ENGINEERING PHYSICS

UNIT - 2

FORMULATION OF QUANTUM MECHANICS

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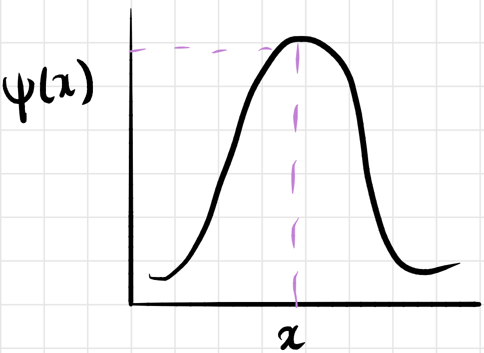
Wavefunction

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

1) ψ must be single-valued, continuous, differentiable



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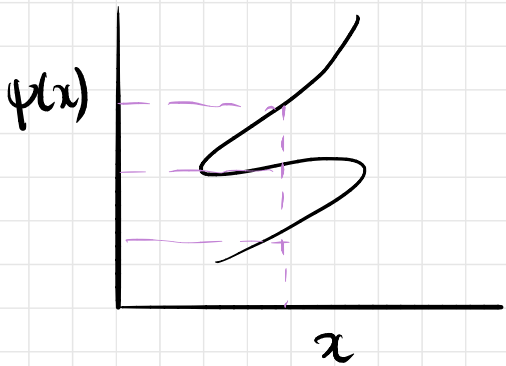

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- probability ($\psi\psi^*$) needs to be defined.

2) The derivatives of ψ should be single-valued, continuous

- $\psi = Ae^{i(kx-\omega t)}$

- To get in terms of p and E

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

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

- Therefore,

$$\psi = Ae^{i/\hbar(px - Et)}$$

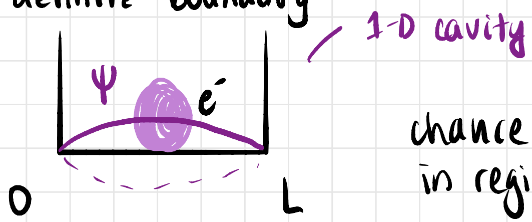
- $\frac{\partial \psi}{\partial x} \longrightarrow p$ and $\frac{\partial \psi}{\partial t} \longrightarrow E$
- $\therefore \frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial t}$ should be continuous

3) Finiteness condition

- ψ should be finite
- as $x \longrightarrow \pm\infty$, $\psi \not\longrightarrow \infty$ but $\psi \longrightarrow 0$

4) ψ should be normalisable

e^- in definite boundary



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

$$\int_0^L \psi \psi^* \, dx = 1$$

free e^- in space (1-D)

$$\int_{-\infty}^{\infty} PD = 1$$ ⟶ normalisation

$$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 1$$ ⟶ particle exists

if $$\int_{-\infty}^{\infty} \psi^* \psi \, dx = 0$$ ⟶ 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

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

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

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

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

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

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

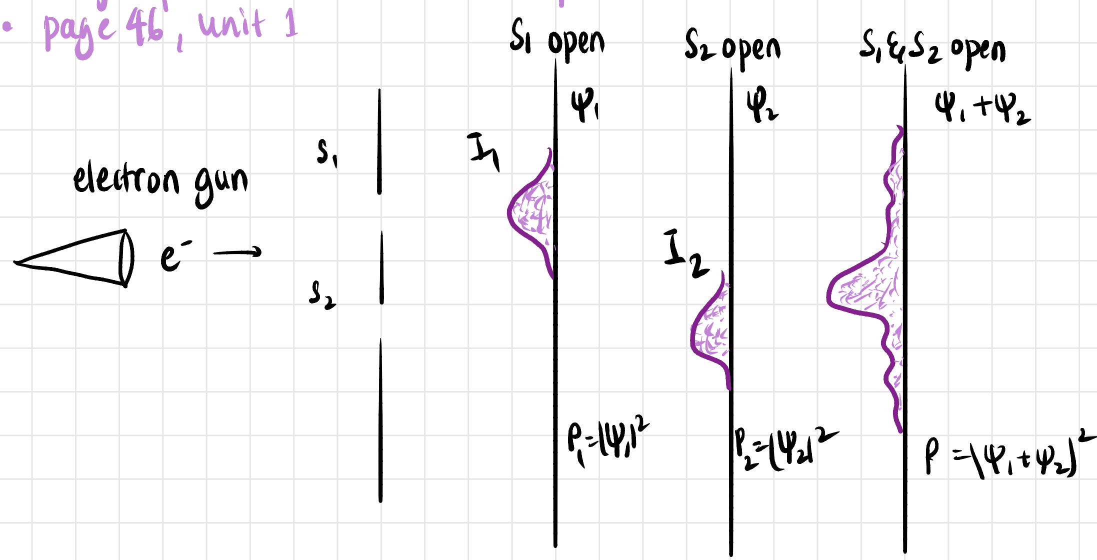
$$\psi = ae^{ikx} \qquad \psi^* = ae^{-ikx}$$

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

$$\boxed{a = 1}$$ (Amplitude is +ve)

Probability Density $|\psi|^2$

- wavefunctions can be added together, but their probabilities cannot be added
- single particle double-slit experiment
- page 46, 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 ($\hat{A}$)

Obervables

- measurable physical parameters
- p, KE, PE

Operators

- to obtain observables, operators on ψ
- operator operates on ψ
- every physical paramater has an associated operator

Eigenvalues

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

operator — eigenvalue

Operator for Observables

1) momentum — $\hat{p}$

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

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

operator

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

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

2) Kinetic energy — $\widehat{KE}$

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

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

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

Dividing by -2m

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

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

3) Total energy — $\hat{H}$

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

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

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

4) Position

$$\hat{x} = x$$

5) Potential energy

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

Observable	Operator
Momentum	$\hat{p} = \frac{\hbar}{i}\frac{\partial}{\partial x}$
Kinetic energy	$\hat{KE} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$
Total energy	$\hat{H} = \frac{-\hbar}{i}\frac{\partial}{\partial t}$
Position	$\hat{x} = x$
Potential energy	$\hat{V}(x) = V(x)$

Hamiltonian Operator ($\hat{H}$)

- used to represent total energy

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

$$\hat{H} = \hat{KE} + \hat{U}(x)$$

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

Q3. The eigenfunction of an operator $\frac{d^2}{dx^2}$ is e^{2x} (ψ). 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 $\sin 3x$

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

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

Expectation Values

- average value
- collection of identical particles (identical ψ)
- multiple attempts - average value
- N_{tot} no. of identical particles (same ψ)

Position

- expectation value of p, position, KE, TE
- $N_1 x_1$, $N_2 x_2$ ... $N_i x_i$

1-D space

- Average value $= \dfrac{N_1 x_1 + N_2 x_2 + N_3 x_3 + \cdots + N_n x_n}{N_1 + N_2 + N_3 + \cdots + N_n}$

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

- $N_i \propto$ probability of finding particle between x_i and $x_i + dx$
- $\dfrac{N_i}{N_{tot}} = P(x)\,dx$ — $P(x)$ is probability density

$$\langle x \rangle = \frac{\sum \frac{N_i}{N_{tot}} x_i}{\sum \frac{N_i}{N_{tot}}} = \frac{\int_{-\infty}^{\infty} P(x)\,dx\,x}{\int_{-\infty}^{\infty} P(x)\,dx}$$

will reduce to 1

will reduce to 1

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

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

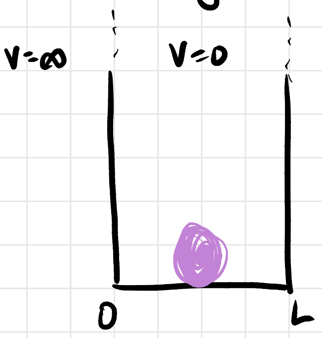
Momentum

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

Kinetic Energy

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

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.



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

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

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

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

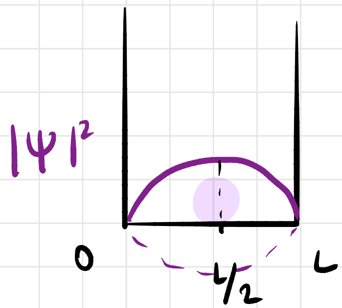
$v = \frac{\sin\frac{2\pi x}{L}}{2\pi/L}$ $u = x$

$dv = \cos\frac{2\pi x}{L}$ $du = dx$

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

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

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



most probable value

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

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

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

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

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

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

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

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

$$\langle p\rangle = 0$$

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

1. Must be consistent with deBroglie-Einstein relation

$$\lambda = \frac{h}{p} \qquad \nu = \frac{E}{h}$$

2. Must be consistent with conservation of energy

$$T.E. = KE + PE$$

3. 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.

$$\psi(x,t) = A\,\psi_1(x,t) + B\,\psi_2(x,t)$$

$$\hat{TE}\psi = \hat{KE}\psi + \hat{PE}\psi$$

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

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

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

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

$$\psi(x,t) = Ae^{\frac{i}{\hbar}(px - Et)}$$

Separation of Variables

$$\psi(x,t) = \underbrace{Ae^{ipx/\hbar}}_{\psi(x)}\ \underbrace{e^{-iEt/\hbar}}_{\phi(t)}$$

$$\psi(x,t) = \psi(x)\,\phi(t)$$

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

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

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

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 ψ where ψ has all the information

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

Applications of SWE (1D)

1) Free Particle — find ψ

- 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 ∞)
- Schrodinger's wave Equation

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

$U_{(x)} = 0$ 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

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

$$D = \pm ik$$

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

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

$$\psi = Ae^{ikx} + Be^{-ikx}$$

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

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

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

The energy of a free particle is given by

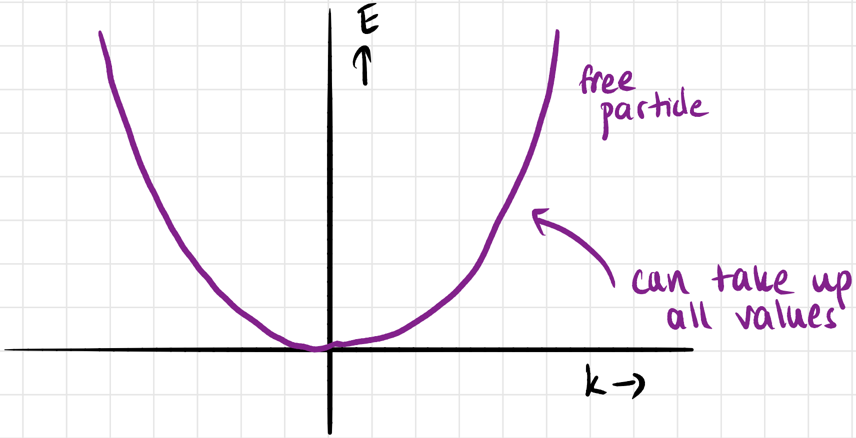
$$\frac{2mE}{\hbar^2} = k^2$$

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

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

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

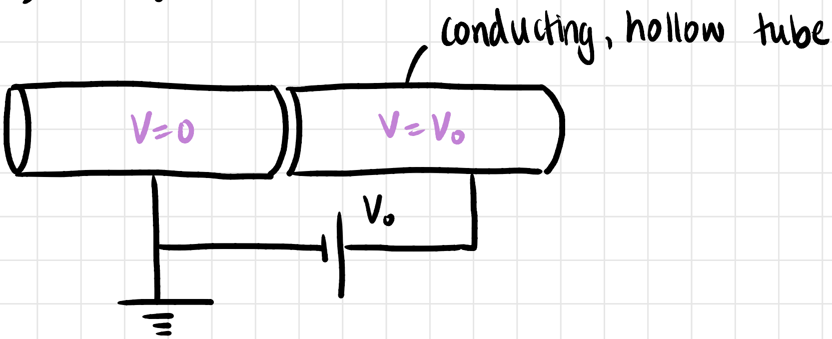
Therefore, energy of a free particle is continuous, not quantised parabola

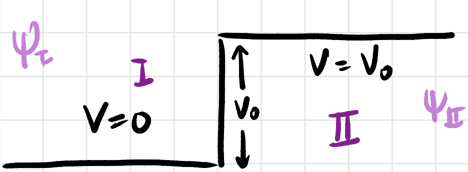


2) Potential Step — find ψ

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 ψ in region I and II for
1) $E > V_0$
2) $E < V_0$





Case I : $E > V_0$

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

Region I

$U_{(x)} = V = 0$ —— ψ_1

Schrödinger wave Equation

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

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

$$k_1^2 = \frac{2m}{\hbar^2}E$$

$$\frac{d^2\psi_I}{dx^2} + k_1^2\psi_I = 0$$

$$\psi_I = \underbrace{Ae^{ik_1x}}_{\text{incident}} + \underbrace{Be^{-ik_1x}}_{\text{reflected}}$$

Since there is a boundary at $x = 0$, Be^{-ik_1x} is the reflected part of the wave

Region II

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

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

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

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

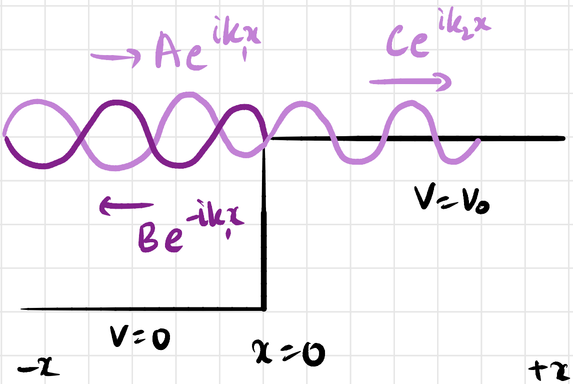
$$\psi_{II} = \underbrace{Ce^{ik_2x}}_{\text{transmitted}} + \underbrace{De^{-ik_2x}}_{\text{reflection}}$$

(D should be = 0)

In region II, Ce^{ik_2x} is the transmitted part of the wave and De^{-ik_2x} is the reflected part.

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

$$\therefore \psi_{II} = Ce^{ik_2x}$$



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

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

$$\psi_{II} = Ce^{ik_2 x}$$

$$R = \frac{\text{reflected flux}}{\text{incident flux}}$$

probability of reflection

$$= \frac{|B|^2 \times v_1}{|A|^2 \times v_1}$$

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

$$= \frac{|C|^2 \times v_2}{|A|^2 \times v_1}$$

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

$$B = C - A$$
$$Ak_1 - Ck_2 = k_1 B$$

$$Ak_1 - Ck_2 = Ck_1 - Ak_1$$

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

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

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

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

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

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

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

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

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

$$k = \frac{2\pi m v}{h} = \frac{mv}{\hbar}$$

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

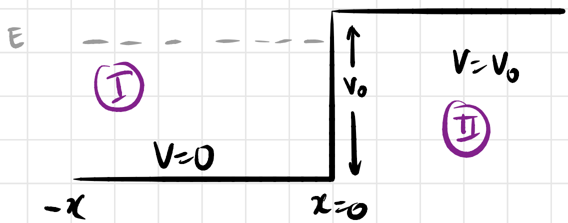
Show that the sum of reflection and transmission probabilities is equal to 1.

$$R + T = 1$$

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

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

Case II : $E < V_0$



$$\lambda_1 = \frac{h}{\sqrt{2mE_k}} \qquad \lambda_2 = \frac{h}{\sqrt{2m(V_0-E)}}$$

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

Region I

$V=0$

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

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

$$k_1^2 = \frac{2mE}{\hbar^2}$$

$$(D^2 + k_1^2)\psi_I = 0$$

$$\boxed{\psi_I = Ae^{ik_1x} + Be^{-ik_1x}}$$

Region II

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

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

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

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

$$ik_2 = \alpha$$

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

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

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

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

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

Finiteness condition

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

as $x \to \infty$, $\psi_{II} \to \infty$ not allowed

The solution is to set $D = 0$

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

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

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

Boundary condition

$$\psi_I(x=0) = \psi_{II}(x=0)$$

$$\frac{d\psi_I(x=0)}{dx} = \frac{d\psi_{II}(x=0)}{dx}$$

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

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

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

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

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

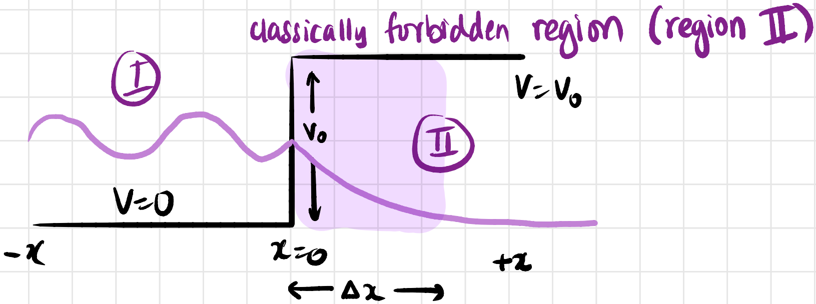
$$R = \frac{|B|^2 \times v_1}{|A|^2 \times v_1} = \frac{(k_2 + ik_1)(k_2 - ik_1)}{(-k_2 + ik_1)(-k_2 - ik_1)}$$

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

$$R = 1$$

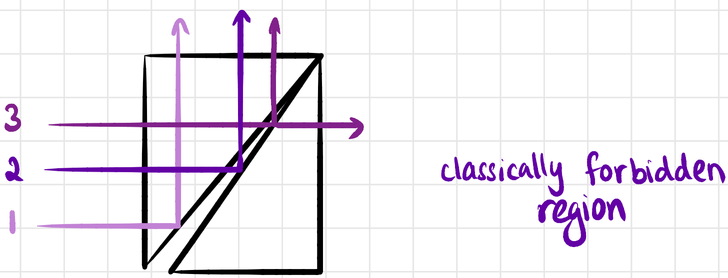
$$R + T = 1 \Rightarrow T = 0$$

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



- $x = 0$ 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 Δx.

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

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

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

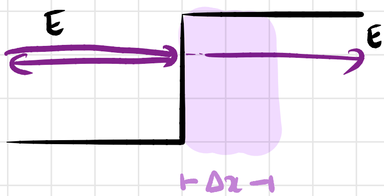
$$e^{-k_2 \Delta x} = e^{-1}$$

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

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

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

- $\Delta E \, \Delta t \sim \hbar$

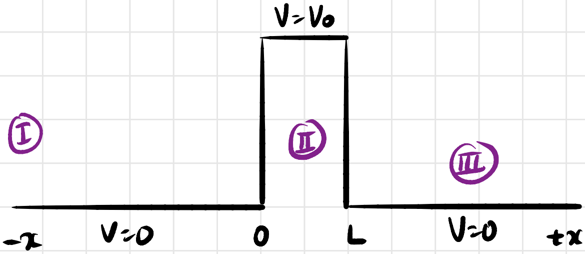


- finite probability of particle penetrating through that region but cannot exist there.

- Penetration into the classically forbidden region is possible because it exhibits wave nature.

3) Potential Barrier

$E < V_0$



Region I

$V=0$

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

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

$$k_1^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi_I}{dx^2} + k_1^2\psi_I = 0$$

$$\psi_I = \underbrace{Ae^{ik_1x}}_{\text{incident}} + \underbrace{Be^{-ik_1x}}_{\text{reflected}}$$

Region II

$E < V_0$

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

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

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

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

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

$\alpha = ik_2$

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

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

$$\psi_{II} = Ce^{-k_2 x} + \cancel{De^{k_2 x}} \xrightarrow{} 0$$

exponentially decaying function cannot oscillate

OR

infinite

Region III

$V = 0$

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

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

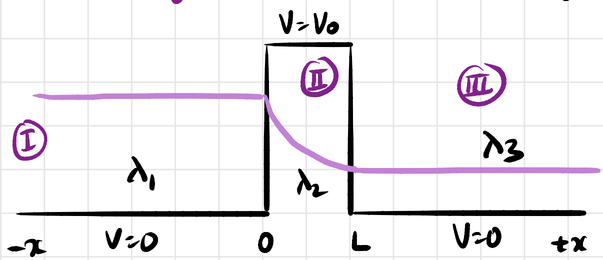
$$k_3^2 = \frac{2mE}{\hbar^2}$$

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

$$\psi_{III} = \underbrace{Ee^{ik_3 x}}_{\text{transmitted}} + \cancel{Fe^{-ik_3 x}} \xrightarrow{} 0$$

cannot reflect (no boundary/force)

region II : CFR $\quad E < V_0$



$\lambda_1 = \lambda_3$, $k_1 = k_3$ (no energy lost/gained)

$$\psi_{I} = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\psi_{II} = Ce^{-k_2x}$$

$$\psi_{III} = Ee^{ik_3x}$$

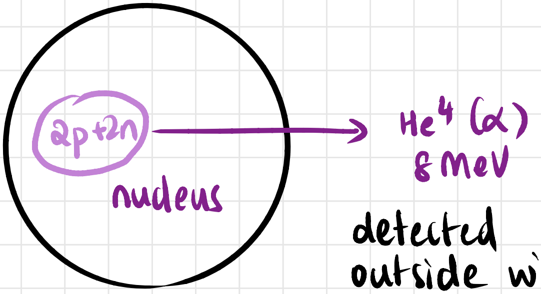
- If exchange of energy takes place in 10^{-4}s (femtoseconds), the particle gains enough energy to penetrate the region and then loses the energy back to the field and emerges from the barrier with the same energy it entered with, therefore not losing or gaining any energy
- Particles are never found 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.

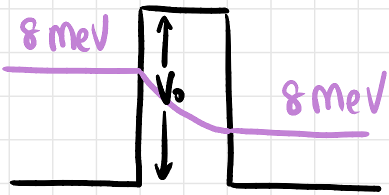
- Seen in α-decay

$V_0 = 22\,MeV$



detected outside with 8 MeV

U-238
V = 22 MeV
or 26



The wavefunctions obtained:

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\psi_{II} = Ce^{-k_2x} \qquad (D=0)$$

$$\psi_{III} = Ee^{ik_3x} \qquad (F=0)$$

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

$= \dfrac{\text{transmitted flux}}{\text{incident flux}}$

$$= \frac{|E|^2 v_3}{|A|^2 v_1} = \frac{|E|^2 \hbar k_3/m}{|A|^2 \hbar k_1/m}$$

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

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

- 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 Δx, 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.

Q7. Electrons with energy 0.4eV are incident on a barrier of height 3eV and width 0.1nm. Find probability of the particle penetrating the barrier.

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

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

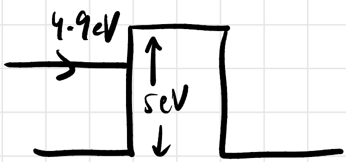
$$k_2 = \frac{\sqrt{2 \times 9.1 \times 10^{-31} (2.6) \times 1.6 \times 10^{-19}}}{(6.626 \times 10^{-34})} (2\pi)$$

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

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

Q8. A current beam 10pA (of identical e^-) is incident on a barrier of height 5eV, 1nm wide. Find the transmitted current strength if the energy of the e^- is 4.9 eV

* note : check KE



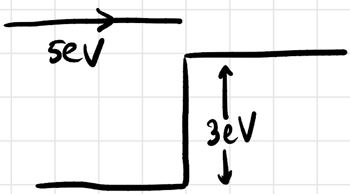
$$k_2 = \frac{\sqrt{2m(V_0 - E)}}{\hbar}$$

$$= 1.618 \times 10^{9}$$

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

$\therefore$ current strength = 0.393 pA

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



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

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

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

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

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

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

$\therefore T = 0.95$

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

$$T = 0, \quad R = 1$$

Q11. Estimate the penetration distance Δx for a small dust particle of radius 10^{-6} m and density $10^{4}\ kg\,m^{-3}$ moving at a very slow velocity $v = 10^{-2} ms^{-1}$; 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.

$$m = (10^{4})\left(\frac{4}{3}\pi 10^{-18}\right) \Rightarrow KE = \frac{1}{2}\,\frac{4}{3}\pi \times 10^{-14} \times 10^{-4}$$

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

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

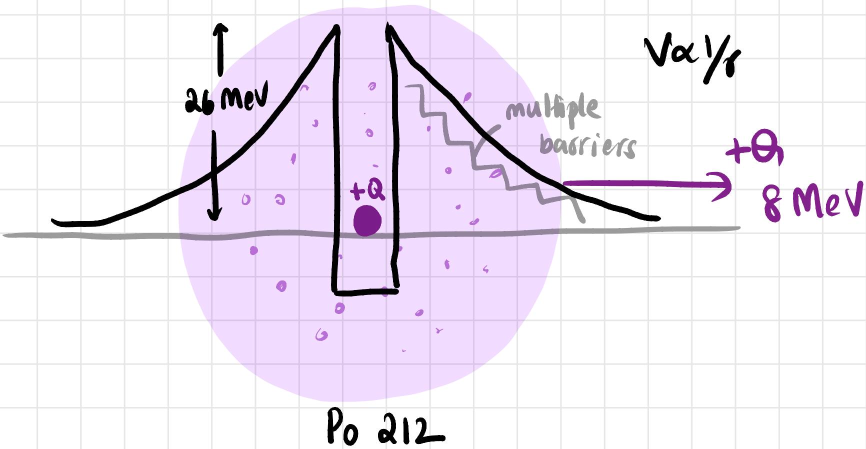
$$\Delta x = \frac{\hbar}{\sqrt{2m(V_0 - E)}} = 2.52 \times 10^{-19} m$$

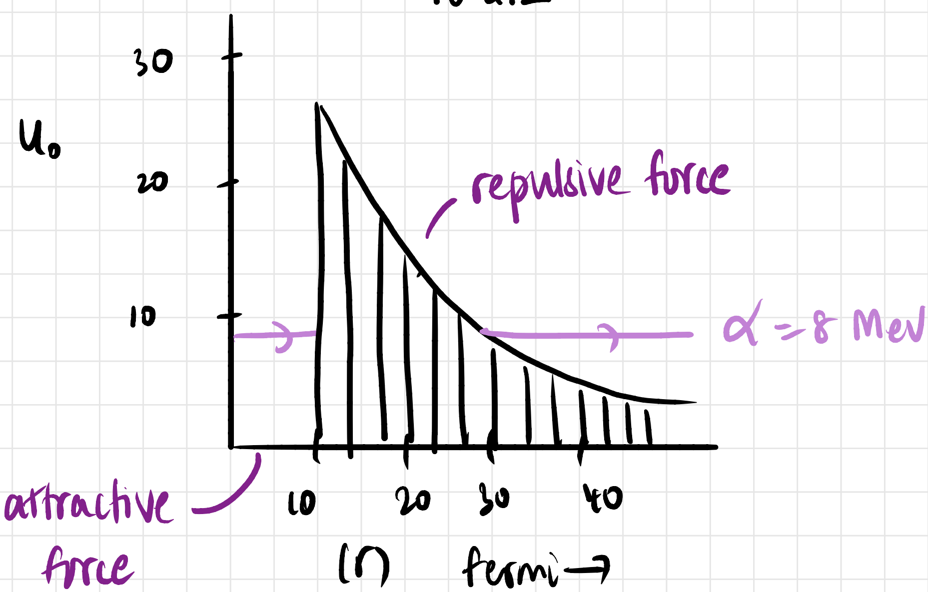
Applications of Barrier Tunneling

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

α- Decay

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





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

Transmission Probability

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

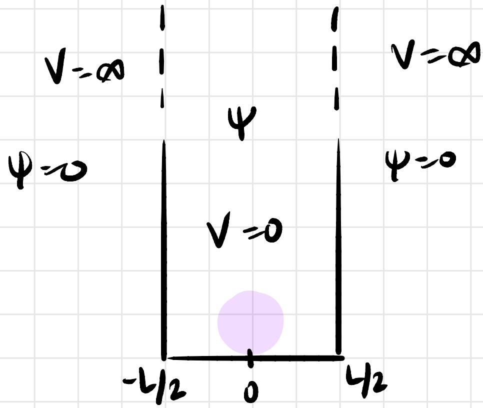
Tunnelling rate is sensitive to small changes in energy and size of the nucleus.

Taking α 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 α particle is emitted out of the nucleus.

The inverse of this probability gives the mean lifetime for α-decay of the radioactive nucleus.

4) Particle in a 1D infinite potential well



Conditions on ψ

$\psi = 0$ at $x \leq -L/2$

$\psi = 0$ at $x \geq L/2$

SWE

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

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

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

$$\psi = Ce^{ikx} + De^{-ikx}$$

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

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

Boundary conditions

$\psi = 0$ at $x = -L/2$

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

$\psi = 0$ at $x = L/2$

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

adding (1) and (2)

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

$$\frac{kL}{2} = (2n_o - 1)\frac{\pi}{2}$$

$$k = (2n_o - 1)\frac{\pi}{L}$$

subtracting (2) from (1)

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

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

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

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

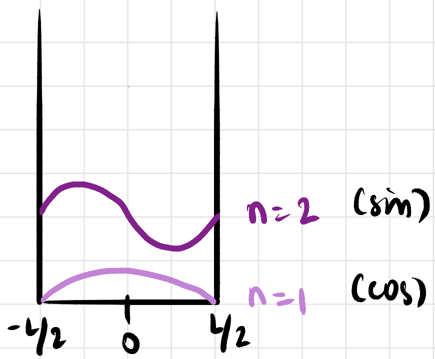
$$\psi = B \sin kx$$

$$\psi = B \sin \left(\frac{2n_0\pi}{L}\right) x \longrightarrow 2n_0 = 2, 4, 6 \ldots = n$$

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

$$\psi = A \cos kx$$

$$\psi = A \cos \frac{(2n_0-1)\pi}{L} x \longrightarrow 2n_0 - 1 = 1, 3, 5 \ldots = n$$



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

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

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

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

Normalising the wavefunctions to find A and B

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

To find A

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

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

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

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

To find B

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

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

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

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

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

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

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

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

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

Energy Eigenvalue

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

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

$$\frac{n^2 \cancel{\pi^2}}{L^2} = \frac{2mE}{h^2} \, 4\cancel{\pi^2}$$

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

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

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

Particle in an infinite box $\longrightarrow$ 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.

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

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

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

standing waves

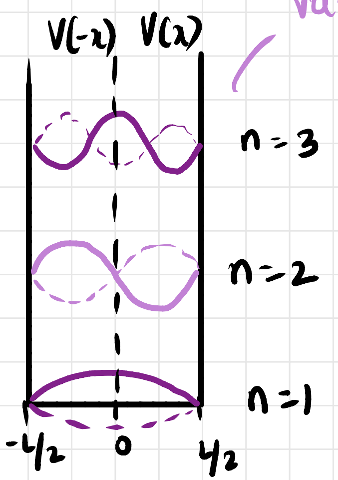
Graphically represent the wavefunction and the corresponding probability density

varying with t

$$\psi_3 = \sqrt{\frac{2}{L}} \cos \frac{3\pi}{L} x$$

$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi}{L} x$$

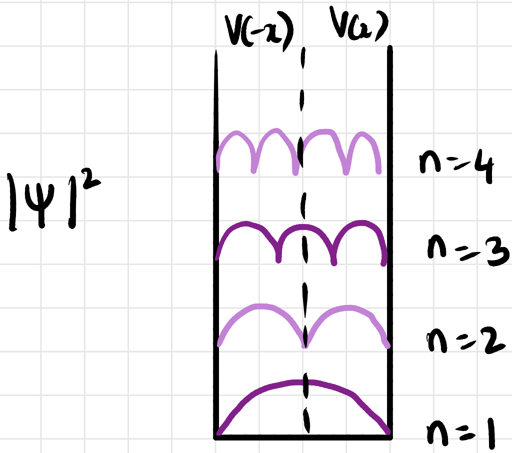
$$\psi_1 = \sqrt{\frac{2}{L}} \cos \frac{\pi}{L} x$$



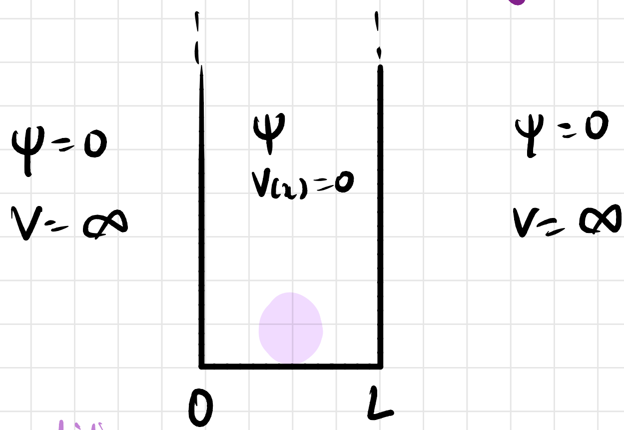
$$V(-x) = V(x)$$

symmetric

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



Find the ψ 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 $x \geq L$, $\psi = 0$

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 $x = L$

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

$\sin kL = 0$ ($B \neq 0$ as particle needs to exist)

$$kL = n\pi$$

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

Normalised

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

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

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

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

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

Energy Eigenvalue

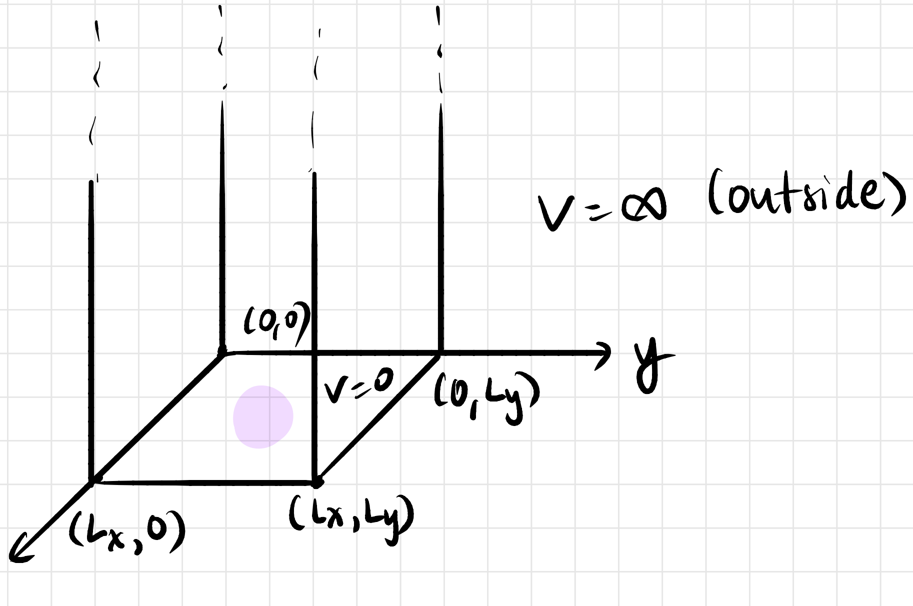
$$k^2 = \frac{2mE}{\hbar^2}$$

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

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

4) Particle in a 2D box

Find ψ 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

$$\psi = Ae^{-i(kx + ky - \omega t)}$$

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

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

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

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

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

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

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

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

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

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

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

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

(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 $x \le 0$, $\psi(x) = 0$
for $x \ge L_x$, $\psi(x) = 0$

for $y \le 0$, $\psi(y) = 0$
for $y \ge L_y$, $\psi(y) = 0$

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

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

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

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

$\sin k_x L_x = 0$

$k_x L_x = n_x \pi$

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

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

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

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

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

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

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

Normalisation

$\psi(x)$:

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

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

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

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

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

$\psi(y)$:

$$\int_0^{L_y} |\psi(y)|^2 \, dy = 1$$

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

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

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

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

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

Energy Eigenvalue

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

$$\frac{2mE\,4\cancel{\pi^2}}{h^2} = \cancel{\pi^2}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right)$$

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

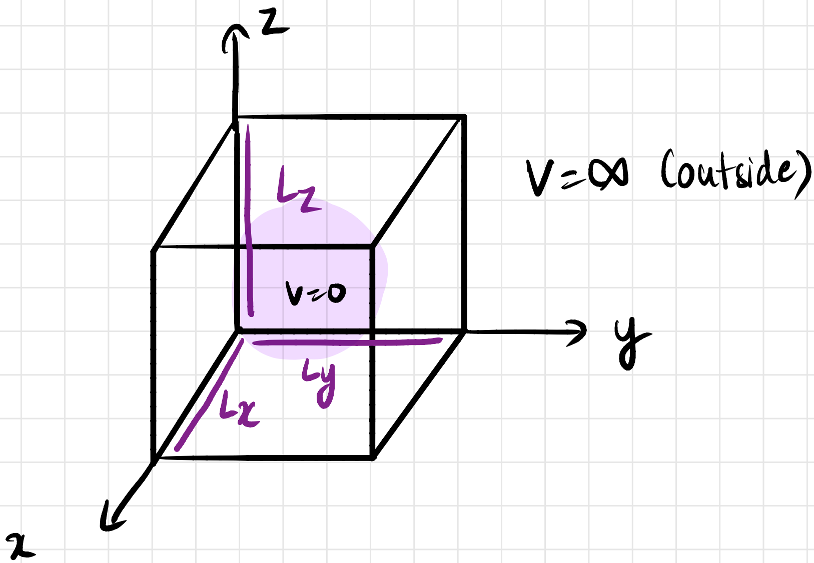
if $L_x = L_y = L$

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

Complete ψ

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

5) Particle in a 3D box



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

Separating the variables

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Normalisation

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

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

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

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

Similarly,

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

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

Energy Eigenvalue

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

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

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

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

if $L_x = L_y = L_z = L$

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

Complete ψ

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

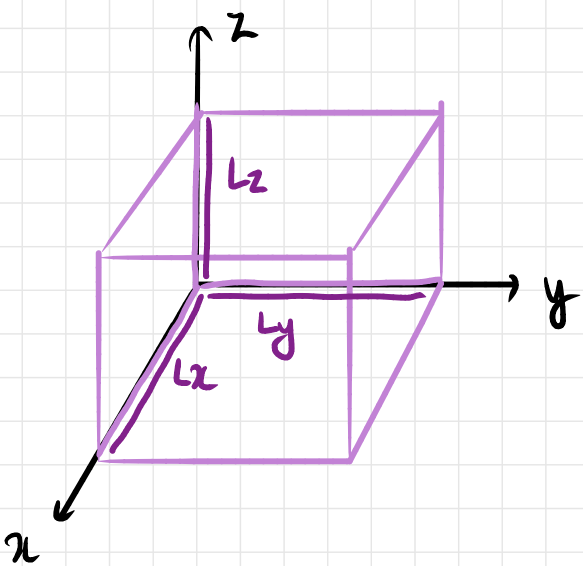
DEGENERACY & NON-DEGENERACY

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

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

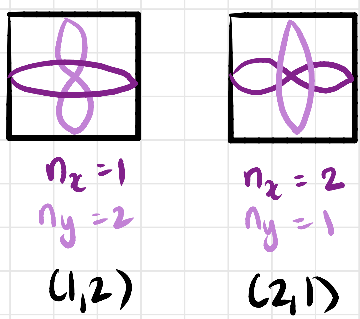
- In a cube (3D), $(L_x = L_y = L_z = L)$

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

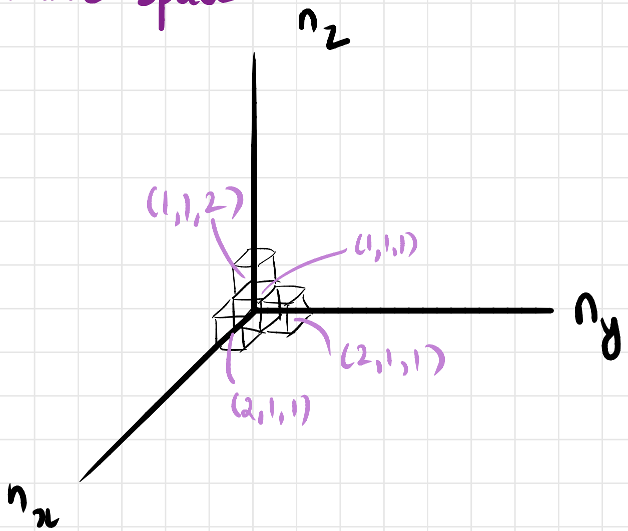


in 2-D

degenerate



Phase Space



Energy of all states in sphere of radius R

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

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.

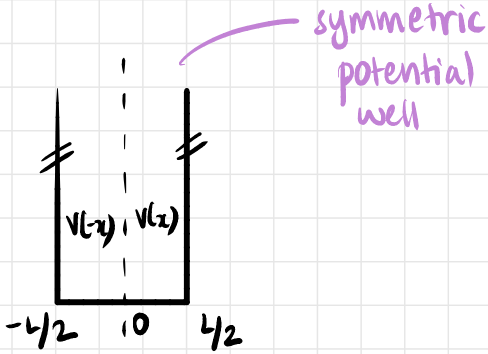
If one of the quantum numbers is different, we have triple degeneracy

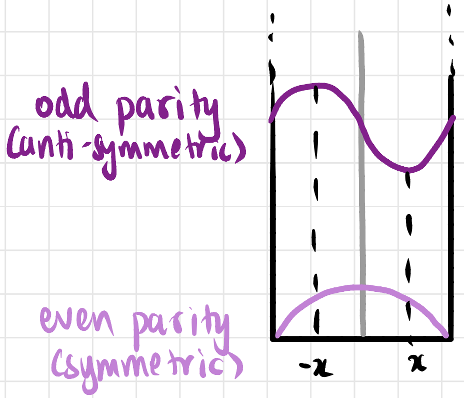
eg: (1,2,1), (2,1,1), (1,1,2)

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





$n=2$ $\quad \psi_2(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{2\pi}{L} x\right)$

$n=1$ $\quad \psi_1(x) = \sqrt{\frac{2}{L}} \cos\left(\frac{\pi}{L} x\right)$

- Parity is exhibited by potentials only if they are symmetric
  Eg: square well potential

  if $\quad V(-x) = V(x)$

- If the origin is at the corner, ψ 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 ψ_m and ψ_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

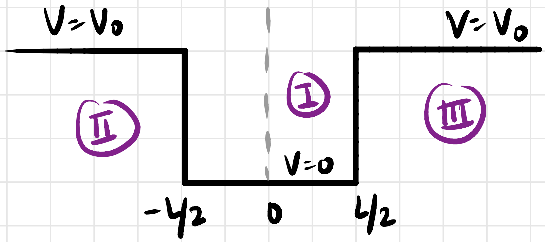
Q12. If $\psi_1 = A\cos x$ and $\psi_2 = B\sin x$, check whether the given wavefunctions are orthogonal in the interval 0 to π

$$\int_0^{\pi} A\cos x \, B\sin x \, dx$$

$$= \frac{AB}{2} \int_0^{\pi} \sin 2x \, dx = \frac{AB}{2} \left[-\frac{\cos 2x}{2} \right]_0^{\pi} = 0$$

The two wavefunctions are orthogonal.

6) Particle in a 1D-Finite Potential well



$(E < V_0)$

Region I

$V=0$

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

$$k_1^2 = \frac{2mE}{\hbar^2}$$

$$\frac{d^2\psi_I}{dx^2} + k_1^2\psi_I = 0$$

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\psi_I = A\cos k_1x + B\sin k_1x$$

Region II

$E < V_0$

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

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

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

$$\alpha = ik_2$$

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

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

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

goes to ∞

Region III

$E < V_0$

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

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

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

$$\beta = ik_3$$

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

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

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

goes to ∞

$$\boxed{\psi_I = Ae^{ik_1x} + Be^{-ik_1x}}$$ — parity (symmetry)

- oscillating wave moving back and forth

Finiteness condition

as $x \to -\infty$, $\psi_{II} \to 0$

$\therefore C = 0$

$$\boxed{\psi_{II} = De^{k_2x}}$$ — exponentially decaying

as $x \to \infty$,

$\therefore F = 0$

$$\boxed{\psi_{III} = Ee^{-k_3x}}$$ — exponentially decaying

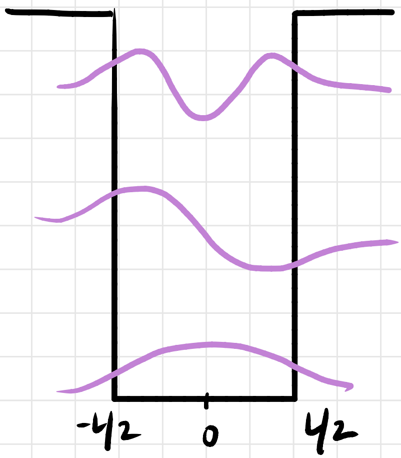
The probability density of finding the particle at the walls is not zero.

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

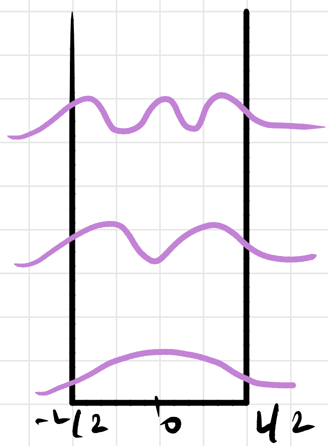
The wavefunction penetrates the walls of the box, losing energy in the process.

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

ψ



$|\psi|^2$

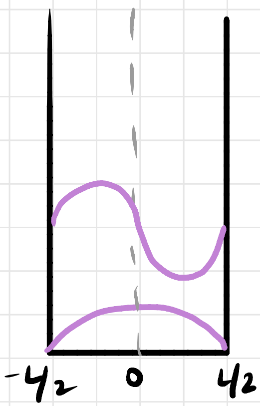


Energy levels are lowered as wavefunction penetrates the walls.

$\psi(L/2) \neq 0$

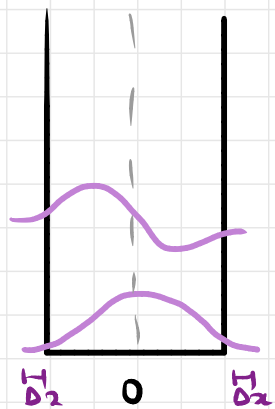
Comparision between infinite and finite potential well

infinite



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

finite



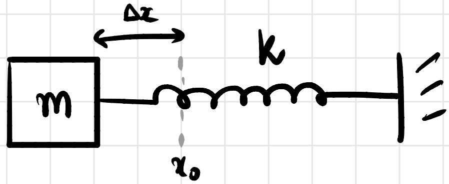
$$\Delta x = \frac{1}{k_2} \qquad E = \frac{n^2h^2}{8M(L+2\Delta x)^2}$$

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

QUANTUM HARMONIC OSCILLATORS

Classical oscillator

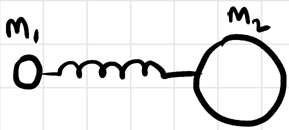
Spring-mass system



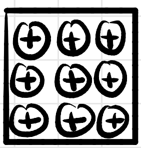
Restoring force tries to bring displaced mass to its equilibrium position

Quantum Oscillators

Diatomic 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

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

$$U = \frac{1}{2}k_0 x^2$$

To find ψ, 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 μ

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

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

$$U = \frac{1}{2}k_0x^2 = \frac{1}{2}\omega^2\mu x^2 \text{ (Hooke's Law)}$$

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

Solution

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

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

$H_n(\xi) \longrightarrow$ Hermite Polynomial

Eigen value

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

$$E_n = \left(n + \frac{1}{2}\right)h\nu \qquad n = 0, 1, 2 \ldots$$

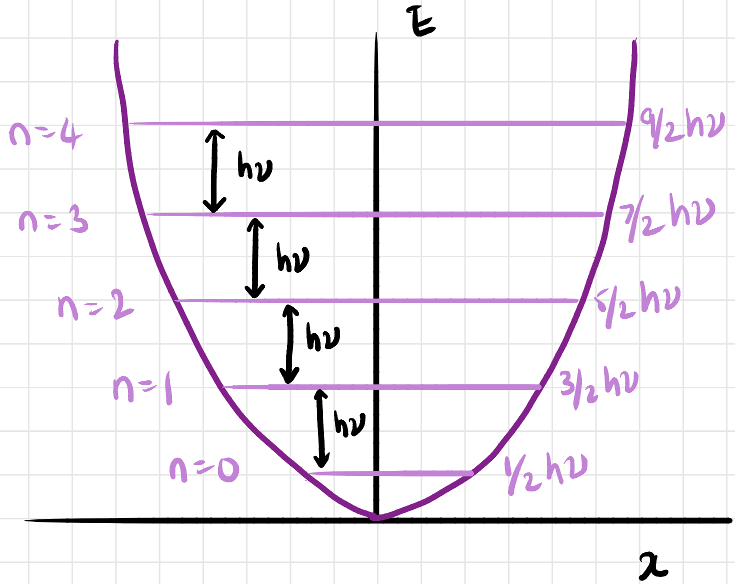
At $n=0$, $E_0 = \frac{1}{2}h\nu \neq 0$, i.e. the particle possesses energy

The particle has nonzero energy at $n=0$, called Zero Point Energy

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

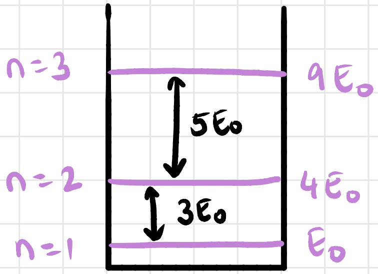
Energy Level Diagram

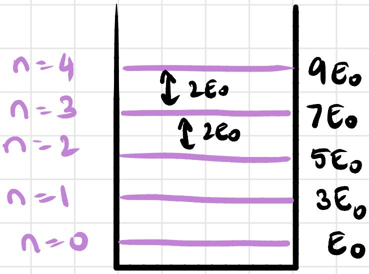
$$U = \frac{1}{2} k_s x^2$$



All vibrational energy states are equally spaced

Difference between IFW and QHO





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

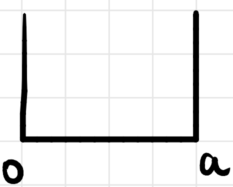
$$E = (n + 1/2)\hbar\omega = (2n+1) E_0$$

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

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

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

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

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

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

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

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

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

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