$\Psi(x, y) \rightarrow \Psi(\varphi)$

Define an operator to measure the Z-component of angular momentum:

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Particle on a ring

What would be the form of the $\widehat{H}$?

$$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{T}} + \widehat{\boldsymbol{V}}$$

For a rigid rotor constrained to move in a plane: V = 0

$$\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{T}}$$

$$\text{KE: } \widehat{T} = \frac{\widehat{L_Z^2}}{2I}; \qquad \text{Thus, } \widehat{\boldsymbol{H}} = -\frac{\hbar^2}{2I}\frac{\delta^2}{\delta\varphi^2}$$

Schröndinger Equation

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}\Phi(\varphi) = E\Phi(\varphi)$$

$$\Rightarrow \frac{d^2}{d\varphi^2}\Phi(\varphi) = -\frac{2I}{\hbar^2}E\Phi(\varphi)$$

Can we guess any solution for this ODE?

2nd derivative of a function is equals the function times a –ve const.

General solution: $\boldsymbol{\Phi(\varphi) = A_{m\pm}\, e^{\pm im\Phi}}$ ..Equn. 1

Work out: Calculate normalization constant of the wave function. N = $\frac{1}{\sqrt{2\pi}}$

Normalized wave function: $\boldsymbol{\Phi(\varphi) = \frac{1}{\sqrt{2\pi}}\, e^{\pm im\Phi}}$

Solves the differential equation but not an acceptable wavefunction

Acceptable wave function

- Requirement that $\Phi(\varphi)$ to be continuous is:

$\Phi\ (\varphi+2\pi) = \Phi(\varphi)$ ....Equn. 2

Substitute Equn. (2) into Equn. (1)

$$A_{m+}\ e^{+im(\Phi+2\pi)} = A_{m+}\ e^{+im\Phi}$$

$$A_{m-}\ e^{-im(\Phi+2\pi)} = A_{m-}\ e^{-im\Phi}$$

$$e^{\pm i2\pi m} = 1$$

$\Rightarrow$ cos(2πm) $\pm$ i sin(2πm) = 1 (cos2πm=1 and sin2πm=0)

$\Rightarrow$ m = 0, $\pm$1, $\pm$2, $\pm$ 3 .... **(m: quantum no => magnetic quantum no.)**

Energy and angular momentum

Wave functions: $$\boldsymbol{\Phi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{\pm im\Phi}}$$

Work out:

- Apply energy operator on $\boldsymbol{\Phi(\varphi)}$ to obtain the energy
- Apply angular momentum operator on $\boldsymbol{\Phi(\varphi)}$ to obtain angular momentum

$$-\frac{\hbar^2}{2I}\frac{d^2}{d\varphi^2}\Phi(\varphi) = E\Phi(\varphi)$$

$$\boldsymbol{E = \frac{m^2\hbar^2}{2I}}$$

- All states with |m| ≥ 1 are doubly degenerate.
- m = 0 is an allowed state.
- Angular momentum would be mħ
- Angular momentum is also quantized.

Wave funcitons

$$\boldsymbol{\Phi}(\boldsymbol{\varphi}) = \frac{1}{\sqrt{2\pi}} \, for \; m = 0$$

General solution for |m| ≥1

$$\boldsymbol{\Phi}(\boldsymbol{\varphi}) = \boldsymbol{A_{m\pm}} \, \boldsymbol{e^{\pm im\Phi}}$$

Work out: (i) Show that linear combinations $(e^{im\Phi} + e^{-im\Phi})$ & $(e^{im\Phi} - e^{-im\Phi})$ are also eigen function of the Hamiltonian of rigid rotor with same eigen value.

(ii) Show: $\cos(m\Phi) = \dfrac{e^{im\Phi} + e^{-im\Phi}}{2}$ and $\sin(m\Phi) = \dfrac{e^{im\Phi} - e^{-im\Phi}}{2i}$

Consequence: Real functions $cos(m\Phi)$ & $sin(m\Phi)$ are having same energy as that of $\Phi(\varphi) = e^{\pm im\Phi}$

Real solution for |m| ≥1

$$\boldsymbol{\Phi}_{|\boldsymbol{m}|}(\boldsymbol{\varphi}) = \frac{1}{\sqrt{2\pi}} \cos|m|\boldsymbol{\varphi} \text{ and } \frac{1}{\sqrt{2\pi}} \sin|m|\boldsymbol{\varphi} \text{ for } |m| \geq 1$$

(will be used in H-atom problem)