

# ENGINEERING PHYSICS

## UNIT-2

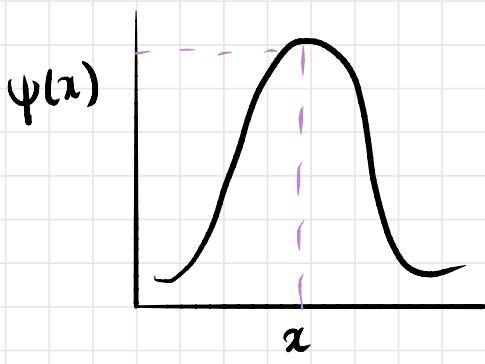
### FORMULATION OF QUANTUM MECHANICS

Vibha Masti

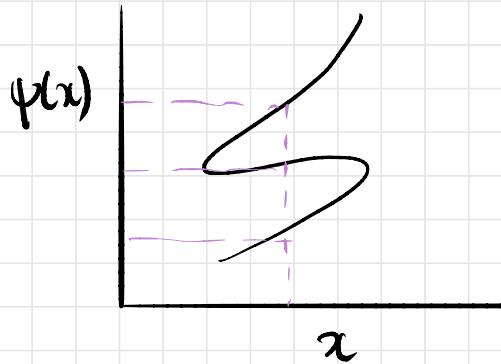
## Wavefunction

- We obtain  $\Psi$  from Schrödinger's equation.
- Refer unit 1 notes (page 50)

1)  $\Psi$  must be single-valued, continuous, differentiable



valid



invalid

- probability ( $\Psi\Psi^*$ ) needs to be defined.

2) The derivatives of  $\Psi$  should be single-valued, continuous

- $\Psi = A e^{i(kx - \omega t)}$
- To get in terms of  $p$  and  $E$

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h}$$

$$\omega = 2\pi f = \frac{2\pi E}{h}$$

- therefore,

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

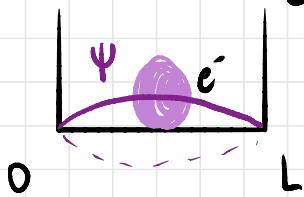
- $\frac{\partial \Psi}{\partial x} \rightarrow p$  and  $\frac{\partial \Psi}{\partial t} \rightarrow E$
- $\therefore \frac{\partial \Psi}{\partial x}, \frac{\partial \Psi}{\partial t}$  should be continuous

### 3) Finiteness condition

- $\Psi$  should be finite
- as  $x \rightarrow \infty$ ,  $\Psi \not\rightarrow \infty$  but  $\Psi \rightarrow 0$

### 4) $\Psi$ should be normalisable

$e^-$  in definite boundary



1-D cavity

chance of finding  $e^-$   
in region  $0-L$  is 1

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

free  $e^-$  in space (1-D)

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1 \quad \xrightarrow{\text{normalisation}}$$

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1 \quad \xrightarrow{\text{particle exists}}$$

$$\text{if } \int_{-\infty}^{\infty} \psi^* \psi dx = 0 \quad \xrightarrow{\text{particle does not exist}}$$

in 3-D space,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} |\psi|^2 dx dy dz = 1$$

- By normalising a wavefunction, we can find the amplitude of the given wavefunction.
- If the wf obeys all these properties, then the wf is said to be a well-behaved wf.

Q1. A particle is trapped in a 1D box of width L. Associated wavefunction is

$$\Psi = A \sin \frac{\pi}{L} x$$

Normalise the wavefunction to find the constant

$$\begin{aligned} & \int_0^L \left( A \sin \frac{\pi}{L} x \right) \left( A \sin \frac{\pi}{L} x \right) dx = 1 \\ &= \frac{A^2}{2} \int_0^L \left( 1 - \cos \frac{2\pi x}{L} \right) dx = 1 \end{aligned}$$

$$\left[ x - \frac{\left( \sin \frac{2\pi x}{L} \right)}{\left( \frac{2\pi}{L} \right)} \right]_0^L = \frac{2}{A^2}$$

$$L - \left( \frac{\sin 2\pi}{2\pi} \right) L = \frac{2}{A^2}$$

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

Q2. Normalise the given wf  $\Psi = ae^{ikx}$  between the limits 0 and 1 to find the constant a.

$$\Psi = ae^{ikx} \quad \Psi^* = ae^{-ikx}$$

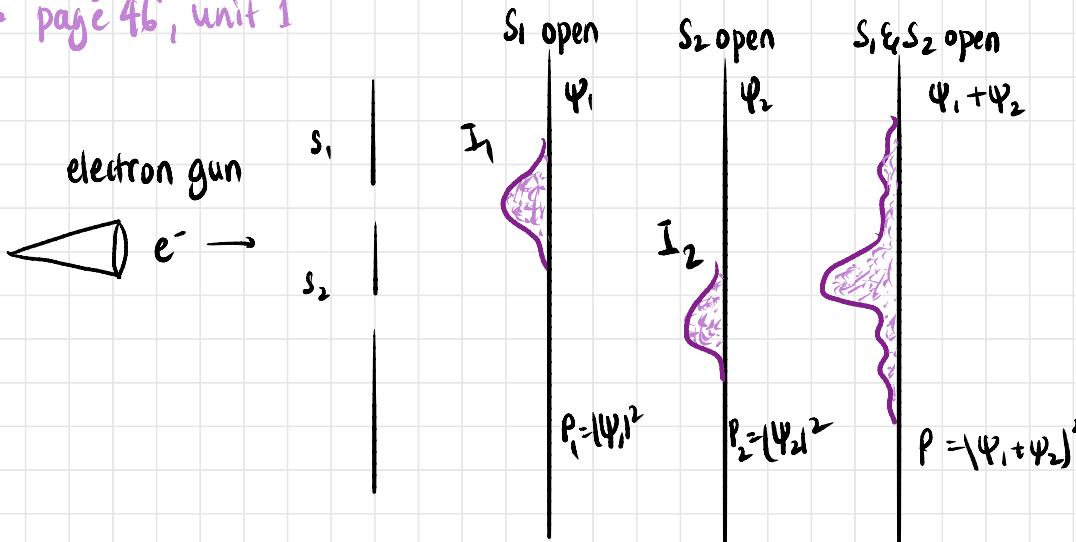
$$\int_0^1 a^2 dx = 1 \Rightarrow a^2 = 1$$

$$a = 1$$

(Amplitude is +ve)

## Probability Density $|\Psi|^2$

- Wavefunctions can be added together, but their probabilities cannot be added
- single particle double-slit experiment
- page 4b, unit 1



- $\Psi = \Psi_1 + \Psi_2$
- probability density =  $|\Psi|^2$   
 $= (\Psi_1 + \Psi_2)^2 = (\Psi_1 + \Psi_2)(\Psi_1^* + \Psi_2^*)$   
 $= (\Psi_1)^2 + (\Psi_2)^2 + \Psi_1\Psi_2^* + \Psi_1^*\Psi_2$   
 $= P_1 + P_2 + \underbrace{\Psi_1\Psi_2^* + \Psi_1^*\Psi_2}_{\text{interference}}$

- the extra term indicates that the wavefunction undergoes interference.
- like any other waves, wavefunctions also undergo interference

## Observables and Operators

- in QM, operators indicated with hat ( $\hat{A}$ )

### Observables

- measurable physical parameters
- $p$ , KE, PE

### Operators

- to obtain observables, operators on  $\Psi$
- operator operates on  $\Psi$
- every physical parameter has an associated operator

## Eigenvalues

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$$\xrightarrow{\text{operator}} \hat{H} \Psi = \xrightarrow{\text{eigenvalue}} E \Psi$$

## Operator for Observables

i) momentum —  $\hat{p}$

$$\text{Take } \psi = A e^{Y_k(Px - Et)}$$

$$\frac{\partial \Psi}{\partial x} = A e^{i/\hbar(px-Et)} \cdot \frac{i}{\hbar} p$$

# operator

$$\cancel{(\text{up})} \quad \frac{\hbar}{i} \frac{\partial \Psi}{\partial x} = p\Psi \Rightarrow \hat{p}\Psi = p\Psi$$

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

## 2) Kinetic energy — KE

$$KE = \frac{P^2}{2m}$$

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{ip}{\hbar} A e^{i\hbar/(px-Et)} \left( \frac{ip}{\hbar} \right)$$

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

Dividing by  $2m$

$$-\frac{\partial^2 \Psi}{\partial x^2} \left( \frac{\hbar^2}{2m} \right) = \frac{p^2}{2m} \Psi = (KE) \Psi$$

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

3) Total energy —  $\hat{H}$

$$\frac{\partial \Psi}{\partial t} = A e^{i/\hbar (px - Et)} \left( \frac{-iE}{\hbar} \right)$$

$$\frac{-i}{\hbar} \frac{\partial \Psi}{\partial t} = E\Psi$$

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

## 4) Position

$$\hat{x} = x$$

## 5) Potential energy

$$\hat{V}(x) = V(x)$$

Observable

Operator

Momentum

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

Kinetic energy

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

Total energy

$$\hat{H} = \frac{-\hbar^2}{i\imath} \frac{\partial}{\partial t}$$

Position

$$\hat{x} = x$$

Potential energy

$$\hat{V}(x) = V(x)$$

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

- used to represent total energy

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

$$\hat{H} = \hat{K}_E + \hat{V}(x)$$

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

Q3. The eigenfunction of an operator  $\frac{d^2}{dx^2}$  is  $e^{2x} \curvearrowleft \Psi$ . Find the corresponding eigenvalue

$$\frac{d^2\Psi}{dx^2} = A\Psi$$

$$\frac{d^2 e^{2x}}{dx^2} = 4e^{2x} = 4\Psi$$

$$\therefore A = 4$$

eigenvalue = 4

Q4. Check whether the given function is a valid eigenvalue function. The eigenfunction of an operator  $\frac{d}{dx}$  is  $\sin 3x$

$$\hat{O} = \frac{d}{dx}, \Psi = \sin 3x$$

$$\hat{O}\Psi = \frac{d\sin 3x}{dx} = 3\cos 3x \longrightarrow \text{invalid eigenfunction.}$$

## Expectation Values

- average value
- collection of identical particles (identical  $\Psi$ )
- multiple attempts - average value
- $N_{\text{tot}}$  no. of identical particles (same  $\Psi$ )

## Position

- expectation value of p, position, KE, TE
- $N_1x_1, N_2x_2 \dots N_ix_i$



$$\text{Average value} = \frac{N_1x_1 + N_2x_2 + N_3x_3 + \dots + N_nx_n}{N_1 + N_2 + N_3 + \dots + N_n}$$

$$\bar{x} = \frac{\sum N_i x_i}{\sum N_i}$$

- $N_i$  & probability of finding particle between  $x_i$  and  $x_i+dx$

$$\frac{N_i}{N_{\text{tot}}} = P(x) dx \quad \text{--- } P(x) \text{ is probability density}$$

$$\langle x \rangle = \frac{\sum \frac{N_i x_i}{N_{\text{tot}}}}{\sum \frac{N_i}{N_{\text{tot}}}} = \frac{\int P(x) dx \cdot x}{\int P(x) dx}$$

$$\frac{\sum \frac{N_i}{N_{\text{tot}}}}{\int P(x) dx} \xrightarrow{\text{will reduce to 1}} \frac{\int P(x) dx}{\int P(x) dx} \xleftarrow{\text{will reduce to 1}}$$

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \psi dx}{\int_{-\infty}^{\infty} \psi^* \psi dx} = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi dx$$

$$\boxed{\langle x \rangle = \int_{-\infty}^{\infty} \psi^* \hat{x} \psi dx}$$

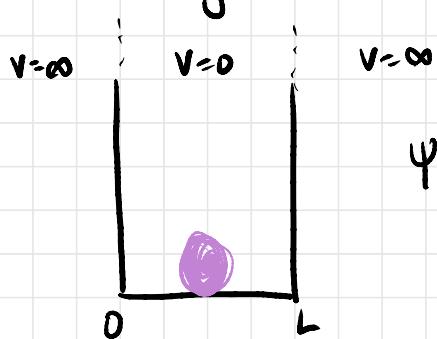
### Momentum

$$\langle p \rangle = \int_{-\infty}^{\infty} \psi^* \hat{p} \psi dx$$

### Kinetic Energy

$$\langle KE \rangle = \int_{-\infty}^{\infty} \psi^* \hat{KE} \psi dx$$

Q5. Find the expectation value of position for a particle in the ground state when it is trapped in an infinite potential well of length L.



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

$$\langle x \rangle = \int_0^L \psi^* \hat{x} \psi dx = \int_0^L \frac{2x}{L} \sin^2\left(\frac{\pi}{L}\right)x dx$$

$$= \frac{2}{L} \int_0^L x \left(1 - \cos\left(\frac{2\pi}{L}x\right)\right) dx = \frac{1}{L} \int_0^L x - x \cos\left(\frac{2\pi}{L}x\right) dx$$

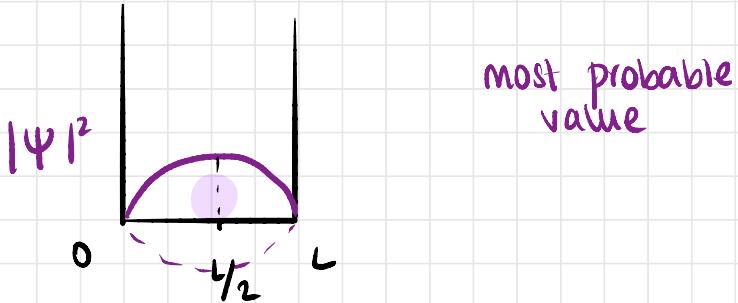
$$= \frac{1}{L} \left[ \frac{x^2}{2} \right]_0^L - \frac{1}{L} \int_0^L x \cos\left(\frac{2\pi}{L}x\right) dx$$

$$v = \frac{\sin 2\pi x}{2\pi L} \quad u = x \\ dv = \cos 2\pi x \quad du = dx$$

$$= \frac{L}{2} - \frac{1}{L} \left( \frac{x \sin \frac{2\pi x}{L}}{\frac{2\pi}{L}} + \frac{\cos \frac{2\pi x}{L}}{\frac{2\pi}{L} \cdot \frac{2\pi}{L}} \right)_0^L$$

$$= \frac{L}{2} - \frac{1}{L} \left( \frac{\cancel{L \sin 2\pi}}{\cancel{2\pi/L}}^0 + \frac{\cancel{\cos 2\pi}}{(\cancel{2\pi})^2}^0 - \frac{\cancel{\cos 0}}{(\cancel{2\pi})^2}^0 \right)$$

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



Q6: For same  $\Psi$ , find  $\langle p \rangle$

$\sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right)$  is not an eigenvalue

$$\langle p \rangle = \int_0^L \Psi^* \hat{P} \Psi dx = \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \hat{P} \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) dx$$

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

$$= \int_0^L \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \frac{\hbar}{i} \frac{\partial}{\partial x} \left( \sqrt{\frac{2}{L}} \sin\left(\frac{\pi x}{L}\right) \right) dx$$

$$= \frac{\pi \hbar k}{L^2 i} \int_0^L \sin \frac{\pi x}{L} \cos \frac{\pi x}{L} dx$$

$$= \frac{\frac{t\pi}{L^2 i}}{\int_0^L \sin \frac{2\pi x}{L} dx}$$

$$= \frac{\frac{t\pi}{L^2 i}}{\left[ -\cos \frac{2\pi x}{L} \right]_0^L} = \frac{\frac{t\pi}{L^2 i}}{(-\cos 2\pi t + \cos 0)}$$

$$\langle p \rangle = 0$$

Since the particle moves back and forth, the average momentum is 0.

## Time-Independent Schrödinger's Wave Equation in 1D Schrödinger's Approach

### Conditions on Wave Equation

- Must be consistent with deBroglie-Einstein relation

$$\lambda = \frac{h}{p} \quad v = \frac{E}{h}$$

- Must be consistent with conservation of energy

$$T \cdot E = KE + PE$$

- Should be linear in  $\Psi(x, t)$

If  $\Psi_1(x, t)$  and  $\Psi_2(x, t)$  are two different solutions for a given system, then the linear combination of solutions is also a solution.

$$\Psi(x, t) = A\Psi_1(x, t) + B\Psi_2(x, t)$$

$$\hat{T}\hat{E}\Psi = \hat{K}\hat{E}\Psi + \hat{P}\hat{E}\Psi$$

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

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

For a steady state system, as total energy is constant, instead of writing  $\hat{T}\hat{E}$ , we can just write  $E$  as the total energy of the system is constant (eigenvalue)

$$E\Psi(x,t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x)\Psi(x,t)$$

$$\Psi(x,t) = A e^{i/\hbar(p_x - Et)}$$

### Separation of Variables

$$\Psi(x,t) = \underbrace{A e^{ipx/\hbar}}_{\Psi(x)} \underbrace{e^{-iEt/\hbar}}_{\Phi(t)}$$

$$\Psi(x,t) = \Psi(x)\Phi(t)$$

Substituting in equation

$$E\Psi(x)\Phi(t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x)\Phi(t)}{\partial x^2} + U(x)\Psi(x)\Phi(t)$$

$$\frac{\hbar^2}{2m} \frac{\partial^2 (\psi(x) \phi(t))}{\partial x^2} + (E - U_{(x)}) \psi(x) \phi(t) = 0$$

$$\phi(t) \left( \frac{\hbar^2}{2m} \frac{\partial^2 \psi(x)}{\partial x^2} + \psi(x)(E - U_{(x)}) \right) = 0$$

where  $\phi(t) \neq 0$

$\psi(x)$  is independent of  $t \Rightarrow$  we can use total derivatives

$$\therefore \frac{\hbar^2}{2m} \frac{d^2 \psi(x)}{dx^2} + (E - U_{(x)}) \psi(x) = 0$$

$$\boxed{\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2} \psi(x)(E - U_{(x)}) = 0}$$

time-independent 1-D Schrödinger's wave equation

$$\nabla^2 \psi(x) + \frac{2m}{\hbar^2} \psi(x)(E - U_{(x)}) = 0$$

in 3-D

Schrödinger's wave equation is used to find the wavefunction  $\Psi$  where  $\Psi$  has all the information.

Note: Dirac's notation (Heisenberg's approach) is one more method (matrix - eigenvectors)

# Applications of SWE (1D)

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## i) Free Particle — find $\psi$

- does not experience any kind of external force
- $F=0 = -\frac{dU}{dx} \Rightarrow U(x) = \text{constant}$
- Potential is = constant
- For mathematical simplicity, the constant potential is taken as 0 (at  $\infty$ )
- Schrödinger's wave Equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - U_{\text{ex}}) \psi = 0$$

$U_{\text{ex}} = 0$  for free particle

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0$$

take  $\frac{2mE}{\hbar^2} = k^2$

$$k = \frac{p}{\hbar} \Rightarrow \frac{p^2}{\hbar^2} = k^2 = \frac{2mE}{\hbar^2}$$

$$(D^2 + k^2) \psi = 0$$

Auxiliary equation

$$D^2 + k^2 = 0$$

$$D = \pm ik$$

$$= A \sin kx + B \cos kx$$

$$\sin \theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$$

$$\cos \theta = \frac{e^{i\theta} + e^{-i\theta}}{2}$$

$e^{ikx}$   $\rightarrow$  plane wave moving in  $+x$

$e^{-ikx}$   $\rightarrow$  plane wave along  $-x$

The energy of a free particle is given by

$$\frac{\partial E}{\partial k^2} = k^2$$

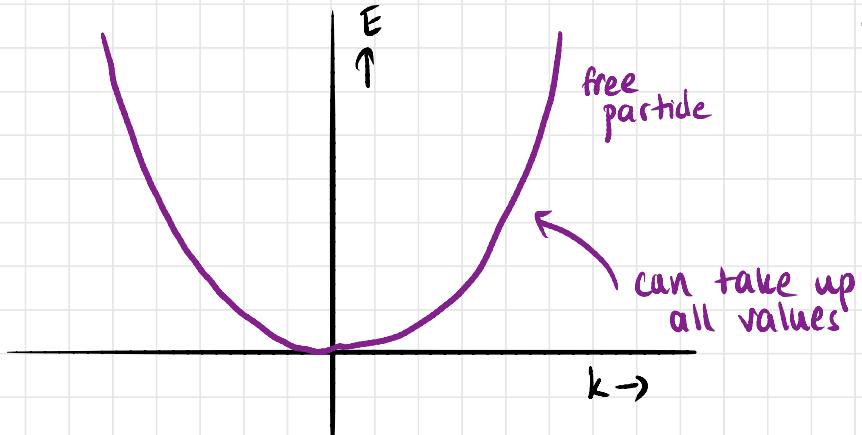
$$E = \frac{\frac{\partial^2 E}{\partial k^2}}{\frac{\partial k^2}{\partial m}} = \frac{p^2}{2m}$$

total energy = kinetic energy ( $U_r = 0$ )

Since  $k$  values are not restricted,  $E$  values are also not restricted.

Therefore, energy of a free particle is continuous, not quantised

parabola

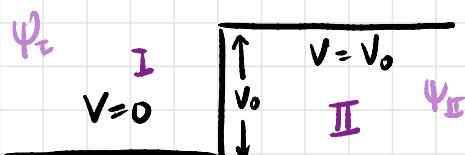
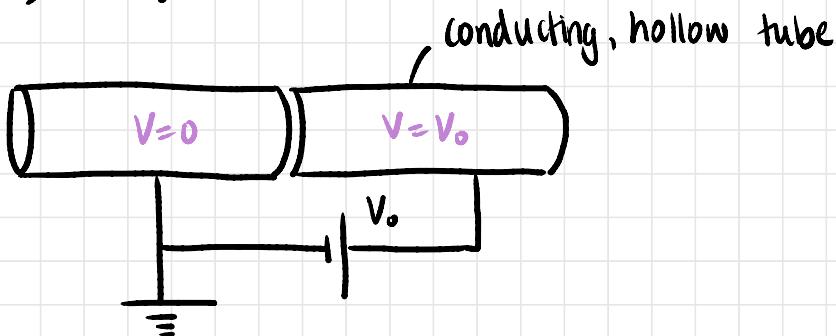


## 2) Potential Step — find $\psi$

Particle is placed in  $-x$  direction of tube. In this region, particle experiences no force (free particle;  $U=0$ ). It suddenly encounters a region of potential at  $x=0$ .

Find  $\psi$  in region I and II for

- 1)  $E > V_0$
- 2)  $E < V_0$



Case I :  $E > V_0$

$$\lambda_I = \frac{\hbar}{\sqrt{2mE_k}} \quad \lambda_{II} = \frac{\hbar}{\sqrt{2m(E - V_0)}}$$

### Region I

$$U_{(x)} = V = 0 \quad \longrightarrow \quad \Psi_I$$

Schrödinger Wave Equation

$$\frac{d^2\Psi_I}{dx^2} + \frac{2m}{\hbar^2} (E - U_{(x)}) \Psi_I = 0$$

$$\frac{d^2\Psi_I}{dx^2} + \frac{2m}{\hbar^2} E_k \Psi_I = 0$$

$$k_I^2 = \frac{2m}{\hbar^2} E$$

$$\frac{d^2\Psi_I}{dx^2} + k_I^2 \Psi_I = 0$$

$$\Psi_I = A e^{ik_I x} + B e^{-ik_I x}$$

( incident )    ( reflected )

Since there is a boundary at  $x=0$ ,  $B e^{-ik_I x}$  is the reflected part of the wave

Region II

$$U_{(2)} = V = V_0$$

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar} (E - V_0) \psi_{II} = 0$$

$$k_2^2 = \frac{2m}{\hbar} (E - V_0)$$

$$\frac{d^2\psi_{II}}{dx^2} + k_2^2 \psi_{II} = 0$$

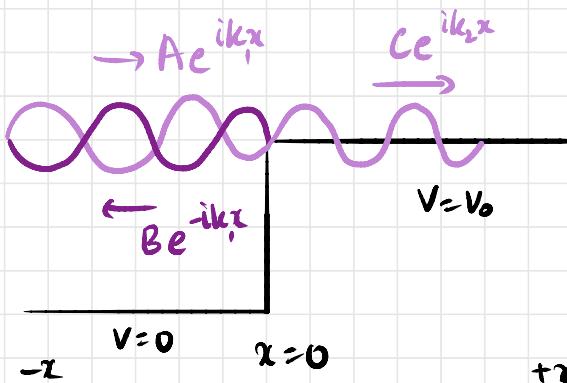
$$\psi_{II} = C e^{ik_2 x} + D e^{-ik_2 x}$$

( transmitted ) reflection  
( D should be = 0 )

In region II,  $C e^{ik_2 x}$  is the transmitted part of the wave and  $D e^{-ik_2 x}$  is the reflected part.

As there is no boundary to reflect off of, we set D=0

$$\therefore \psi_{II} = C e^{ik_2 x}$$



## Continuity condition/ Boundary condition

at  $x = 0$ ,

$$\Psi_I = \Psi_{II} \quad \text{and} \quad \frac{\partial \Psi_I}{\partial x} = \frac{\partial \Psi_{II}}{\partial x}$$

By using the boundary condition, we can find reflection and transmission coefficient

$$\Psi_I = A e^{ik_1 x} + B e^{-ik_1 x}$$

$$\Psi_{II} = C e^{ik_2 x}$$

$$R = \frac{\text{reflected flux}}{\text{incident flux}} \quad \text{--- probability of reflection}$$

$$= \frac{|B|^2 \times v_i}{|A|^2 \times v_i}$$

$$T = \frac{\text{transmitted flux}}{\text{incident flux}}$$

$$= \frac{|C|^2 \times v_2}{|A|^2 \times v_i}$$

Condition I

$$\Psi_I(0) = \Psi_{II}(0)$$

$$A + B = C \longrightarrow (1)$$

Condition II

$$\frac{d\Psi_I}{dx} = ik_1 A e^{ik_1 x} - ik_1 B e^{-ik_1 x}$$

$$\frac{d\Psi_{II}}{dx} = ik_2 C e^{ik_2 x}$$

$$\frac{d\Psi_I(0)}{dx} = \frac{d\Psi_{II}(0)}{dx}$$

$$k_1 A - k_1 B = k_2 C \longrightarrow (2)$$

To find R and T

Eliminating C

$$A + B = \frac{k_1 A - k_1 B}{k_2}$$

$$Ak_2 + Bk_2 = Ak_1 - Bk_1$$

$$B(k_2 + k_1) = A(k_1 - k_2)$$

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2}$$

## Eliminating B

$$B = C - A$$

$$Ak_1 - Ck_2 = k_1 B$$

$$Ak_1 - Ck_2 = Ck_1 - Ak_1$$

$$C(k_1 + k_2) = A(2k_1)$$

$$\frac{C}{A} = \frac{2k_1}{k_1 + k_2}$$

$$R = \frac{|B|^2}{|A|^2} = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2}$$

$$R = \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2}$$

$$T = \frac{4k_1^2}{(k_1 + k_2)^2} \times \frac{v_2}{v_1}$$

$$= \frac{4k_1^2}{(k_1 + k_2)^2} \times \frac{m k_2 / m}{k_1 k_1 / m}$$

$$T = \frac{4k_1 k_2}{(k_1 + k_2)^2}$$

$$k = \frac{2\pi}{\lambda}$$

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

$$k = \frac{2\pi mv}{h} = \frac{mv}{\lambda}$$

$$v = \frac{\lambda k}{m}$$

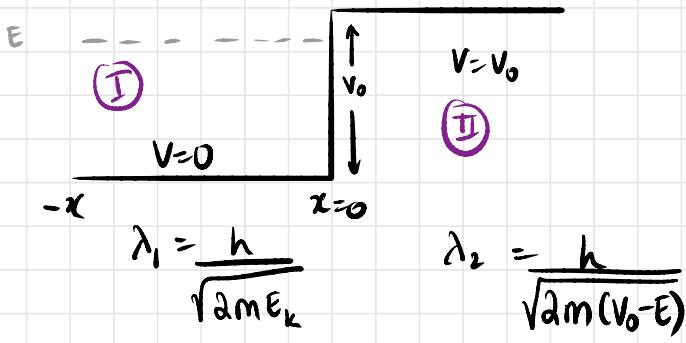
Show that the sum of reflection and transmission probabilities is equal to 1.

$$R + T = 1$$

$$= \frac{(k_1 - k_2)^2}{(k_1 + k_2)^2} + \frac{4k_1 k_2}{(k_1 + k_2)^2}$$

$$= \frac{(k_1 + k_2)^2}{(k_1 + k_2)^2} = 1$$

Case II :  $E < V_0$



here,  $E = E_k + V_0$   
 but  $V_0 > E$   
 $\therefore E_k < 0$   
 which is not  
 possible  
 classically

Region I

$$V=0$$

$$\text{SWE: } \frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi_I = 0$$

$$\frac{d^2\psi_I}{dx^2} + \frac{2mE}{\hbar^2} \psi_I = 0$$

$$k_I^2 = \frac{2mE}{\hbar^2}$$

$$(D^2 + k_I^2) \psi_I = 0$$

$$\boxed{\psi_I = A e^{ik_I x} + B e^{-ik_I x}}$$

## Region II

$$V = V_0 \quad , \quad E < V_0$$

SWE :  $\frac{d^2 \Psi_{II}}{dx^2} + \underbrace{\frac{2m}{\hbar^2} (E - V_0)}_{-\text{ve value}} \Psi_{II} = 0$

$$k_2^2 = \frac{2m(V_0 - E)}{\hbar^2} \quad (k_2^2 \text{ must be +ve})$$

$$\frac{d^2 \Psi_{II}}{dx^2} + (ik_2)^2 \Psi_{II} = 0$$

$$ik_2 = d$$

$$\frac{d^2 \Psi_{II}}{dx^2} + \alpha^2 \Psi_{II} = 0$$

$$(D^2 + \alpha^2) \Psi_{II} = 0$$

$$\Psi_{II} = C e^{i\alpha x} + D e^{-i\alpha x}$$

$$\Psi_{II} = C e^{-k_2 x} + D e^{k_2 x}$$

Since the wavefunction obtained has both an increasing and exponentially decaying part, we must check for finiteness

### Finiteness condition

$$\Psi_{\text{II}} = Ce^{-k_2 x} + De^{k_2 x}$$

as  $x \rightarrow \infty$ ,  $\Psi_{\text{II}} \rightarrow \infty$

not allowed

The solution is to set  $D=0$

$$\boxed{\Psi_{\text{II}} = Ce^{-k_2 x}}$$

The wavefunction in region II is an exponentially decaying function, not an oscillating function.

To find the reflection and transmission coefficients, we have to apply continuity/boundary condition.

### Boundary condition

$$\Psi_I(x=0) = \Psi_{\text{II}}(x=0)$$

$$\frac{d\Psi_I}{dx}(x=0) = \frac{d\Psi_{\text{II}}}{dx}(x=0)$$

$$A + B = C \longrightarrow (1)$$

$$ik_1 A - ik_1 B = -k_2 C \longrightarrow (2)$$

$$ik_1 A - ik_1 B = -k_2 A - k_2 B$$

$$A(k_2 + ik_1) = B(-k_2 + ik_1)$$

$$\frac{B}{A} = \frac{k_2 + ik_1}{-k_2 + ik_1}$$

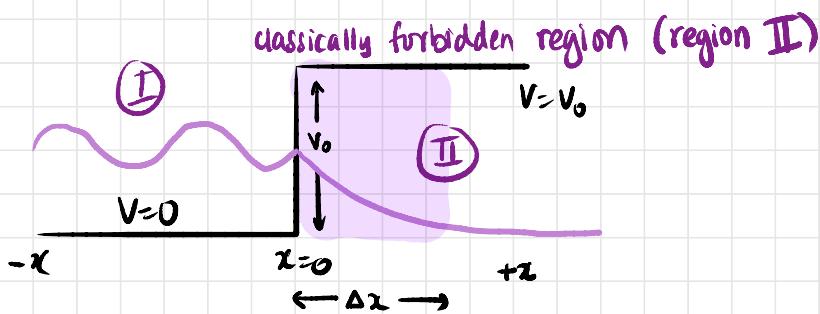
$$R = \frac{|B|^2 \times V_i}{|A|^2 \times V_i} = \frac{(k_2 + ik_1)(k_2 - ik_1)}{(-k_2 + ik_1)(-k_2 - ik_1)}$$

$$R = \frac{k_2^2 + k_1^2}{k_2^2 + k_1^2}$$

$$R = 1$$

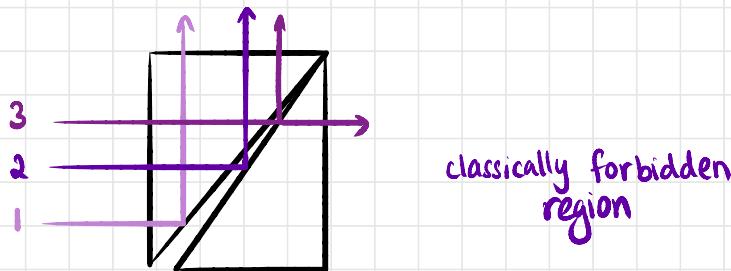
$$R + T = 1 \Rightarrow T = 0$$

- According to this, 100% of incoming waves get reflected and nothing gets transmitted.



- $x \geq 0$  is a region of -ve K.E. How can the wave exist here and further penetrate?
- Wavefunction penetrates but particle never actually found.

### Frustrated Total Internal Reflection (FTIR)



- ray 2 should not exist in the classically forbidden region.

## Penetration Depth

- The wavefunction has a finite value and decays exponentially in region II
- This function is significant until it decays to  $1/e$  of the value at  $x=0$ .
- The changes in this function become insignificant at some distance  $\Delta x$ .

$$\Psi_{II} = C e^{-k_2 x}$$

$$\Psi_{II}(\Delta x) = \frac{1}{e} \Psi_I(0)$$

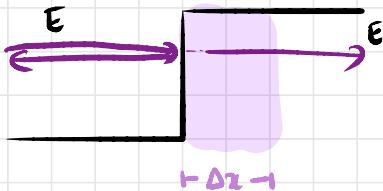
$$C e^{-k_2 \Delta x} = \frac{1}{e} C$$

$$e^{-k_2 \Delta x} = e^{-1}$$

$$\Delta x = \frac{1}{k_2}$$

$$\boxed{\Delta x = \frac{\hbar}{\sqrt{2m(V_0 - E)}}}$$

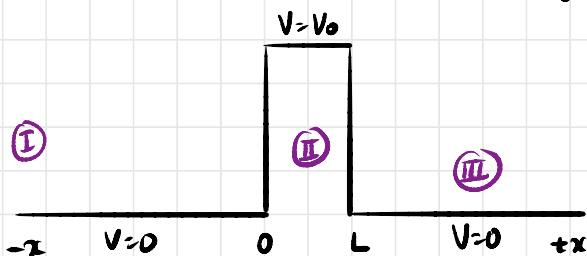
- if  $\Delta t \sim 10^{-9}$  to  $10^{-10}$  s, particle can gain and lose energy (exchange energy)
- $\Delta E \Delta t \sim \hbar$



- finite probability of particle penetrating through that region but cannot exist there.
- Penetration into the classically forbidden region is possible because it exhibits wave nature.

### 3) Potential Barrier

$$E < V_0$$



Region I  
 $V=0$

$$\text{SWE: } \frac{d^2\psi_i}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_i = 0$$

$$\frac{d^2\psi_I}{dx^2} + \frac{2mE}{\hbar^2} \psi_I = 0$$

$$k_I^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi_I}{dx^2} + k_I^2 \psi_I = 0$$

$$\psi_I = \underbrace{A e^{ik_I x}}_{\text{incident}} + \underbrace{B e^{-ik_I x}}_{\text{reflected}}$$

Region II

$$E < V_0$$

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2} (E - V_{in}) \psi_{II} = 0$$

$$\frac{d^2\psi_{II}}{dx^2} - \frac{2m}{\hbar^2} (V_0 - E) \psi_{II} = 0$$

$$k_2^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

$$\frac{d^2\psi_{II}}{dx^2} - k_2^2 \psi_{II} = 0$$

$$\frac{d^2\psi_{II}}{dx^2} + (ik_2)^2 \psi_{II} = 0$$

$$\alpha = ik_2$$

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$$\frac{d^2\psi_I}{dx^2} + \alpha^2 \psi_I = 0$$

$$\psi_I = C e^{i\alpha x} + D e^{-i\alpha x}$$

$$\psi_I = C e^{-k_2 x} + D e^{k_2 x}$$

exponentially decaying  
function cannot oscillate

(OR)  
infinite

### Region III

$$V=0$$

$$SWE: \frac{d^2\psi_{III}}{dz^2} + \frac{2m}{\hbar^2} (E - V_n) \psi_{III} = 0$$

$$\frac{d^2\psi_{III}}{dz^2} + \frac{2mE}{\hbar^2} \psi_{III} = 0$$

$$k_3^2 = \frac{2mE}{\hbar^2}$$

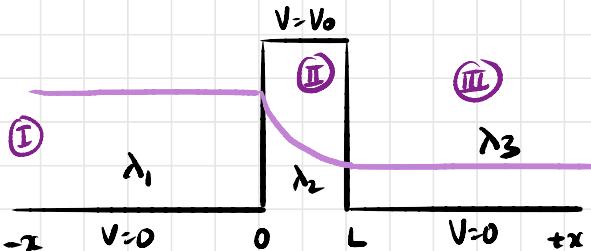
$$\frac{d^2\psi_{III}}{dz^2} + k_3^2 \psi_{III} = 0$$

$$\psi_{III} = \underbrace{E e^{ik_3 z}}_{\text{transmitted}} + F e^{-ik_3 z}$$

cannot reflect  
(no boundary/  
force)

## region II: CFR

$E < V_0$



$$\lambda_1 = \lambda_3, \quad k_1 = k_3 \text{ (no energy lost/gained)}$$

$$\Psi_I = Ae^{ik_1 x} + Be^{-ik_1 x}$$

$$\Psi_{II} = Ce^{-k_2 x}$$

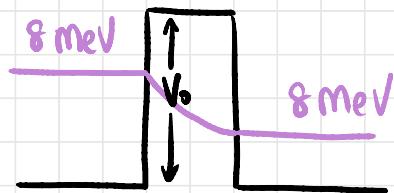
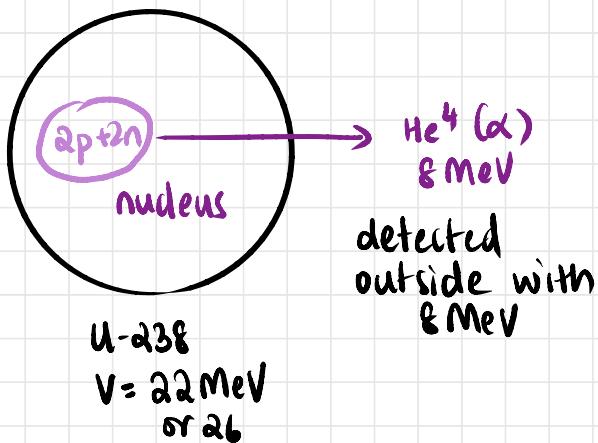
$$\Psi_{III} = De^{ik_3 x}$$

- If exchange of energy takes place in  $10^{-4}$ 's (femtoseconds), the particle gains enough energy to penetrate the region and then loses the energy back to the field and emerges from the barrier with the same energy it entered with, therefore not losing or gaining any energy
  - Particles are never found in region II; they are sometimes detected in region III
  - This effect is known as Quantum Tunneling
  - If exchange of energy happens in the order of  $\Delta t \sim \frac{\hbar}{\Delta E}$ , tunneling effect is observed
- $\Delta E \cdot \Delta t \sim \hbar$
- If the width of the barrier  $L < \Delta x$ , particle can tunnel.

- Seen in  $\alpha$ -decay

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$$V_0 = 22 \text{ MeV}$$



The wavefunctions obtained:

$$\Psi_I = Ae^{ik_1 x} + Be^{-ik_1 x}$$

$$\Psi_{II} = Ce^{-ik_2 x} \quad (D=0)$$

$$\Psi_{III} = Ee^{ik_3 x} \quad (F=0)$$

Boundary conditions

$$1) x=0$$

$$\Psi_I(0) = \Psi_{II}(0)$$

$$\frac{d\Psi_I(0)}{dx} = \frac{d\Psi_{II}(0)}{dx}$$

$$2) x=L$$

$$\Psi_{II}(L) = \Psi_{III}(L)$$

$$\frac{d\Psi_{II}(L)}{dx} = \frac{d\Psi_{III}(L)}{dx}$$

$T$  = transmission coefficient

= tunneling probability

= transmitted flux  
incident flux

$$= \frac{|E|^2 V_3}{|A|^2 V_1} = \frac{|E|^2 \pi k_3/m}{|A|^2 \pi k_1/m}$$

- Solving for  $T$ , we get (no working here)

$$T = e^{-2k_2 L}$$

- The probability of transmission is more if  $k_2$  or  $L$  is small
- Smaller  $k_2$  implies smaller  $V_0 - E$ .
- Thus, the particle will have higher transmission probability through the barrier.
- If the width of the barrier is less than the penetration depth  $\Delta z$ , then there is a finite probability that the particle is transmitted across the barrier.
- This process of transmission through a potential barrier even when the energy of the particle is less than the barrier potential is known as barrier tunneling or quantum tunneling.

Q1. Electrons with energy 0.4 eV are incident on a barrier of height 3 eV and width 0.1 nm. Find probability of the particle penetrating the barrier.

$$T = e^{-2k_2 L}$$

$$k_2 = \frac{\sqrt{2m_e(V_0 - E)}}{\hbar}$$

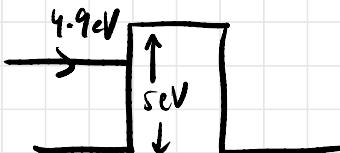
$$k_2 = \frac{\sqrt{2 \times 9.1 \times 10^{-31} (2.6) \times 1.6 \times 10^{-19}}}{(6.626 \times 10^{-34})} (2\pi)$$

$$= 8.25 \times 10^9 \text{ m}^{-1}$$

$$T = e^{-2k_2 L} = e^{-2 \times 8.25 \times 10^9 \times 0.1 \times 10^{-9}} = 0.192 = 19.2\%$$

Q2. A current beam 10 pA (of identical  $e^-$ ) is incident on a barrier of height 5 eV, 1 nm wide. Find the transmitted current strength if the energy of the  $e^-$  is 4.9 eV

\* note: check KE



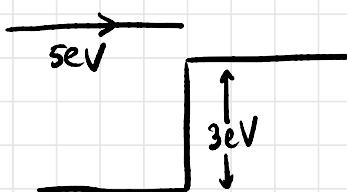
$$k_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

$$= 1.618 \times 10^9$$

$$T = e^{-2k_2 L} = 3.93\%$$

$\therefore$  current strength = 0.393 pA

- Q9. A particle with energy 5eV encounters a potential step of height 3eV. Find the reflection and transmission probabilities.



$$R = \left( \frac{k_1 - k_2}{k_1 + k_2} \right)^2$$

$$k_1 = \frac{\sqrt{2mE}}{\hbar} \quad k_2 = \frac{\sqrt{2m(E-V_0)}}{\hbar}$$

$$(k_1 - k_2)^2 = \frac{2m}{\hbar^2} \left( \sqrt{E} - \sqrt{E-V_0} \right)^2$$

$$(k_1 + k_2)^2 = \frac{2m}{\hbar^2} \left( \sqrt{E} + \sqrt{E-V_0} \right)^2$$

$$R = \frac{\left( \sqrt{E} - \sqrt{E-V_0} \right)^2}{\left( \sqrt{E} + \sqrt{E-V_0} \right)^2} = \frac{2E - V_0 - 2\sqrt{E}\sqrt{E-V_0}}{2E - V_0 + 2\sqrt{E}\sqrt{E-V_0}}$$

$$= \frac{10 - 3 - 2\sqrt{5}\sqrt{2}}{10 - 3 + 2\sqrt{5}\sqrt{2}} = \frac{7 - 2\sqrt{10}}{7 + 2\sqrt{10}} = 0.05$$

$$\therefore T = 0.95$$

Q10. A bunch of particles  $E = 0.2 \text{ eV}$  impinges on a pot step of height  $0.5 \text{ eV}$ . What is probability of trans & ref.

$$T=0, R=1$$

Q11. Estimate the penetration distance  $\Delta x$  for a small dust particle of radius  $10^{-6} \text{ m}$  and density  $10^4 \text{ kg m}^{-3}$  moving at a very slow velocity  $v = 10^{-2} \text{ ms}^{-1}$ , if the particle impinges on a potential step of height equal to twice its kinetic energy in the region to the left of the step

$$m = (10^4) \left( \frac{4}{3} \pi r^3 \right) \Rightarrow KE = \frac{1}{2} \frac{4}{3} \pi r^3 \times 10^{-14} \times 10^{-4}$$

$$KE = 6.67 \times 10^{-19} \text{ J} = E$$

$$V_0 = 1.33 \times 10^{-18} \text{ J}$$

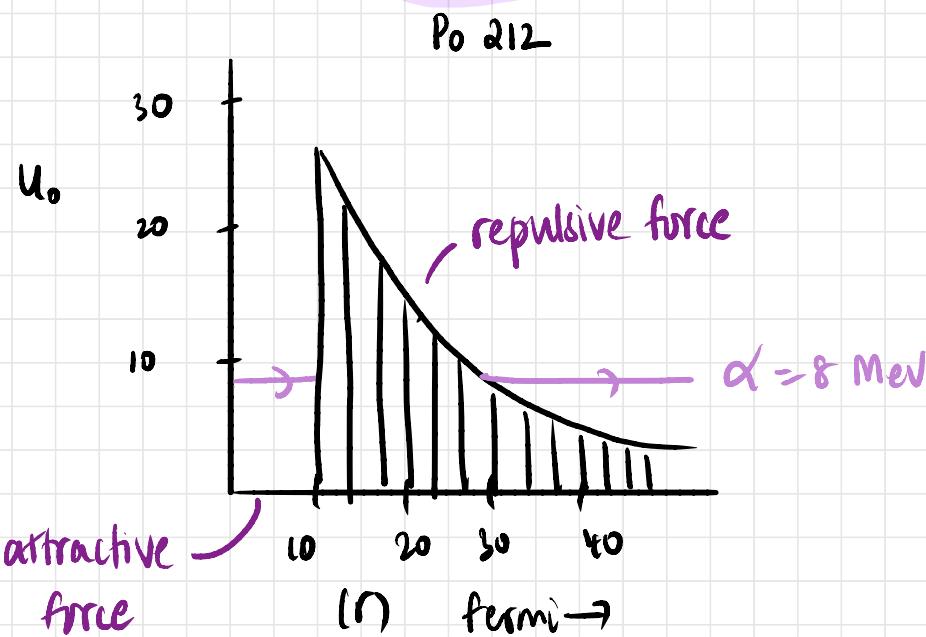
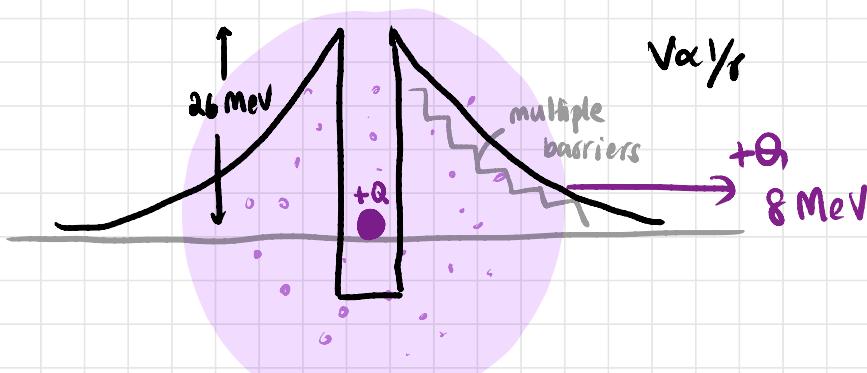
$$\Delta x = \frac{k}{\sqrt{2m(V_0 - E)}} = 2.52 \times 10^{-11} \text{ m}$$

## Applications of Barrier Tunneling

1. Inversion of ammonia
2. Scanning tunneling microscope (STM)
3. Tunnel diodes
4. Alpha decay.

## $\alpha$ -Decay

- Disintegration of heavy nuclei
- $2p + 2n \rightarrow \text{He}^4$
- Below 9.1 fermi, nuclear force dominates over electrostatic force (-ve potential)
- Gamow suggested that at  $r=9.1$  fermi, it is like a barrier potential of 26.4 MeV.



- For Po-212 nuclei,  $\alpha$  particle found with energy 8 MeV
- Has to cross barrier of 26 MeV
- Only way it can be explained: Barrier tunnelling
- $\alpha$ -particle tunnels through the barrier because it is associated with a wave

## Transmission Probability

$$T = e^{-2k_2 L}$$

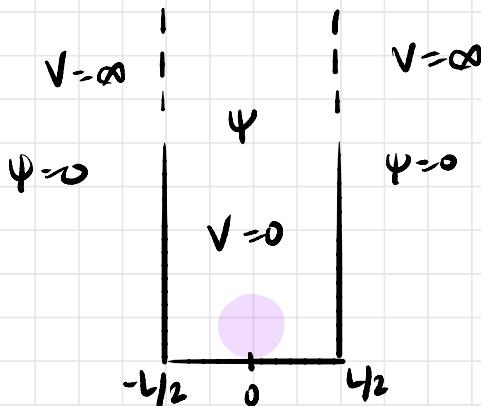
Tunnelling rate is sensitive to small changes in energy and size of the nucleus.

Taking  $\alpha$  particle to be in a state of constant motion with a very high KE, the frequency of approach to the nuclear surface can be estimated to be the diameter of the nucleus divided by the velocity of the particles.

This frequency, when multiplied by the transmission coefficient gives us the probability that an  $\alpha$  particle is emitted out of the nucleus.

The inverse of this probability gives the mean lifetime for  $\alpha$ -decay of the radioactive nucleus.

#### 4) Particle in a 1D infinite potential well



Conditions on  $\Psi$

$$\Psi = 0 \quad \text{at} \quad x \leq -L/2$$

$$\Psi = 0 \quad \text{at} \quad x \geq L/2$$

SWE

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2} (E) \Psi = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\Psi}{dx^2} + k^2 \Psi = 0$$

$$\Psi = C e^{ikx} + D e^{-ikx}$$

$$= (C+D) \cos kx + (C-D)i \sin kx$$

$$\boxed{\Psi = A \cos kx + B \sin kx}$$

# Boundary conditions

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$$\psi=0 \text{ at } x=-L/2$$

$$0 = A \cos \frac{kL}{2} - B \sin \frac{kL}{2} \longrightarrow (1)$$

$$\psi=0 \text{ at } x=L/2$$

$$0 = A \cos \frac{kL}{2} + B \sin \frac{kL}{2} \longrightarrow (2)$$

adding (1) and (2)

$$2A \cos \frac{kL}{2} = 0 \Rightarrow \cos \frac{kL}{2} = 0 \quad \text{or} \quad A=0$$

$$\frac{kL}{2} = (2n+1)\frac{\pi}{2}$$

$$k = (2n+1) \frac{\pi}{L}$$

subtracting (2) from (1)

$$2B \sin \frac{kL}{2} = 0 \Rightarrow \sin \frac{kL}{2} = 0 \quad \text{or} \quad B=0$$

$$\frac{kL}{2} = n\pi$$

$$k = \frac{2n\pi}{L}$$

$$\text{If } A=0, \quad \sin \frac{kL}{2} = 0$$

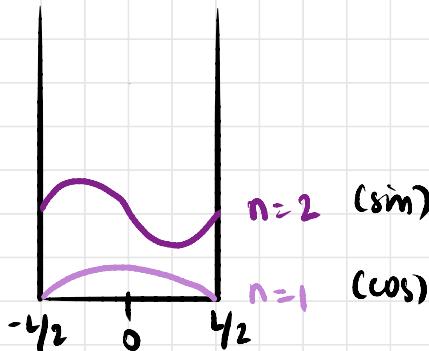
$$\Psi = B \sin kx$$

$$\Psi = B \sin \left( \frac{2n\pi}{L} x \right) \rightarrow 2n = 2, 4, 6 \dots = n$$

$$\text{If } B=0, \quad \cos \frac{kL}{2} = 0$$

$$\Psi = A \cos kx$$

$$\Psi = A \cos \left( \frac{2n_0\pi}{L} x \right) \rightarrow 2n_0 = 1, 3, 5 \dots = n$$



$$\Psi = A \cos \frac{n\pi}{L} x, \quad B=0$$

$$n = 1, 3, 5, 7 \dots$$

$$\Psi = B \sin \frac{n\pi}{L} x, \quad A=0$$

$$n = 2, 4, 6, 8 \dots$$

Normalising the wavefunctions to find A and B

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$$\int_{-L/2}^{L/2} \psi^* \psi dx = 1$$

To find A

$$\int_{-L/2}^{L/2} A^2 \cos^2\left(\frac{n\pi}{L}x\right) dx , n=1,3,5\dots$$

$$\frac{A^2}{2} \int_{-L/2}^{L/2} 1 + \cos \frac{2n\pi}{L} x = 1$$

$$\frac{A^2}{2} \left[ x + \frac{\sin \frac{2n\pi}{L} x}{\frac{2n\pi}{L}} \right]_{-L/2}^{L/2}$$

$$\frac{A^2 L}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{L}}$$

To find B

$$\int_{-L/2}^{L/2} |\psi|^2 dx = 1$$

$$\int_{-\frac{L}{2}}^{\frac{L}{2}} B^2 \sin^2\left(\frac{n\pi}{L}x\right) dx = 1$$

$$\frac{B^2}{2} \int_{-\frac{L}{2}}^{\frac{L}{2}} \left( 1 - \cos \frac{2n\pi x}{L} \right) dx = 1$$

$$\frac{B^2}{2} \left[ x - \frac{\sin \frac{2n\pi x}{L}}{\frac{2n\pi}{L}} \right]_{-\frac{L}{2}}^{\frac{L}{2}} = 1$$

$$\frac{B^2}{2} L = 1$$

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

Therefore, the eigenfunction/wavefunction of particle trapped in a box is given by

$$\Psi = \sqrt{\frac{2}{L}} \cos \frac{n\pi}{L} x, \quad n=1, 3, 5, \dots$$

$$\Psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x, \quad n=2, 4, 6, \dots$$

## Energy Eigenvalue

$$k^2 = \frac{2mE}{\hbar^2}$$

$$n = \frac{m\pi}{L}$$

$$\frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2\hbar^2}{8mL^2}$$

If  $n=0$ ,  $k=0$  &  $E=0$  and particle does not exist

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

Particle in an infinite box  $\rightarrow$  quantised energy states

since  $k$  values are restricted,  $E$  values are also restricted and therefore energy is quantised.

Any kind of confinement/localisation of particle leads to quantisation

Show that the deBroglie waves inside the well are actually standing wave packets.

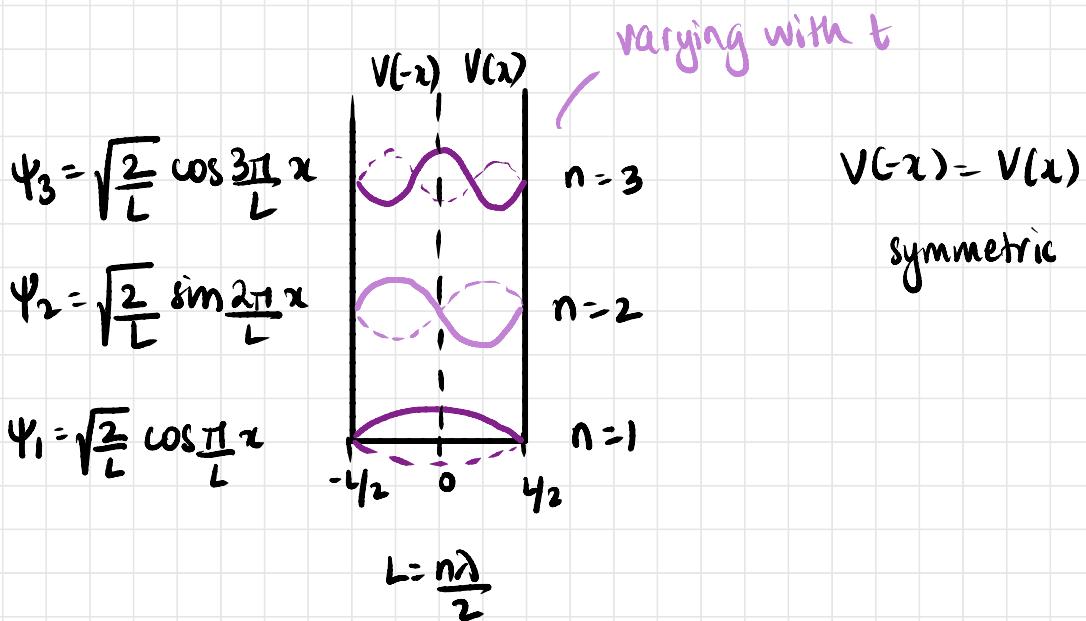
$$k = \frac{n\pi}{L}, n=1, 2, 3 \dots$$

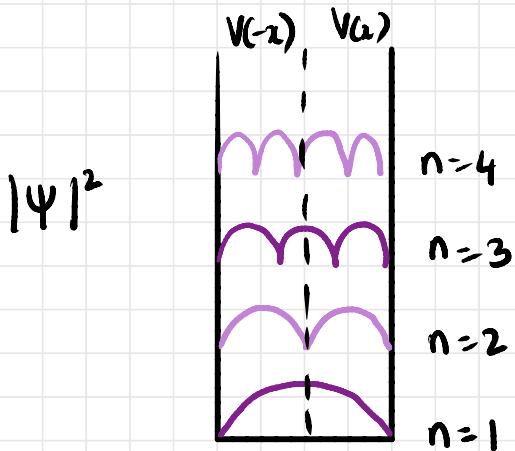
$$\frac{2\pi}{\lambda} = \frac{n\pi}{L}$$

$$L = \frac{n\lambda}{2}$$

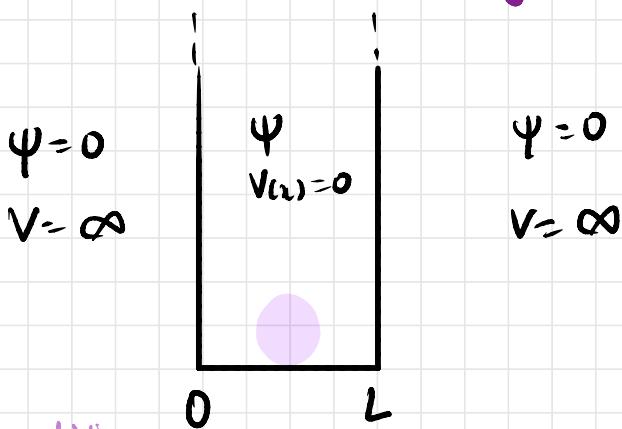
standing waves

Graphically represent the wavefunction and the corresponding probability density





Find the  $\psi$  and the corresponding eigenvalue for a particle in an infinite box if the origin is shifted to the corner.



Boundary condition

- (1) at  $x \leq 0$ ,  $\psi = 0$
- (2) at  $x \geq L$ ,  $\psi = 0$

$$\text{SWE: } \frac{d^2\psi}{dx^2} + \frac{2mE}{\hbar^2} \psi = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

$$\psi = A \cos kx + B \sin kx$$

At  $x=0$

$$A=0$$

$$\psi = B \sin kx$$

At  $x=L$

$$\psi = B \sin kL = 0$$

$$\sin kL = 0 \quad (B \neq 0 \text{ as particle needs to exist})$$

$$kL = n\pi$$

$$k = \frac{n\pi}{L} \rightarrow \text{standing waves}$$

Normalised

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

$$\int_0^L B^2 \sin^2 kx = 1$$

$$\frac{B^2}{2} \int_0^L 1 - \cos 2kx \, dx = 1$$

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

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

## Energy Eigenvalue

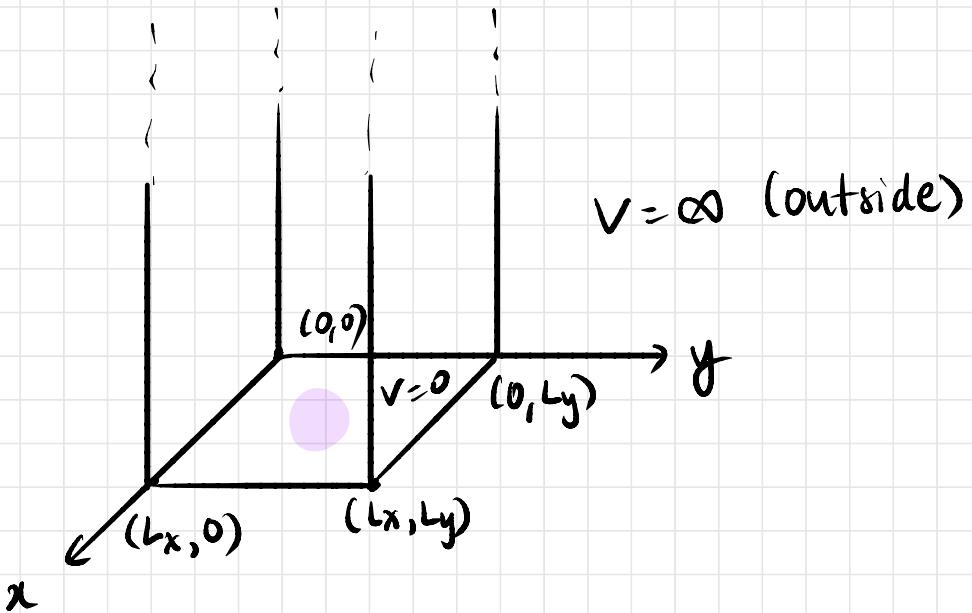
$$k^2 = \frac{2mE}{\hbar^2}$$

$$\frac{n^2\pi^2}{L^2} = \frac{2mE}{\hbar^2} 4\pi^2$$

$$E = \frac{\hbar^2 n^2}{8mL^2}$$

#### 4) Particle in a 2D box

Find  $\Psi$  and the corresponding eigenvalue for a particle trapped in a 2D infinite potential box.



SWE:

$$\frac{\partial^2 \Psi(x,y)}{\partial x^2} + \frac{\partial^2 \Psi(x,y)}{\partial y^2} + \frac{2m}{\hbar^2} (E - V_0) \Psi(x,y) = 0$$

separating the variables

$$\Psi = A e^{-i(kx+ky-\omega t)}$$

$$\Psi(x,y) = \Psi(x)\Psi(y)$$

$$\frac{\partial^2}{\partial x^2} (\psi(x) \psi(y)) + \frac{\partial^2}{\partial y^2} (\psi(x) \psi(y)) + \frac{2m(E - V_0)}{\hbar^2} \psi(x) \psi(y) = 0$$

$$\psi(y) \frac{d^2 \psi(x)}{dx^2} + \psi(x) \frac{d^2 \psi(y)}{dy^2} + \frac{2m(E - V_0)}{\hbar^2} \psi(x) \psi(y) = 0$$

Dividing by  $\psi(y) \psi(x)$

$$\frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + \frac{1}{\psi(y)} \frac{d^2 \psi(y)}{dy^2} + \frac{2m(E - V_0)}{\hbar^2} = 0$$

Inside the 2D well,  $V_0 = 0$  (free)

Outside,  $V_0 = \infty$

$$\frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + \frac{1}{\psi(y)} \frac{d^2 \psi(y)}{dy^2} + \frac{2mE}{\hbar^2} = 0$$

$$k^2 = \frac{2mE}{\hbar^2} \quad \longrightarrow \quad (1)$$

$$\frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} + \frac{1}{\psi(y)} \frac{d^2 \psi(y)}{dy^2} = -k^2$$

$$-k_x^2 = \frac{1}{\psi(x)} \frac{d^2 \psi(x)}{dx^2} \quad \longrightarrow \quad (2)$$

$$-k_y^2 = \frac{1}{\psi(y)} \frac{d^2 \psi(y)}{dy^2} \quad \longrightarrow \quad (3)$$

$$k_x^2 + k_y^2 = k^2$$

$$(2) \frac{d^2\psi(x)}{dx^2} + k_x^2 \psi(x) = 0$$

$$\psi(x) = A \cos k_x x + B \sin k_x x$$

$$(3) \frac{d^2\psi(y)}{dy^2} + k_y^2 \psi(y) = 0$$

$$\psi(y) = C \cos k_y y + D \sin k_y y$$

### Boundary conditions

for  $x \leq 0, \psi(x) = 0$   
 for  $x \geq L_x, \psi(x) = 0$

for  $y \leq 0, \psi(y) = 0$   
 for  $y \geq L_y, \psi(y) = 0$

$x=0, \psi(x) = A = 0$

$$\psi(x) = B \sin k_x x$$

$$x=L_x, \Psi(x) = B \sin k_x L_x = 0$$

$B \neq 0$  (particle will not exist)

$$\sin k_x L_x = 0$$

$$k_x L_x = n_x \pi$$

$$k_x = \frac{n_x \pi}{L_x}$$

$$y=0, \Psi(y) = C = 0$$

$$\Psi(y) = D \sin k_y y$$

$$y=L_y, \Psi(y) = D \sin k_y L_y = 0$$

$$D \neq 0 \Rightarrow \sin k_y L_y = 0$$

$$k_y = \frac{n_y \pi}{L_y}$$

$$k^2 = k_x^2 + k_y^2 = \pi^2 \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

## Normalisation

$$\Psi(x) : \int_0^{L_x} |\Psi(x)|^2 dx = 1$$

$$\int_0^{L_x} B^2 \sin^2\left(\frac{n\pi}{L_x} x\right) dx = 1$$

$$\frac{B^2}{2} \int_0^{L_x} 1 - \cos\left(\frac{2n\pi x}{L_x}\right) dx = 1$$

$$\frac{B^2 L_x}{2} = 1$$

$$B = \sqrt{\frac{2}{L_x}}$$

$$\Psi(y) : \int_0^{L_y} |\Psi(y)|^2 dy = 1$$

$$\int_0^{L_y} D^2 \sin^2\left(\frac{n\pi}{L_y} y\right) dy = 1$$

$$\frac{D^2}{2} \int_0^{L_y} 1 - \cos\left(\frac{2n\pi y}{L_y}\right) dy = 1$$

$$D = \sqrt{\frac{2}{L_y}}$$

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

$$\psi(y) = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi}{L_y} y\right)$$

Energy Eigenvalue

$$k^2 = \frac{2mE}{\hbar^2} = \pi^2 \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$\frac{2mE}{\hbar^2} = \pi^2 \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

$$E = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right)$$

if  $L_x = L_y = L$

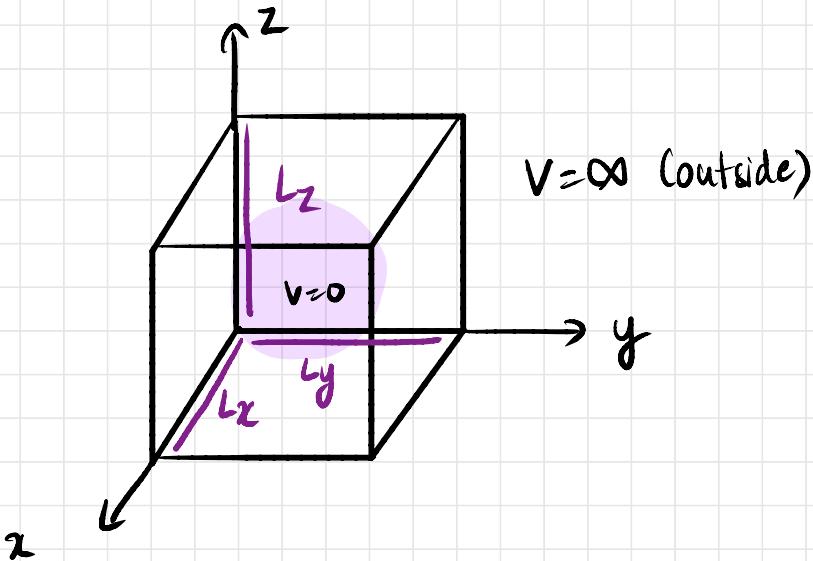
$$E = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2)$$

Complete  $\Psi$

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

### 5) Particle in a 3D box

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$$SWE: \nabla^2 \Psi(x, y, z) + \frac{2m}{\hbar^2} E \Psi(x, y, z) = 0$$

Separating the variables

$$\Psi(x, y, z) = \Psi(x) \Psi(y) \Psi(z)$$

$$\begin{aligned} \Psi(y) \Psi(z) \frac{d^2 \Psi(x)}{dx^2} + \Psi(x) \Psi(z) \frac{d^2 \Psi(y)}{dy^2} + \Psi(x) \Psi(y) \frac{d^2 \Psi(z)}{dz^2} \\ + \Psi(x) \Psi(y) \Psi(z) \frac{2m}{\hbar^2} E = 0 \end{aligned}$$

Dividing by  $\Psi(x) \Psi(y) \Psi(z)$

$$\frac{1}{\Psi(x)} \frac{d^2 \Psi(x)}{dx^2} + \frac{1}{\Psi(y)} \frac{d^2 \Psi(y)}{dy^2} + \frac{1}{\Psi(z)} \frac{d^2 \Psi(z)}{dz^2} + \frac{2mE}{\hbar^2} = 0$$

$$k^2 = \frac{2mE}{\hbar^2}$$

$$\frac{1}{\Psi(x)} \frac{d^2\Psi(x)}{dx^2} = -k_x^2 \longrightarrow (1)$$

$$\frac{1}{\Psi(y)} \frac{d^2\Psi(y)}{dy^2} = -k_y^2 \longrightarrow (2)$$

$$\frac{1}{\Psi(z)} \frac{d^2\Psi(z)}{dz^2} = -k_z^2 \longrightarrow (3)$$

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

(1)  $\frac{d^2\Psi(x)}{dx^2} + k_x^2 \Psi(x) = 0$

$$\Psi(x) = A \sin k_x x + B \cos k_x x$$

(2)  $\frac{d^2\Psi(y)}{dy^2} + k_y^2 \Psi(y) = 0$

$$\Psi(y) = C \sin k_y y + D \cos k_y y$$

(3)  $\frac{d^2\Psi(z)}{dz^2} + k_z^2 \Psi(z) = 0$

$$\Psi(z) = E \sin k_z z + F \cos k_z z$$

## Boundary conditions

$$(1) \quad x \leq 0, \quad \psi(x) = 0$$

$$(2) \quad x \geq L_x, \quad \psi(x) = 0$$

$$(3) \quad y \leq 0, \quad \psi(y) = 0$$

$$(4) \quad y \geq l_y, \quad \psi(y) = 0$$

$$(5) \quad z \leq 0, \quad \psi(z) = 0$$

$$(6) \quad z \geq L_z, \quad \psi(z) = 0$$

$$x=0, \quad \psi(x) = B = 0$$

$$x=L_x, \quad \psi(x) = A \sin k_x L_x = 0$$

$$A \neq 0 \Rightarrow k_x = \frac{n_x \pi}{L_x}$$

$$y=0, \quad \psi(y) = D = 0$$

$$y=l_y, \quad \psi(y) = C \sin k_y l_y = 0$$

$$C \neq 0 \Rightarrow k_y = \frac{n_y \pi}{l_y}$$

$$z=0, \quad \psi(z) = F = 0$$

$$z=L_z, \quad \psi(z) = E \sin k_z L_z = 0$$

$$E \neq 0 \Rightarrow k_z = \frac{n_z \pi}{L_z}$$

$$\psi(x) = A \sin\left(\frac{n_x \pi x}{L_x}\right)$$

$$\psi(y) = C \sin\left(\frac{n_y \pi y}{L_y}\right)$$

$$\psi(z) = E \sin\left(\frac{n_z \pi z}{L_z}\right)$$

### Normalisation

$$\psi(x) : \int_0^{L_x} |\psi(x)|^2 dx = 1$$

$$\int_0^{L_x} A^2 \sin^2\left(\frac{n_x \pi}{L_x} x\right) dx = 1$$

$$\frac{A^2}{2} \int_0^{L_x} 1 - \cos\left(2 \frac{n_x \pi x}{L_x}\right) dx = 1$$

$$A = \sqrt{\frac{2}{L_x}}$$

Similarly,

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

$$E = \sqrt{\frac{2}{L_z}}$$

## Energy Eigenvalue

$$k^2 = k_x^2 + k_y^2 + k_z^2$$

$$\frac{2mE}{\hbar^2} = \pi^2 \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$\frac{8mE}{\hbar^2} = \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

$$E = \frac{\hbar^2}{8m} \left( \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right)$$

if  $L_x = L_y = L_z = L$

$$E = \frac{\hbar^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2)$$

## Complete $\Psi$

$$\Psi(x, y, z) = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi y}{L_y}\right) \sqrt{\frac{2}{L_z}} \sin\left(\frac{n_z \pi z}{L_z}\right)$$

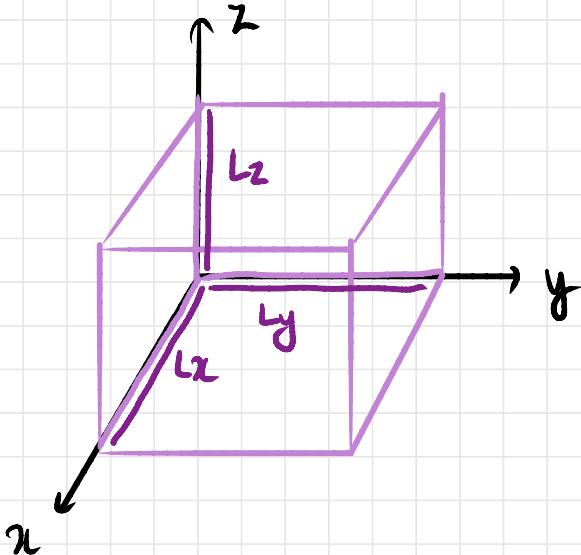
## DEGENERACY & NON-DEGENERACY

- 1D states are non-degenerate
- In a square plane (2D), ( $L_x = L_y = L$ )

$$E = \frac{(n_x^2 + n_y^2) \hbar^2}{8mL^2}$$

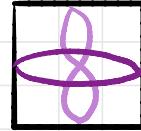
- In a cube (3D), ( $L_x = L_y = L_z = L$ )

$$E = \frac{(n_x^2 + n_y^2 + n_z^2) \hbar^2}{8mL^2}$$



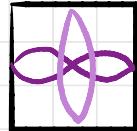
in 2-D

degenerate



$$\begin{aligned} n_x &= 1 \\ n_y &= 2 \end{aligned}$$

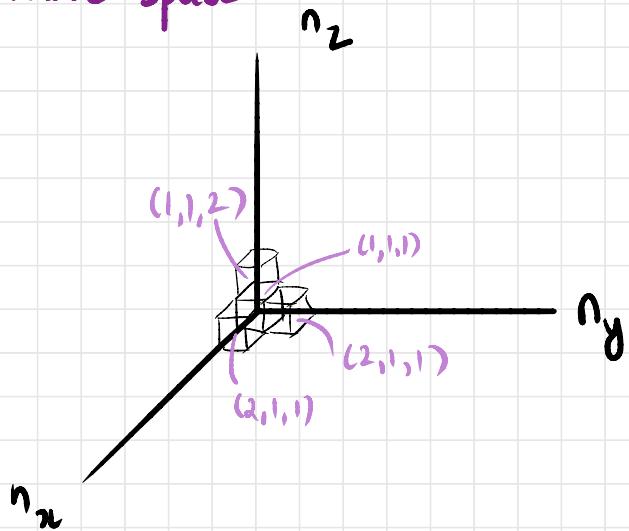
$$(1,2)$$



$$\begin{aligned} n_x &= 2 \\ n_y &= 1 \end{aligned}$$

$$(2,1)$$

## Phase Space



Energy of all states  
in sphere of radius R

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

$$\text{where } R^2 = n_x^2 + n_y^2 + n_z^2$$

For a set of quantum numbers  $n_x$ ,  $n_y$  and  $n_z$ , if the energy of those states remains the same and their wavefunctions are different, then such states are called degenerate states.

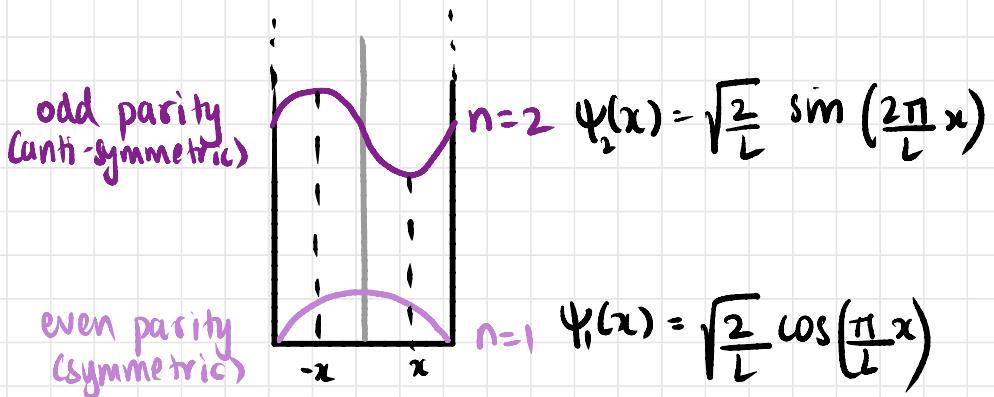
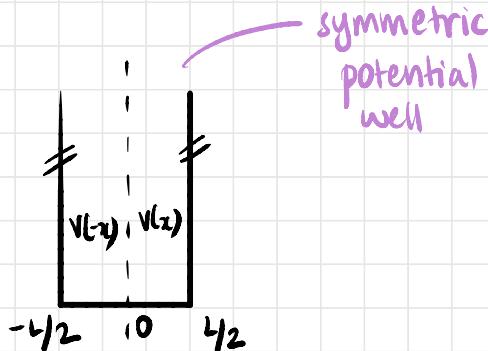
If one of the quantum numbers is different, we have triple degeneracy

eg:  $(1,2,1)$ ,  $(2,1,1)$ ,  $(1,1,2)$

If all the quantum numbers are different, we have sixfold degeneracy ( $3!$ )

eg:  $(1,2,3)$ ,  $(1,3,2)$ ,  $(2,1,3)$ ,  $(2,3,1)$ ,  $(3,1,2)$ ,  $(3,2,1)$

## PARITY



- Parity is exhibited by potentials only if they are symmetric  
Eg: square well potential  
if  $V(-x) = V(x)$
- If the origin is at the corner,  $\Psi$  does not exhibit parity
- For  $n=1$ ,  $\Psi_1(-x) = \Psi_1(x)$  — even parity  
(cos functions show even parity)
- For  $n=2$ ,  $\Psi_2(-x) = -\Psi_2(x)$  — odd parity
- Alternating even and odd parities in symmetric potential wells.

## ORTHOGONALITY PROPERTY OF WAVEFUNCTIONS

Two wavefunctions  $\Psi_m$  and  $\Psi_n$ ,  $m \neq n$  are said to be orthogonal if

$$\int_{-\infty}^{\infty} \Psi_m^* \Psi_n dx = \int_{-\infty}^{\infty} \Psi_n^* \Psi_m dx = 0$$

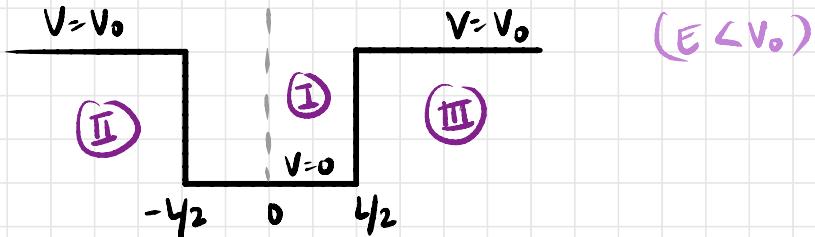
If  $m=n$ ,  $\Psi_m=\Psi_n=\Psi$  and the integral gives us the normalisation condition

Q12. If  $\Psi_1 = A \cos x$  and  $\Psi_2 = B \sin x$ , check whether the given wavefunctions are orthogonal in the interval  $0$  to  $\pi$

$$\begin{aligned} & \int_0^\pi A \cos x B \sin x dx \\ &= \frac{AB}{2} \int_0^\pi \sin 2x dx = \frac{AB}{2} \left[ -\frac{\cos 2x}{2} \right]_0^\pi = 0 \end{aligned}$$

The two wavefunctions are orthogonal.

## 6) Particle in a 1D-Finite Potential Well



Region I

$$V = 0$$

$$\text{SWE: } \frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2} E \psi_I = 0$$

$$k_I^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi_I}{dx^2} + k_I^2 \psi_I = 0$$

$$\psi_I = A e^{ik_I x} + B e^{-ik_I x}$$

$$\psi_I = A \cos k_I x + B \sin k_I x$$

Region II

$$E < V_0$$

SWE:

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_{II} = 0$$

$$k_{II}^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

$$\frac{d^2\psi_{\text{I}}}{dx^2} - k_2^2 \psi_{\text{I}} = 0$$

$$\alpha = ik_2$$

$$\frac{d^2\psi_{\text{II}}}{dx^2} + \alpha^2 \psi_{\text{II}} = 0$$

$$\psi_{\text{II}} = Ce^{-i\alpha x} + De^{i\alpha x}$$

$$\psi_{\text{II}} = Ce^{-k_2 x} + De^{k_2 x}$$

Region III

$$E < V_0$$

$$\frac{d^2\psi_{\text{III}}}{dx^2} + \frac{2m}{\hbar^2} (E - V_0) \psi_{\text{III}} = 0$$

$$k_3^2 = \frac{2m}{\hbar^2} (V_0 - E)$$

$$\frac{d^2\psi_{\text{III}}}{dx^2} - k_3^2 \psi_{\text{III}} = 0$$

$$\beta = ik_3$$

$$\frac{d^2\psi_{\text{III}}}{dx^2} + \beta^2 \psi_{\text{III}} = 0$$

$$\psi_{\text{III}} = Ee^{-i\beta x} + Fe^{i\beta x}$$

$$\psi_{\text{III}} = Ee^{-k_3 x} + Fe^{k_3 x}$$

$\rightarrow$  goes to  $\infty$

$$\Psi_I = Ae^{ik_1x} + Be^{-ik_1x} \quad \text{--- parity (symmetry)}$$

- oscillating wave moving back and forth

Finiteness Condition

as  $x \rightarrow -\infty$ ,  $\Psi_{II} \rightarrow 0$

$$\therefore C=0$$

$$\Psi_{II} = De^{-k_2x} \quad \text{--- exponentially decaying}$$

as  $x \rightarrow \infty$ ,

$$\therefore F=0$$

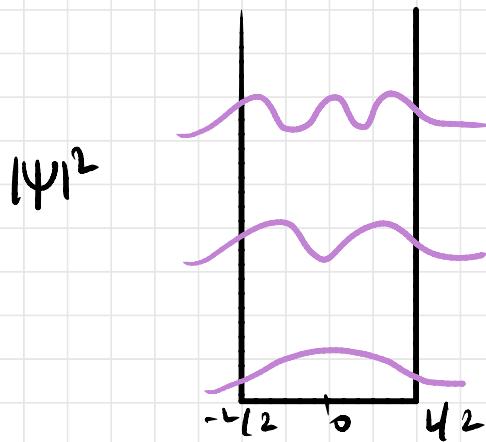
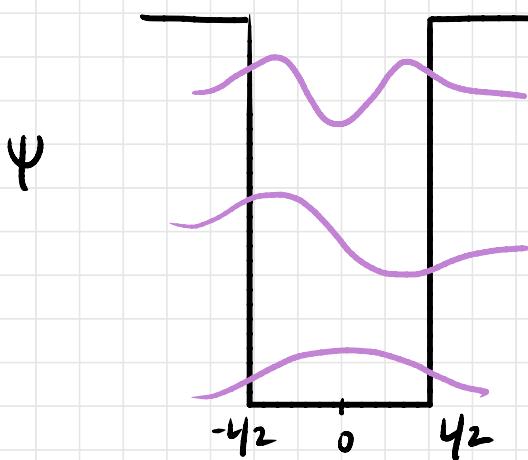
$$\Psi_{III} = Ee^{-k_3x} \quad \text{--- exponentially decaying}$$

The probability density of finding the particle at the walls is not zero.

There is a finite probability of finding the particle beyond the walls of the well.

The wavefunction penetrates the walls of the box, losing energy in the process.

Graphical representation of wavefunction and corresponding probability density for a particle in a finite potential box.



Energy levels are lowered as wavefunction penetrates the walls.

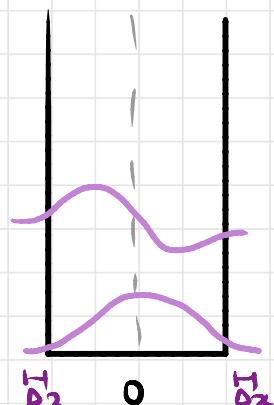
$$\Psi(4/2) \neq 0$$

# Comparision between infinite and finite potential well

infinite



finite



$$E = \frac{n^2 h^2}{8 M L^2}$$

$$\Delta x = \frac{1}{k_2}$$

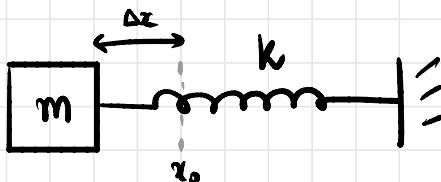
$$E = \frac{n^2 h^2}{8 M (L + 2\Delta x)^2}$$

Particle has more energy in infinite potential well than in a finite potential well

# QUANTUM HARMONIC OSCILLATORS

## Classical oscillator

spring-mass system



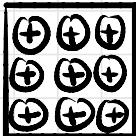
Restoring force tries to bring displaced mass to its equilibrium position

## Quantum Oscillators

Diatomc molecule



Solids



constant motion  
(vibration)

In any oscillator, a restoring force is present where  $F \propto x$

For quantum harmonic oscillators, we approximate the force using Hooke's Law (for small displacements)  
(vibrational spectroscopy)

Application: IR spectroscopy

For a classical system

$$F = -kx = ma$$

$$\frac{d^2x}{dt^2} + \frac{k}{m}x = 0$$

$$\omega^2 = \frac{k}{m} \Rightarrow \omega = \sqrt{\frac{k}{m}}$$

$$x = A \cos \omega t$$

For a quantum system

$$F = -\frac{k_0}{r}x = -\frac{dU}{dx}$$

$$U = \frac{1}{2}k_0x^2$$

To find  $\Psi$ , we write SWE

$$\frac{d^2\Psi}{dx^2} + \frac{2m}{\hbar^2}(E - U)\Psi = 0$$

For a diatomic molecule, we use reduced mass  $\mu$

$$\mu = \frac{m_1 m_2}{m_1 + m_2}; \quad \omega^2 = \frac{k_0}{\mu}$$

$$\frac{d^2\Psi}{dx^2} + \frac{2\mu}{\hbar^2}(E - U)\Psi = 0$$

$$U = \frac{1}{2} k x^2 = \frac{1}{2} \omega^2 \mu x^2 \quad (\text{Hooke's Law})$$

$$\frac{d^2\psi}{dx^2} + \frac{2\mu}{\hbar^2} \left( E - \frac{1}{2} \mu \omega^2 x^2 \right) \psi = 0$$

Solution

$$\psi = N_n H_n(\xi) e^{\frac{1}{2}\xi^2}$$

$$\text{where } \xi = \gamma x, \quad \gamma = \sqrt{\frac{\mu m}{\hbar}}, \quad N_n = \sqrt{\frac{\nu}{2^n n! \sqrt{\pi}}}$$

$H_n(\xi) \rightarrow$  Hermite Polynomial

Eigen value

$$E_n = \left(n + \frac{1}{2}\right) \hbar \nu$$

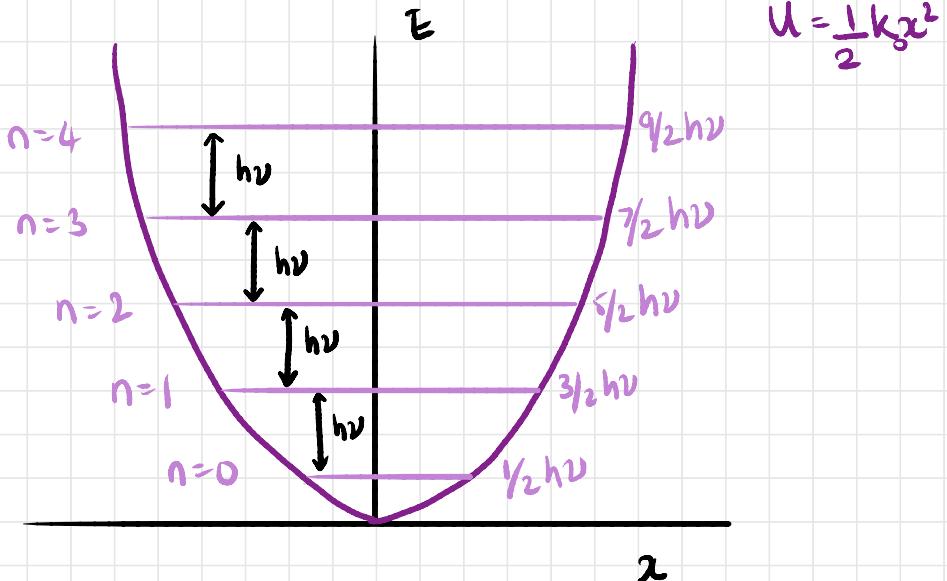
$$E_n = \left(n + \frac{1}{2}\right) \hbar \nu \quad n = 0, 1, 2, \dots$$

At  $n=0$ ,  $E_0 = \frac{1}{2} \hbar \nu \neq 0$ , i.e. the particle possesses energy

The particle has nonzero energy at  $n=0$ , called zero point energy

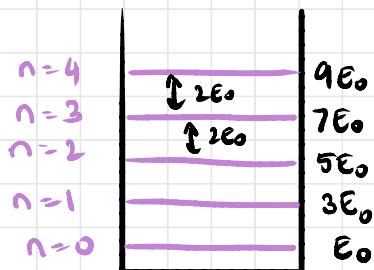
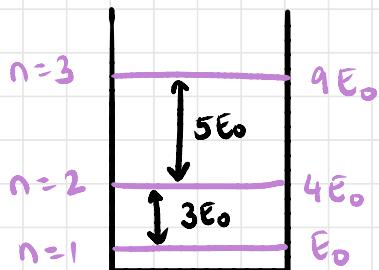
Therefore, vibration always occurs and particle is never at rest.

# Energy Level Diagram



All vibrational energy states are equally spaced

Difference between IFW and QHO



$$E = \frac{n^2 h^2}{8ML^2} = n^2 E_0$$

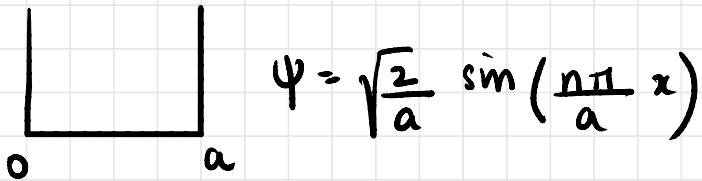
$$E = (n+\frac{1}{2})\hbar\omega = (2n+1)E_0$$

Q13. What is the minimum energy of an electron trapped in a 1D region of an atomic nucleus? The width of the nucleus is  $L = 10^{-14} \text{ m}$  ( $m = 9.1 \times 10^{-31} \text{ kg}$ )

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

$$E_1 = \frac{h^2}{8mL^2} = 6.03 \times 10^{-10} \text{ J} = 3.77 \text{ GeV}$$

Q14. A particle is in an IPW of width  $a$ . Find the prob. of finding the particle between  $a/3$  and  $2a/3$  in the ground and third excited state



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

$$1) n=1, \quad \Psi = \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right)$$

$$P = \int_{a/3}^{2a/3} \frac{2}{a} \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{1}{a} \int_{a/3}^{2a/3} 1 - \cos\left(\frac{2\pi x}{a}\right) dx$$

$$= \frac{1}{a} \left[ x - \frac{\sin\left(\frac{2\pi x}{a}\right)}{\frac{2\pi}{a}} \right]_{a/3}^{2a/3}$$

$$= \frac{1}{a} \left( \frac{2a}{3} - \frac{a}{3} - \frac{\sin\left(\frac{2\pi}{a} \cdot \frac{2a}{3}\right)}{2\pi/a} + \frac{\sin\left(\frac{2\pi}{a} \cdot \frac{a}{3}\right)}{2\pi/a} \right)$$

$$= \frac{1}{a} \left( \frac{a}{3} + \frac{a}{2\pi} \left( -\sin\left(\frac{4\pi}{3}\right) + \sin\left(\frac{2\pi}{3}\right) \right) \right)$$

$$= \left( \frac{1}{3} + \frac{1}{2\pi} \left( \frac{\sqrt{3}}{2} + \frac{\sqrt{3}}{2} \right) \right)$$

$$= \frac{1}{3} + \frac{\sqrt{3}}{2\pi} = 0.609 = 60.9\%$$