UNIT 2: Quantum Mechanics

→ For classical particles,

$$f = ma \longrightarrow$$ basic formula for classical mechanics

$$\Rightarrow -\frac{dV(x)}{dx} = m\frac{d^2x}{dt^2}$$ — underivable

m, x, p → well known (definite)

Since, they are particles → have to obey the conservation of momentum & energy.

→ For quantum particles,

$$\Delta x \Delta p \geq \hbar/2$$ (either x or p is known)

1. wave particle duality → $\lambda = h/p$
2. General wave eq^n → $\frac{\partial^2 f}{\partial t^2} = v^2 \frac{\partial^2 f}{\partial x^2}$
3. Conservation of momentum & energy hold good

→ Schrödinger's time-dependent equation:

Total Energy($\hat{E}$) = KE ($\hat{T}$) + PE ($V(x)$)

$$i\hbar \frac{\partial \psi(x,t)}{\partial t} = \frac{-\hbar^2}{2m}\frac{d^2\psi(x,t)}{dx^2} + V(x)\psi(x,t) \quad \text{—} (1)$$

$$\psi(x,t) = Ae^{i(kx-\omega t)} \quad \text{—} (2)$$

$$\psi(x,t) = Ae^{ikx} \cdot e^{-i\omega t}$$

$$\psi(x,t) = \psi(x) \cdot e^{-i\omega t} \quad \text{—} (3)$$

$$\frac{\partial \psi(x,t)}{\partial t} = \psi(x) \cdot (-i\omega) \cdot e^{-i\omega t} \quad \text{—} (4)$$

$$\frac{\partial^2 \psi(x,t)}{\partial x^2} = e^{-i\omega t} \frac{\partial^2 \psi(x)}{\partial x^2} \quad \text{—} (5)$$

Sub. (5) & (4) in (1)

$$(1) \Rightarrow i\hbar(-i\omega) \cdot \cancel{e^{-i\omega t}}\, \psi(x) = \frac{-\hbar^2}{2m}\left(\cancel{e^{-i\omega t}} \cdot \frac{\partial^2 \psi(x)}{\partial x^2}\right) + V(x)\psi(x)\cancel{e^{-i\omega t}}$$

$$\hbar\omega \cdot \psi(x) = \frac{-\hbar^2}{2m}\left(\frac{d^2\psi(x)}{dx^2}\right) + V(x) \cdot \psi(x)$$

$$\left\{\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x} + Vx\right\}\psi(x) = \hbar\omega\,\psi(x)$$

$$\left\{\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + Vx\right\}\psi(x) = \frac{h}{2\pi}\times 2\pi\nu\,\psi(x)$$

$$\left\{\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + Vx\right\}\psi(x) = E\,\psi(x) \quad -⑥$$

$$\left(\underset{\text{operator}}{\text{Total Energy}}\right)\psi(x) = \left(\underset{\text{values}}{\text{Energy}}\right)\psi(x)$$

↓

Hamiltonian

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

→ Schrödinger's time-independent equation

↓ (stationary state equation)

Eigenvalue equation

$$⑥ \times \frac{-2m}{\hbar^2} \Rightarrow \frac{d^2\psi(x)}{dx^2} + \frac{2m}{\hbar^2}\left(E - V(x)\right)\psi(x) = 0$$

→ Properties of Wave Function:

→ Wave function should be finite, continuous & differentiable.

→ First derivative of $\psi(x)$ should be continuous & differentiable.

→ Wave function should be single-valued.

→ Wave function should be normalisable.

If all the four properties stated are satisfied then wave function → well-behaved/eigen function.

→ Expectation value of an operator:

$$\frac{\sum x_i |\psi_i|^2}{\sum |\psi_i|^2} = \frac{\int_{-\infty}^{\infty} \hat{O}|\psi|^2\,dV}{\int_{-\infty}^{\infty} |\psi^2|\,dx}$$

$\hat{O}$ → position operator

$$|\psi|^2 = \psi^*\psi \qquad = \frac{\int_{-\infty}^{\infty} \hat{O}\,\psi^*\psi\,dV}{\int_{-\infty}^{\infty} \psi^*\psi\,dV}$$

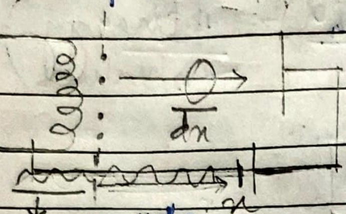
Expectation value of an operator

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

→ Application of Schrödinger's eqn:

Ex 1: Free particle : $F = 0$, $\therefore V(x) = \text{constant}$

$V(x) = 0$ for convenience



$$\frac{d^2 \psi(x)}{dx^2} + \frac{2m}{\hbar^2}(E - V(x))\psi(x) = 0 \quad \text{— (1)}$$

-ve x- direction (ignored in this case as e^- moving only in +ve x) $x=0$

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

$$\frac{d^2 \psi(x)}{dx^2} + k^2 \psi(x) = 0 \quad \text{(3)} \longrightarrow \text{General soln} \quad \text{(2)}$$

$[k^2 = 2mE/\hbar^2]$

~~$\psi(x) = Ae^{ikx}$ $\phi(x) = Be^{-ikx}$~~

$$\psi(x) = \underbrace{Ae^{ikx}}_{\text{represents electron moving in +ve x direction}} + \underbrace{Be^{-ikx}}_{\text{rep. } e^- \text{ moving in -ve x direction (meaningless in this case)}} \quad \text{— (4) is a general soln of (3).}$$

So, Be^{-ikx} → neglected.

$$\psi(x) = Ae^{ikx} \quad \text{— (5)}, \quad \psi^*(x) = Ae^{-ikx}$$

Probability of finding e^- in dx,

$$P\,dx = \int_0^{\infty} |\psi(x)|^2 \, dx = \int_0^{\infty} \psi \psi^* \, dx$$

~~$P\,dx = (Ae^{ikx})(Ae^{-ikx}) \, dx$~~

$$P\,dx = \int_0^{\infty} (A\cancel{e^{ikx}}) \cdot (A\cancel{e^{-ikx}}) \, dx$$

$P\,dx = |A|^2$ → means there is equal probability of finding e^- at all points. (contradicts the assumption that e^- is a wave) where P is not equal)

This tells us that once ejected, e^- moves like a particle.

(2) $\Rightarrow$ $E = \dfrac{k^2\hbar^2}{2m}$

$E = \dfrac{p^2}{2m}$ $\left[\because k = \dfrac{2\pi p}{h}\right]$

Total Energy $= \dfrac{p^2}{2m} + V(x)$ $[\because \hbar = h/2\pi]$

Here $V(x) = 0$ assumed, so,

Total Energy $= \dfrac{p^2}{2m}$.

Uncertainity in Energy:

$\Delta E . \Delta t \geq \hbar/2$

But, here $e^- \rightarrow$ particle so $\Delta t = 0$.

Only, wave eqn has $\Delta t \neq 0$.

$\therefore$ for e^-, $\Delta E \times 0 \geq \hbar/2$

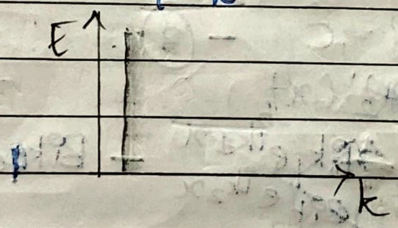
$\downarrow$

No uncertainity in energy.

|||ly no uncertainity in Δp, Δx also. So, free $e^- \rightarrow$ behaves like a ~~wave~~ particle.

NOTE: Energy is continuous not quantised.

E v/s k



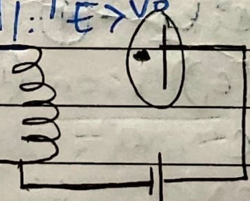
$|E| = \dfrac{\hbar^2 k^2}{2m}$

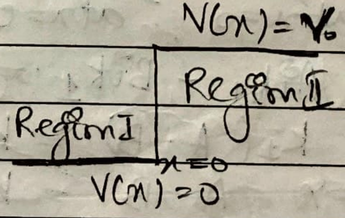
as k uniform and $\hbar k = p$

P is x-uniform.

Ex 2: Step potential:

Case 1: $E > V_0$





$V(x) = \begin{cases} 0, & x < 0 \\ V_0, & x > 0 \end{cases}$

Solving Schrödinger's eqⁿ in Region I,

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

$$\psi_1(x) = \underbrace{Ae^{ik_1x}}_{\text{incident wave}} + \underbrace{Be^{-ik_1x}}_{\text{reflected wave}} \quad -(1) \qquad k_1^2 = 2mE/\hbar^2$$

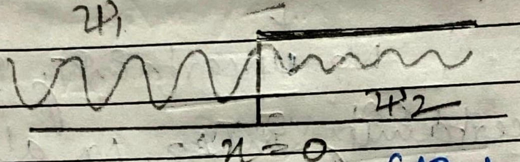
Solving Schrödinger's eqⁿ in Region II,

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

put $k_2^2 = 2m/\hbar^2 \, (E - V_0)$

$$\psi_2(x) = Ce^{ik_2x} + De^{-ik_2x} \quad -(2)$$

$De^{-ik_2x} \rightarrow$ neglected



Boundary condition : $\psi_1' = \psi_2'$ (first derivative)

$$\psi_1(x) = \psi_2(x)$$
at $x=0$ at $x=0$

$$A + B = C \quad -(3)$$

$$\psi_1'(x) = \psi_2'(x)$$

$$\psi_1'(x) = Aik_1e^{ik_1x} - Bik_1e^{-ik_1x}$$

$$\psi_2'(x) = Cik_2e^{ik_2x}$$

$$\psi_1'(x) = \psi_2'(x)$$
at $x=0$ at $x=0$

$$Aik_1 - Bik_1 = Cik_2 \quad -(4)$$

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

$$\Rightarrow A - B = \frac{k_2C}{k_1}$$

$$B = \frac{k_1 - k_2A}{k_1 + k_2} \quad \& \quad C = \frac{2k_1}{k_1 + k_2}A$$

(a)   (b)

Reflection coefficient (R) = $\frac{\text{Reflected flux}}{\text{Incident flux}}$

Transmission coefficient = $\frac{\text{Transmitted flux}}{\text{Incident flux}}$

Flux = no. of particles/unit area/time

Flux = particle density (n) x velocity (v)

$n \propto I \propto |Amp|^2$, $v = \frac{p}{m} = \frac{\hbar k}{m}$

$$R = \frac{|B|^2 \times \cancel{\hbar k_1/m}}{|A|^2 \times \cancel{\hbar k_1/m}}$$

$$R = \frac{|B|^2}{|A|^2}$$

$$R = \left|\frac{k_1 - k_2}{k_1 + k_2}\right|^2 \quad \text{(from a)}$$

$$T = \frac{|C|^2 \times \cancel{\hbar} k_2 \cancel{/m}}{|A|^2 \cancel{\hbar} k_1 \cancel{/m}}$$

$$T = \frac{|C|^2}{|A|^2} \times \frac{k_2}{k_1}$$

$$T = \frac{|2k_1|^2}{|k_1 + k_2|^2} \times \frac{k_2}{k_1} \quad \text{(from b)}$$

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

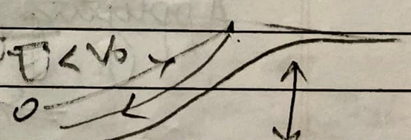
$$T = \frac{4k_1 k_2}{(k_1 + k_2)^2}$$

$R + T = 1$

5 10

Case 2: $E < V_0$

$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$ — (1)



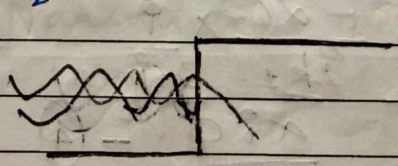
$\psi_2 = Ce^{ik_2x}$

$\psi_2 = Ce^{i(i\alpha x)}$

$\psi_2 = Ce^{-\alpha x}$ — (2)

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

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

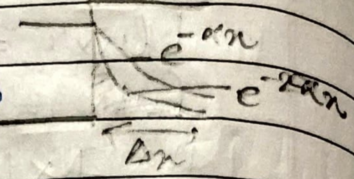


$k_2 = i\alpha$

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

$$|\psi_2|^2 = \psi^* \psi$$
$$|\psi_2|^2 = Ce^{-\alpha x} \cdot Ce^{-\alpha x}$$
$$|\psi_2|^2 = C^2 e^{-2\alpha x}$$

$$\psi(\Delta x) = e^{-\alpha \Delta x}$$



$$\psi(\Delta x) = \frac{1}{e^{\alpha \Delta x}}$$

$$\Delta x \cdot \alpha = 1$$
$$\Delta x = \frac{1}{\alpha}$$

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

$$\Delta p = \frac{\hbar}{2\Delta x}$$
$$\Delta p = \frac{\cancel{\hbar} \times \sqrt{2m(V_0 - E)}}{2\cancel{\hbar}}$$
$$\Delta p = \frac{\sqrt{2m(V_0 - E)}}{2}$$
$$\Delta E = p^2/2m$$
$$\Delta E = \frac{\cancel{2m}(V_0 - E)}{4 \times \cancel{2m}}$$

$$\Delta E \propto (V_0 - E).$$

Applying boundary condition,
$$\psi_1(x=0) = \psi_2(x=0)$$
$$\Rightarrow A + B = C \quad \text{—(3) (from (1) \& (2))}$$
$$\psi'_1(x=0) = \psi'_2(x=0)$$
$$ik_1(A - B) = -\alpha C$$
$$A - B = \frac{-\alpha C}{ik_1} \times \frac{i}{i}$$
$$A - B = \frac{\alpha i C}{k_1} \quad \text{—(4)}$$

$$③ + ④ \Rightarrow 2A = C\left(1 + \frac{\alpha i}{k_1}\right) \Rightarrow A = \frac{C}{2}\left(1 + \frac{\alpha i}{k_1}\right)$$

$$③ - ④ \Rightarrow 2B = C\left(1 - \frac{\alpha i}{k_1}\right) \Rightarrow B = \frac{C}{2}\left(1 - \frac{\alpha i}{k_1}\right)$$

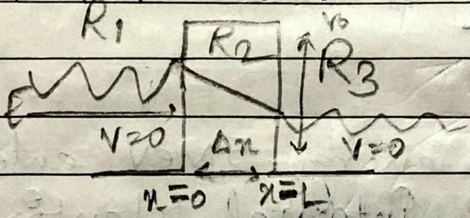
R: Reflection coefficient.

$$R = \left|\frac{B}{A}\right|^2 = \frac{B^*B}{A^*A}$$ [as A & B are imaginary no.]

$$R = \frac{\cancel{\frac{C}{2}}\cancel{\left(1 + \frac{\alpha i}{k_1}\right)} \times \cancel{\left(1 - \frac{\alpha i}{k_1}\right)}}{\cancel{\frac{C}{2}}\cancel{\left(1 - \frac{\alpha i}{k_1}\right)} \times \cancel{\left(1 + \frac{\alpha i}{k_1}\right)}}$$

$R = 1$ (means 100% reflection & 0% transmission).

Ex 3: Potential barrier



$$V(x) = \begin{cases} 0, & x<0 \ \& \ x>L \\ V_0, & 0<x<L \end{cases}$$

$$\psi_1 = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\psi_2 = Ce^{-\alpha x}$$

$$\psi_3 = De^{ikx} + Fe^{-ikx}$$

ψ_3 can't be reflected back so, $Fe^{-ikx} = 0$

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

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

at $x=0$, $\psi_1 = \psi_2 \Rightarrow A+B=C$

at $x=0$, $\psi_1' = \psi_2' \Rightarrow ik_1(A-B) = -\alpha C$

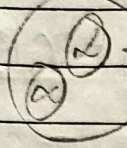
at $x=L$, $\psi_2 = \psi_3 \Rightarrow Ce^{-\alpha L} = De^{ik_1L}$

at $x=L$, $\psi_2' = \psi_3' \Rightarrow -\alpha Ce^{-\alpha L} = ik_1 De^{ik_1L}$

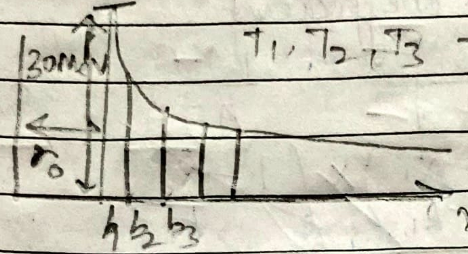
Transmission coefficient $T \propto e^{2\alpha L}$

$$T \propto e^{2\alpha L} = \left[1 + \frac{\sinh^2(\alpha L)}{4\frac{E}{V_0}\left(1 - \frac{E}{V_0}\right)}\right]^{-1} = \frac{16E}{V_0}\left[1 - \frac{E}{V_0}\right]e^{-2\alpha L}$$

Application: α-Decay.



— α – 4-10 MeV



T_1, T_2, T_3 → Transmission coefficient of b_1, b_2, b_3

$b_1 \rightarrow n_1 = nT_1$

$b_2 \rightarrow n_2 = n\,T_1T_2$

$b_3 \rightarrow n_3 = nT_1T_2T_3$

$$T = T_1 \times T_2 \times T_3 \ldots$$

$$T = e^{-2\alpha \int_{r_0}^{r_{max}} \Delta L}$$

Half life → $\lambda \propto 1/T$

Q- A neutron of energy 5 MeV enters a nucleus of an internal potential of -50 MeV compared to external potential of $V=0$. Estimate the probability that this neutron is reflected.

Ans:

$$T = \frac{4k_1k_2}{(k_1+k_2)^2} \qquad k_1 = \frac{\sqrt{2mE}}{\hbar}$$

$$R = 1 - T \qquad k_2 = \frac{\sqrt{2m(V_0-E)}}{\hbar}$$

$$R = 1 - \frac{4k_1k_2}{(k_1+k_2)^2} \qquad k_2 = \frac{\sqrt{2mE}}{\hbar}\frac{\sqrt{V_0-E}}{\sqrt{E}}$$

$$R = \frac{(k_1+k_2)^2 - 4k_1k_2}{(k_1+k_2)^2}$$

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

$$R = \left(\frac{\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2} - \left(\frac{2m}{\hbar^2}(V_0-E)\right)^{1/2}\right]}{\left[\left(\frac{2mE}{\hbar^2}\right)^{1/2} + \left(\frac{2m}{\hbar^2}(V_0-E)\right)^{1/2}\right]} \right)^2$$

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

$$R = 0.29$$

Q- e^- of energy E are made to fall on potential barrier height 6eV & width 0.2nm. T = 1%. Calculate energy of incident e^-?

Ans:

$$T = e^{-2\alpha L}$$

$$\ln(T) = |2\alpha L|$$

$$\frac{\ln T}{2L} = \alpha = \sqrt{\frac{2m(V_0-E)}{\hbar^2}}$$

$$\left(\frac{\ln T}{2L}\right)^2 = \frac{2m(V_0-E)}{\hbar^2}$$

$$\frac{\hbar^2}{2m}\left(\frac{\ln T}{2L}\right)^2 = V_0 - E$$

$$V_0 - \left[\left(\frac{\hbar^2}{2m}\right)\left(\frac{\ln T}{2L}\right)^2\right] = E.$$

$$6\times1.6\times10^{-19} - \left[\frac{1.113\times10^{-68}}{2\times9.1\times10^{-31}}\times\left(\frac{\ln(0.01)}{2\times0.2\times10^{-9}}\right)^2\right] = E$$

$$6\times1.6\times10^{-19} - \left[\frac{1.13\times10^{-68}}{2\times9.1\times10^{-31}}\times\left(\frac{-4.605}{2\times0.2\times10^{-9}}\right)^2\right] = E$$

$$6\times1.6\times10^{-19} - \left[\frac{1.13\times10^{-68}}{2\times9.1\times10^{-31}}\times1.32\times10^{20}\right] = E$$

$$9.6\times10^{-19} - 0.081\times10^{-17} = E$$

$$9.6\times10^{-19} - 8.1\times10^{-19} = E$$

$$E = 1.5\times10^{-19}\,J$$

$$E = 0.9375\,eV.$$

Q- Some e⁻ encounter a potential height of 6eV & width of 0.5 nm, after transmission were found to have a λ of 3nm, Calculate the energy with which the e⁻ were impinched on the potential step.

Ans:
$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}$$

$$k = \frac{\cancel{2 \times 3.14}^{\,2.093} \times 10^9}{\cancel{3}\,1.5}$$

$$k = 2.093 \times 10^9$$

$$2.093 \times 10^9 = \sqrt{\frac{2 \times 9.1 \times 10^{-31} \times (6 \times 10^{-19} \times 1.6 - E)}{1.13 \times 10^{-68}}}$$

$$4.380 \times 10^{18} = \frac{2 \times 9.1 \times 10^{-31} \times (9.6 \times 10^{-19} - E)}{1.13 \times 10^{-68}}$$

$$\frac{4.380 \times 1.13 \times 10^{-50}}{2 \times 9.1 \times 10^{-31}} = 9.6 \times 10^{-19} - E$$

$$0.271 \times 10^{-19} = 9.6 \times 10^{-19} - E$$

$$E = 9.329 \times 10^{-19}\,J$$

$$E = 5.83\,eV$$

Q- The input current for a forward-biased diode is 10 mA. The e^- in the diode are made to fall on the depletion region idealised as 5eV height & 1nm width potential barrier. Calculate the leakage current if the energy of the input electrons is 4.9eV.

Ans: $I_{leakage} = T \times I_{input}$

$T = e^{-2\alpha L}$

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

$$\alpha = \sqrt{\frac{2 \times 9.1 \times 10^{-31} \times 10^{-1} \times 1.6 \times 10^{-19}}{(1.055 \times 10^{-34})^2}}$$

$$\alpha = \sqrt{\frac{2 \times 9.1 \times 1.6 \times 10^{-51}}{1.13 \times 10^{-68}}}$$

$$\alpha = \sqrt{25.76 \times 10^{+17}}$$

$$\alpha = 1.602 \times 10^{+9}\ m^{-1}$$

$T = e^{-2 \times 1.6 \times 10^{9} \times \cancel{10^{-9}}}$

$\cancel{\ln(T) = \ldots -3.2}$

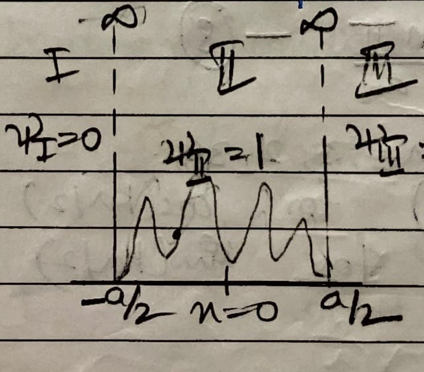
$T = e^{-3.2}$

$T = 0.04$, $T = 4\%$

$I_{leakage} = \frac{4}{100} \times \frac{10}{1000}$

$I_{leakage} = 0.4\ mA$

Ex4: Particle in infinite potential well



In region II,
$F = 0$, $V = 0$.
Solving Schrödinger's eqn in region II,

$$\frac{d^2\psi}{dx^2} + \frac{2M}{\hbar^2}E\psi = 0 \quad (1)$$

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put $k^2 = 2mE/\hbar^2$ — (2)

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0 \quad — (3)$$

Solving (3), $\psi(x) = Ae^{ikx} + Be^{-ikx}$

$\psi(x) = A\sin kx + B\cos kx$ — (4)

$$\left[\begin{aligned} &\because e^{ikx} = \cos kx + i\sin kx \\ &\frac{e^{ikx}+e^{-ikx}}{2} = \cos kx \rightarrow Re\,\psi(x) \\ &\frac{e^{ikx}-e^{-ikx}}{2i} = \sin kx \rightarrow Im\,\psi(x) \end{aligned}\right]$$

Applying boundary conditions,

at $x = -a/2$, $\psi(x) = 0$

(4) $\Rightarrow$ $\psi(-a/2) = A\sin(k(-a/2)) + B\cos(k(-a/2))$

$0 = A\sin(k(-a/2)) + B\cos(k(a/2))$ — (5)

at $x = a/2$, $\psi(x) = 0$

(4) $\Rightarrow$ $\psi(a/2) = A\sin(k(a/2)) + B\cos(k(a/2))$

$0 = A\sin(k(a/2)) + B\cos(k(a/2))$ — (6)

$$\left.\begin{aligned} &(5)+(6) \Rightarrow 2B\cos(ka/2) = 0 \\ &(5)-(6) \Rightarrow -2A\sin(ka/2) = 0 \\ &\qquad +2A\sin(ka/2) = 0 \end{aligned}\right\} (7)$$

Let $A = 0$ & $\cos(ka/2) = 0$

$ka = (2\theta+1)\pi$ (odd multiple)

$\Rightarrow k = \frac{(2\theta+1)\pi}{a}$

Let $B = 0$ & $\sin(ka/2) = 0$

$ka = (2\theta)\pi$ (even multiple)

$\Rightarrow k = (2\theta)\pi/a$

General condition for k:

$$k = \frac{n\pi}{a} \quad — (8)$$

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

$n = (2\theta + 1)$ for $\cos(ka/2)$

& $n = (2\theta)$ for $\sin(ka/2)$

from ② & ⑧,

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

$$\Rightarrow \frac{n^2\cancel{\pi^2}}{a^2} = \frac{2mE \times 4\cancel{\pi^2}}{h^2} \quad \left[\because \hbar = \frac{h}{2\pi}\right]$$

$$\Rightarrow E = \frac{n^2h^2}{8ma^2}, \quad n = 1, 2, 3, \ldots$$

$\downarrow$ claims that energy is quantised.

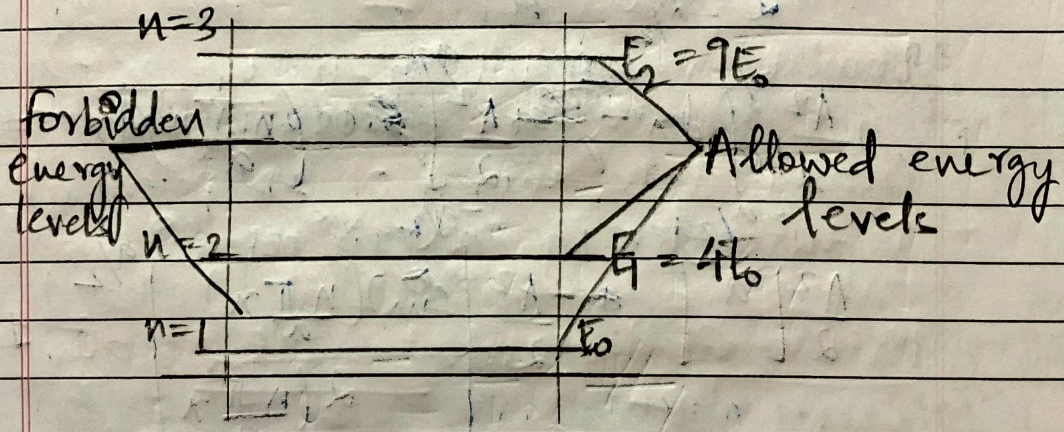
$n = 1, \quad E_0 = \frac{h^2}{8ma^2}$

~~$n=2$, $E = \frac{h^2 \times 4}{8ma^2 \times 8} \Rightarrow E = n^2 E_0$~~

$n = 2, \quad E = 4\left(\frac{h^2}{8ma^2}\right) \Rightarrow E_1 = 4E_0$

$n = 3, \quad E = 9\left(\frac{h^2}{8ma^2}\right) \Rightarrow E_2 = 9E_0$

$\therefore \quad E_n = n^2 E_0$



Quantisation of energy is possible due to the binding of particles (boundary conditions). Energy is continuous due to absence of boundary conditions.

General form: $E_{n-1} = n^2 E_0, \quad n = 1, 2, 3, \ldots$

$\downarrow$ Eigen energy values $\quad E_0 = \frac{h^2}{8ma^2}$

$E_0 \rightarrow$ zeropoint energy / Ground-state

$\downarrow$ least possible energy for quantum sys

$E_1 \longrightarrow$ First excited state
$E_2 \longrightarrow$ Second excited state

→ To estimate the constant A & B:
Normalisation condition:

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

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

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

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

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

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

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

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

$$\frac{A^2 a}{2} = 1$$

$$A^2 = 2/a$$

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

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

$$\psi_n(x) = \begin{cases} \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi}{a}x\right), & n \rightarrow \text{even} \\ \sqrt{\frac{2}{a}} \cos\left(\frac{n\pi}{a}x\right), & n \rightarrow \text{odd} \end{cases}$$

$\psi_n(x) \downarrow$ Eigen functions

→ Eigenvalue equation: $\hat{O}\psi = O\psi$

ψ → wave function

$\hat{O}$ ↓ operator, O ↓ eigenvalues

$$\left[\frac{p^2}{2m} + V\right]\psi_n(x) = E_n \psi_n(x)$$

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]\psi_n(x) = E_n \psi_n(x)$$

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \quad \text{---} (1)$$

$\hat{H}$ ↓ Hamiltonian

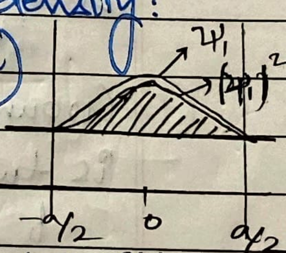
(1) → Energy-eigen equation for particle in ~~box~~ an infinite box.

→ **Wave function & probability density:**

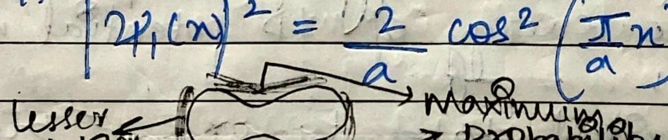
$n = 1$, $\psi_1(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi}{a}x\right)$

$P = 1/1 = 1$, for $n=1$

$$|\psi_1(x)|^2 = \frac{2}{a}\cos^2\left(\frac{\pi}{a}x\right)$$

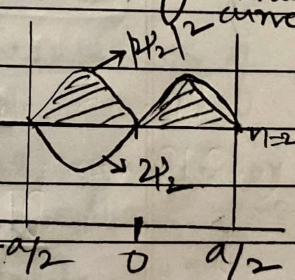


Probability → area under curve

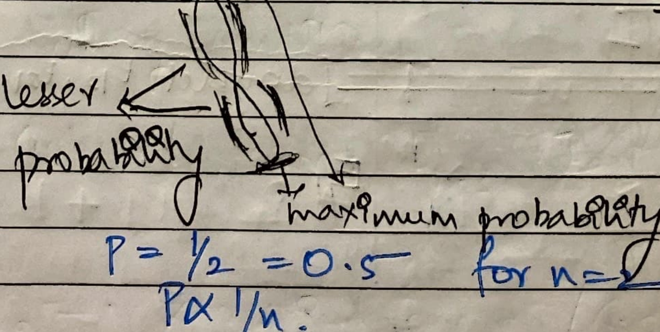


$n=2$, $\psi_2(x) = \sqrt{\frac{2}{a}} \sin(\pi/a\, x)$

$$|\psi_2(x)|^2 = \frac{2}{a}\sin^2\left(\frac{\pi}{a}x\right)$$



Shaded region → probability



$P = 1/2 = 0.5$ for $n=2$

$P \propto 1/n$.

→ 2D & 3D Infinite Potential Well:

In 2D → $\left(\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2}\right) + \frac{2m(E-V_0)}{\hbar^2}\psi = 0$

In x-direction → $E_x = \frac{n_x^2 h^2}{8ma^2}$, $n_x = 1, 2$

In y-direction → $E_y = \frac{n_y^2 h^2}{8ma^2}$ $n_y = 1, 2, 3$

Total energy $E_{xy} = E_x + E_y$

$E_{xy} = \frac{h^2(n_x^2 + n_y^2)}{8ma^2}$

$E_{xy} = \frac{h^2 n^2}{8ma^2}$ $\because \underbrace{n^2 = n_x^2 + n_y^2}_{\text{Represents a circle.}}$

↓

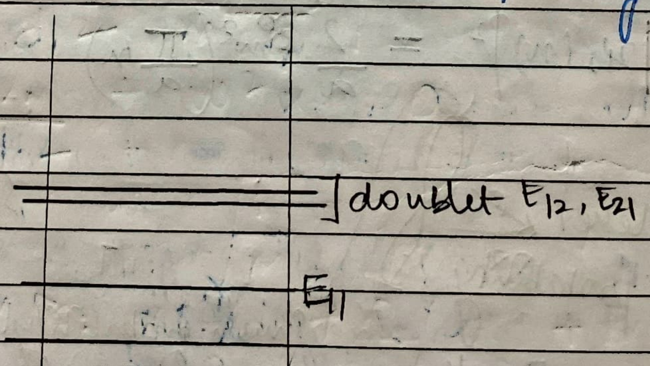
Degenerate energy state

↳ several particles/states having same energy. Ex: d_{px}, d_{py}, d_{pz} - orbitals

Lowest Energy state in 2D: $\underbrace{E_{11}}_{\text{singlet}} = \frac{h^2(2)}{8ma} = 2E_0$

Ground-state energy of 2D potential well is twice energy of 1D potential well.

First excited state: $\underbrace{E_{12} \text{ or } E_{21}}_{\text{Doublet/doubly degenerate}} = 5E_0$



$$\psi(x) = \sqrt{\frac{2}{a}} \begin{cases} \sin\left(\frac{n\pi x}{a}\right), & \text{odd parity} \\ \cos\left(\frac{n\pi}{a}x\right), & \text{even parity} \end{cases}$$

$$\psi(y) = \sqrt{\frac{2}{a}} \begin{cases} \sin\left(\frac{n\pi}{a}y\right), & \text{odd parity} \\ \cos\left(\frac{n\pi}{a}y\right), & \text{even parity} \end{cases}$$

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

$$\psi_{n_x n_y}(x,y) = \frac{2}{a} \begin{cases} \sin\left(\frac{n\pi}{a}x\right) \\ \cos\left(\frac{n\pi}{a}x\right) \\ \sin\left(\frac{n\pi}{a}y\right) \\ \cos\left(\frac{n\pi}{a}y\right) \end{cases}$$

$n_x = n_y = 1$,

$$\psi_{11}(x,y) = \frac{2}{a}\cos\left(\frac{\pi}{a}x\right)\cos\left(\frac{\pi}{a}y\right) \rightarrow E_{11}$$

$n_x = 1, n_y = 2$

$$\psi_{12}(x,y) = \frac{2}{a}\cos\left(\frac{\pi}{a}x\right)\sin\left(\frac{2\pi}{a}y\right) \rightarrow E_{12}$$

$n_x = 2, n_y = 1$

$$\psi_{21}(x,y) = \frac{2}{a}\sin\left(\frac{2\pi}{a}x\right)\cos\left(\frac{\pi}{a}y\right) \rightarrow E_{21}$$

$\psi_{12}(x,y) \neq \psi_{21}(x,y)$ but, $E_{12} = E_{21}$.

In 3D $\longrightarrow$ $E_{xyz} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$

for $n_x = n_y = n_z = 1$

$E_{111} = 3E_0$

Ground-state of 3D is three times energy of 1D.

for $n_x = n_y = 1, n_z = 2$ or $n_x = 2, n_y = n_z = 1$ or $n_x = n_z = 1, n_y = 2$,

$E_{112} = E_{121} = E_{211} = 6E_0$ } triplet

$$\psi_{111} = \left(\frac{2}{a}\right)^{3/2} \begin{cases} \sin\left(\frac{n\pi}{a}x\right) \\ \sin\left(\frac{n\pi}{a}y\right) \\ \sin\left(\frac{n\pi}{a}z\right) \\ \cos\left(\frac{n\pi}{a}x\right) \\ \cos\left(\frac{n\pi}{a}y\right) \\ \cos\left(\frac{n\pi}{a}z\right) \end{cases}$$

~~→ Potential in finite potential~~

→ Energy of particle in finite potential.

$$E_{finite} = \frac{n^2h^2}{8m(a+2\Delta l)^2}$$

$$E_{finite} < E_{infinite}$$

$$a+2\Delta l \approx 2a$$

$$E_{finite} \approx E_{infinite}/4$$

→ Harmonic oscillation → class of periodic oscill

Simple harmonic oscillation is periodic oscillat with single frequency & restoring force $F \propto -x$

$$F = -kx \qquad k \rightarrow \text{spring constant}$$

$$F = -\frac{dV}{dx}$$

$$-\int F\,dx = \int dV$$

$$-\int(-kx\,dx) = \int dV$$

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

$$\text{Total energy} = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$

→ Classical eqn of motion:

$$F = ma = -kx$$

$$m\frac{d^2x}{dt^2} = -kx$$

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

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

$$\therefore \omega = \sqrt{\frac{k}{m}}$$

Soln is: $x(t) = A\sin(\omega t) + B\cos(\omega t)$

→ Quantum eq^n of motion:

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

For centre of mass system:

reduced mass (M) : $\frac{1}{M} = \frac{1}{m_1} + \frac{1}{m_2}$

$$\Rightarrow M = \frac{m_1 m_2}{m_1+m_2}$$

Thus, the Schrödinger's eq^n takes the form:

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

Let $\frac{2M}{\hbar^2} = \gamma$, $X = x/\alpha$

$$\frac{d^2\psi(X)}{dX^2} + (\varepsilon - X^2)\psi(X) = 0$$

where, $\varepsilon = \gamma\alpha^2E$ & $\frac{1}{2}\alpha^4\gamma M\omega^2 = 1$

If $X \ggg \varepsilon$, $\frac{d^2\psi(X)}{dX^2} - X^2\psi(X) = 0$

sol^n: $\psi(X) = Ae^{-X^2/2} + Be^{X^2/2}$

As a general sol^n, A can be function of X, $H_n(X)$

$\psi(X) = NH_n(X)e^{-X^2/2}$, normalisation constant

$$N = \frac{1}{\sqrt{2^n n!\sqrt{\pi}}}$$

$H_n(X)$ → Hermite polynomial → needed because nature of differential eqn is not constant

$H_0(X) = 1$

$H_1(X) = 2X$

$H_2(X) = -2(1-2X^2)$

$\psi_0(X) = Ne^{-X^2/2}$

→ The series sol^{n}s of Schrödinger eqn should terminate to have any physical meaning, that leads to, $\frac{2E}{\hbar\omega} = 2n+1$; $E = (n+\frac{1}{2})\hbar\omega$

Energy levels are equidistant.

Date
Page

→ When there is constrained motion Energy gets quantised.

→ For harmonic oscillator at high en quantum & classical probability is same

→ Qualitative discussion of Hydrogen atom
H-atom is spherically symmetrical with e^- & p^+ which are relative in motion
Their reduced mass $\mu = \frac{m_e m_p}{m_e + m_p}$

Schrödinger used polar coordinate system.
→ Spherical polar coordinate system:

$r = \sqrt{x^2+y^2+z^2}$ → radius vector
$\theta = \cos^{-1}\left(\frac{z}{\sqrt{x^2+y^2+z^2}}\right)$ → zenith ~~vector~~ angle
$\phi = \tan^{-1}\left(\frac{y}{x}\right)$ → azimuth angle

$x = r\sin\theta\cos\phi$
$y = r\sin\theta\sin\phi$
$z = r\cos\theta$

→ Schrödinger's wave eq^n in r, θ, ϕ:

$$\frac{\hbar^2}{2\mu r^2\sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]+(E-V(r))\psi(r,\theta,\phi)=0$$

Wave eq^n can be resolved into three independent components in three independent variables: r, θ, ϕ.

$\psi(r,\theta,\phi) = R(r).\Theta'(\theta).\Phi'(\phi)$.

for Φ' : $d^2\Phi'/d\phi^2 + m_l^2\Phi = 0$

for Θ': $\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta'}{d\theta}\right)+\left[l(l+1)+\frac{m_l^2}{\sin^2\theta}\right]\Theta'=0$

for R: $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\left[\frac{2m}{\hbar^2}\left(\frac{ke^2}{r}+E\right)-\frac{l(l+1)}{r^2}\right]R=0$

→ Quantum numbers:
Principal quantum no. (n) → 1, 2, 3, ... (quantises energy)
Orbital / Azimuthal quantum no. (l) → 0, 1, 2 ... (n-1)
(quantises magnitude of angular momentum).
Magnetic quantum no. (m_l) → 0, ±1, ±2, ... ±l
(quantises direction of angular momentum).

→ $a = \frac{4\pi \varepsilon_0 \hbar^2}{Me^2} = 0.529 \times 10^{-10} m$ → Bohr's radius

→ Energy of e^- in different states can be written as: $E_n = -\frac{\hbar^2 k^2}{2m} = -\frac{Me^4}{8\pi^2 \varepsilon_0^2 h^2 f^2}$

Q- Find the ground state energy ~~for an atom~~ for an e^- in an atom if the e^- resides in first Bohr orbital (infinite potential)

Ans: $E_0 = \frac{h^2}{8ma_0^2}$ $a_0 = 5.29 \times 10^{-9} m$

$E_0 = 2.41 \times 10^{-17} J$

$E_0 = 150 eV$.

$E_1 = 4 \times 150 eV$

$E_1 = 600 eV$.

$E_2 = 9 \times 150 eV$

$E_2 = 1350 eV$

Q- In a finite potential well of height 3eV and width 3nm, calculate 1st three energy states for an e^- with energy 2.5 eV. Compare ground state energy with that of an infinite potential well of same width.

Ans: $E = \frac{n^2 h^2}{8m(a + 2\Delta x)^2}$

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

$\Delta x = 2.76\,A^\circ = 2.76 \times 10^{-10}\,m$

$E_0 = 0.03\,eV$

$E_1 = 4E_0 = 0.12\,eV$, $E_2 = 9E_0 = 0.27$

for infinite,

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

$E = 0.04\,eV$

Q- Calculate energy diff. b/w E_{111} & next excited state for an e^- in a Cu ~~qd~~ quantum dot of diameter 7nm. what would be the difference for similar states in a block of Cu of $1\,mm^3$.

Ans: ~~$E_{111} = 3E$~~

$E_0 = 0.0307\,eV$

$E_{111} = 3E_0$

$E_{111} = 0.0921\,eV$ — (1)

$E_{121} / E_{211} / E_{112} = 0.1842\,eV$ — (2)

Energy diff = (2) − (1) = $0.0921\,eV$