Lecture 4

Wednesday, September 20, 2023 10:28

Particle in a Box Wavefunctions

$$\psi_{II} = \left(\frac{2}{\ell}\right)^{1/2} \sin\left(\frac{n\pi x}{\ell}\right),$$

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

$$\psi_i = \left(\frac{2}{\ell}\right)^{\frac{1}{2}} \sin\left(\frac{n_i \pi x}{\ell}\right), \quad \underline{0 < x < \ell}$$

$$\underline{\psi_i = 0 \quad \text{elsewhere}}$$

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = 1 \quad \text{if } i = j$$

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = 0 \quad \text{if } i \neq j$$

$$\int_0^l \underbrace{\boxed{\left(\frac{2}{l}\right)^{1/2}} \sin\left[\underbrace{\boxed{\frac{n_i\pi x}{l}}}_{a}\right] \boxed{\left(\frac{2}{l}\right)^{1/2}}}_{2/l} \sin\left[\underbrace{\boxed{\frac{n_j\pi x}{l}}}_{b}\right] dx$$

$n_i \neq n_j$

Integral table

$$\int \sin ax \sin bx \, dx$$

$$= \frac{\sin[(a-b)x]}{2(a-b)} - \frac{\sin[(a+b)x]}{2(a+b)}$$

$a^2 \neq b^2$

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = \frac{2}{l} \left| \frac{\sin[(n_i-n_j)\pi \overset{l}{x}/l]}{2(n_i-n_j)\pi/l} - \frac{\sin[(n_i+n_j)\pi \overset{l}{x}/l]}{2(n_i+n_j)\pi/l} \right|_0^l$$

$$= \frac{2}{l}\left\{ \cancel{\frac{\sin[(n_i-n_j)\pi]}{2(n_i-n_j)\pi/l}} - \cancel{\frac{\sin[(n_i+n_j)\pi]}{2(n_i+n_j)\pi/l}} \right\}$$

$\sin(m\pi) = 0$ for m integer

$= 0$

$$\therefore \int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = 0 \quad \text{if } i \neq j$$

↑ if this condition holds, ψ_i and ψ_j are orthogonal to each other

$$\int_{-\infty}^{\infty} \psi_i^* \psi_j \, dx = \delta_{ij}$$

δ_{ij} : Kronecker delta

$$\delta_{ij} \underset{\substack{\uparrow \\ \text{definition}}}{\equiv} \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

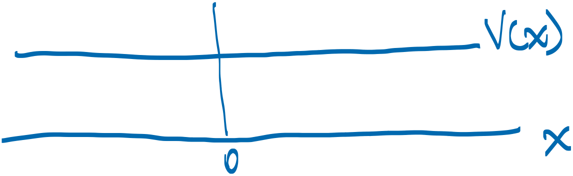
if a set of wavefunctions satisfy this property, it is said to be orthonormal (orthogonal and normalized)

2.3 The Free Particle in One Dimension

free particle: particle experiencing no forces whatsoever.

$$F = -\frac{dV(x)}{dx} = 0$$

V(x) constant



Set $V(x) = 0$

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

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

divide by $-\frac{\hbar^2}{2m}$

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

$$y'' + \frac{2mE}{\hbar^2} y = 0$$

$$\boxed{r^2 + \frac{2mE}{\hbar^2} = 0}$$

auxiliary equation

$$y'' + py' + qy = 0$$

$$r^2 + pr + q = 0$$

$$r^2 = -\frac{2mE}{\hbar^2}$$

$$r = \pm \frac{\sqrt{2mE}}{\hbar} i$$

$$r = \pm \sqrt{\frac{2mE}{\hbar^2}}\, i$$

$$\psi = c_1 e^{\boxed{(2mE)^{1/2}/\hbar \cdot ix}} + c_2 e^{-(2mE)^{1/2}/\hbar \cdot ix}$$

Impose boundary conditions:

- postulate ψ remains finite as x approaches $+\infty$ and $-\infty$

What happens when $E < 0$?

$$(2mE)^{\frac{1}{2}} i = (-2m|E|)^{1/2} i$$

$$= (2m|E|)^{1/2} i \cdot i$$

$$= -(2m|E|)^{1/2}$$

$$\psi = c_1 e^{-(2m|E|)^{1/2}/\hbar \cdot x} + c_2 e^{(2m|E|)^{1/2}/\hbar \cdot x}$$

at $x \to -\infty$,
ψ goes to ∞

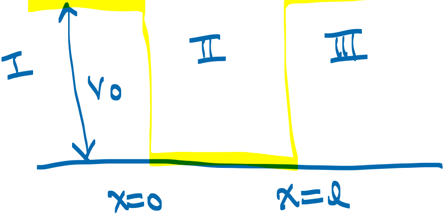
at $x \to +\infty$
ψ goes to ∞

Thus, the boundary condition requires

$$E \geq 0$$

the energy levels of a free particle are not quantized

2.4 Particle in a Rectangular Well



Consider the case where $\boxed{E<V_0}$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2}+V_0\psi=E\psi$$

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

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

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

$$a^2-\frac{2m}{\hbar^2}\underline{(V_0-E)}=0$$

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

$$a=\pm\left(\frac{2m}{\hbar^2}\right)^{1/2}(V_0-E)^{1/2}$$

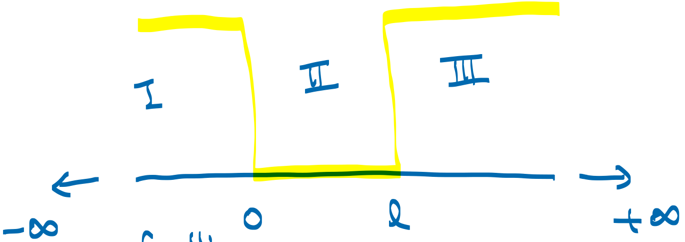
$$\psi_{I} = Ce^{(2m/\hbar^2)^{1/2}(V_0-E)^{1/2}x} + De^{-(2m/\hbar^2)^{1/2}(V_0-E)^{1/2}x}$$

$$\psi_{III} = Fe^{(2m/\hbar^2)^{1/2}(V_0-E)^{1/2}x} + Ge^{-(2m/\hbar^2)^{1/2}(V_0-E)^{1/2}x}$$

$$\text{let } a = \left(\frac{2m}{\hbar^2}\right)^{1/2}(V_0-E)^{1/2}$$

$$\psi_{I} = Ce^{ax} + \cancel{De^{-ax}} \qquad \psi_{I} = Ce^{ax}$$

$$\psi_{III} = \cancel{Fe^{ax}} + Ge^{-ax} \qquad \psi_{III} = Ge^{-ax}$$



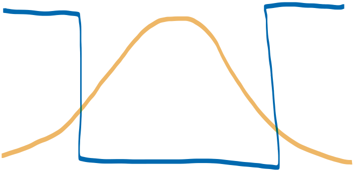
solution for ψ_{II}:

$$\psi_{II} = A\cos\left[\left(\frac{2m}{\hbar^2}\right)^{1/2}E^{1/2}x\right] + B\sin\left[\left(\frac{2m}{\hbar^2}\right)^{1/2}E^{1/2}x\right]$$

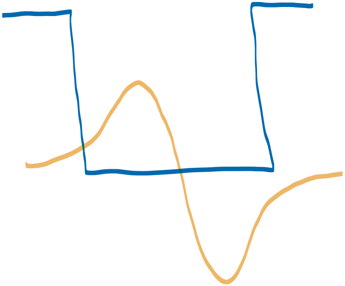
$$\boxed{(2E-V_0)\sin\left[\frac{(2mE)^{1/2}l}{\hbar}\right] = 2(V_0E-E^2)^{1/2}\cos\left[\frac{(2mE)^{1/2}l}{\hbar}\right]}$$

constraint on ψ_{II}

energy levels are quantized because of this constraint

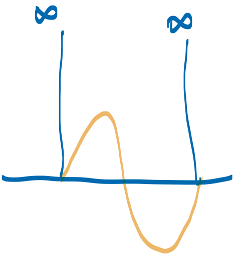


n=1



n=2

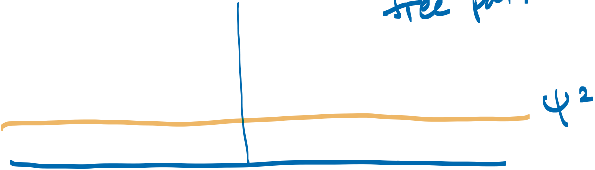
- even though $E<V_0$, the particle has some finite probability of being found outside of the box → tunnelling; strictly a quantum mechanical effect



if $\psi \to 0$ as $x \to \infty$ and $x \to -\infty$:

bound state

otherwise : unbound state ← free particle



$E < V_0$: bound

$E > V_0$: unbound