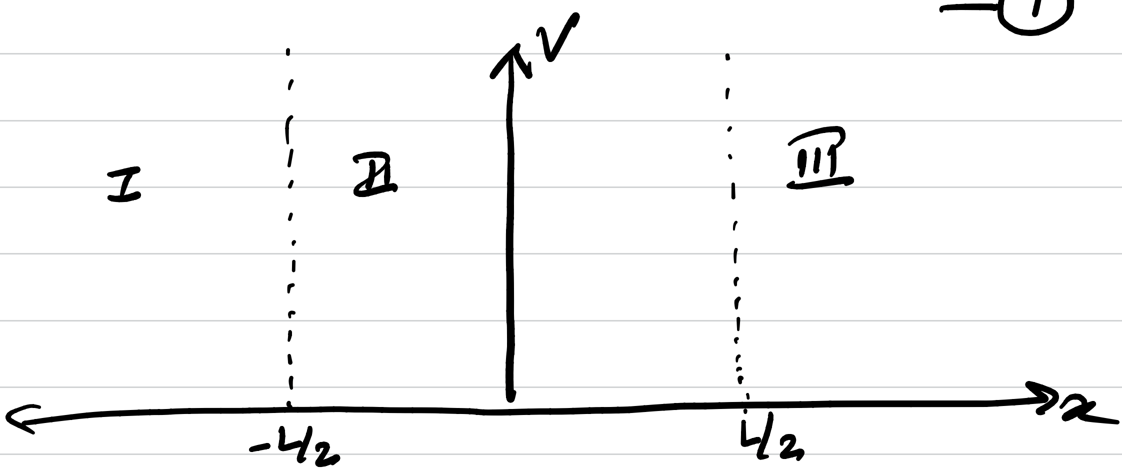
16/9/2025 Day 21. Particle in a square well

Next we take up a situation where the potential energy $V(x)$ has a simple but non-trivial dependence on x.

$$V(x) = \begin{cases} 0 & |x| \leq L/2 \\ \infty & |x| > L/2 \end{cases} \quad \text{—(1)}$$



The potential changes discontinously at $x = \pm L/2$, but stays constant in the 3 regions I, II, & III, albeit having a different value in each interval. Such a potential with finite number of discontinuities is called a piecewise continuous potential.

We note that the TISE, in the position representation, is a local equation satisfied by the wavefunction at every point x, decided by the potential at that point.

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

This means that we can solve the equation separately in the 3 regions I, II & III, obtaining a wavefunction defined differently in each region, all the same corresponding to the same energy E. After solving thus, we will impose continuity of ψ to piece together the solutions.

Moreover, we will look for solutions with $E \geq 0$ since $E<0$, as we have seen, will give us a trivial solution $\psi=0$.

Regions I & III: For both these regions the wavefunction $\psi^{I/III}(x)$ satisfy:

$$\frac{1}{\psi^{I/III}}\frac{d^2\psi^{I/III}(x)}{dx^2} = \frac{2m}{\hbar^2}(E-V_0) \qquad — (3)$$

where $V_0 \to \infty$

In the entire region, the potential remains uniform (but large). This means we expect ψ, ψ' & ψ'' to be continuous and hence finite. Therefore, RHS of (3) being infinite is only consistent with

$$\psi^{I/III}(x) = 0 \qquad — (4)$$

That is, the wavefunction corresponding to any energy (E) state vanishes in region I & III.

- P.T.O -

Region II: The TISE here can be written as:

$$\frac{d^2\psi^{II}(x)}{dx^2} + k^2 \psi^{II}(x) = 0 \quad — (5)$$

where $k^2 = \frac{2m}{\hbar^2} E$ — (6)

$E \geq 0$

$$\Rightarrow k = \sqrt{\left(\frac{2m}{\hbar^2}\right) E} \text{ or } E = \frac{\hbar^2 k^2}{2m} \quad — (7)$$

As we have seen earlier, the general solution to (5) is:

$$\psi^{II}(x) = c_1 e^{ikx} + c_2 e^{-ikx} \quad — (8)$$

For this problem it is more convenient to recast (8) as

$$\psi^{II}(x) = A_1 \cos kx + A_2 \sin kx \quad — (9)$$

(easily shown by the substitution

$$e^{\pm ikx} = \cos(kx) \pm i \sin(kx) \quad — (10)$$

Now, the A_1 & A_2 can be determined by matching (9) at the boundaries $x = \pm \frac{L}{2}$ with ψ^{I} & ψ^{II}, respectively.

i.e.
$$\left.\begin{aligned} \psi^{II}(L/2) &= \psi^{III}(L/2) \\ \psi^{I}(-L/2) &= \psi^{III}(-L/2) \end{aligned}\right\} \quad (11)$$

Accordingly, we have

$$A_1 \cos(kL/2) + A_2 \sin\left(\frac{kL}{2}\right) = 0 \quad -(12)$$

$$A_1 \cos(kL/2) - A_2 \sin\left(\frac{kL}{2}\right) = 0 \quad -(13)$$

where in (13) we have used the fact that $\cos x$ is an even function of x, while $\sin x$ is odd.

(12) + (13) $\Rightarrow$ $2A_1 \cos\left(\frac{kL}{2}\right) = 0 \quad -(14)$

(12) − (13) $\Rightarrow$ $2A_2 \sin\left(\frac{kL}{2}\right) = 0 \quad -(15)$

(14) $\Rightarrow$ either $A_1 = 0$ or $\cos\left(\frac{kL}{2}\right) = 0$

(15) $\Rightarrow$ either $A_2 = 0$ or $\sin\left(\frac{kL}{2}\right) = 0$

Since A_1 & A_2 cannot be simultaneously zero (trivial solution), we must have two sets of solutions:

(i) $A_1 \neq 0$, $A_2 = 0$ & $\cos\left(\frac{kL}{2}\right) = 0$

$$\Rightarrow \frac{kL}{2} = \frac{m\pi}{2}, \quad m = 1, 3, 5, 7, \ldots$$

$$\text{or } k = \frac{m\pi}{L}, \quad m = 1, 3, 5, \ldots \qquad (16)$$

and

(ii) $A_1 = 0$, $A_2 \neq 0$ & $\sin\left(\frac{kL}{2}\right) = 0$

$$\Rightarrow \frac{kL}{2} = m\pi, \quad m = 0, 1, 2, 3, \ldots$$

$$\text{or } k = \frac{(2m)\pi}{L}, \quad (2m) = 0, 2, 4, \ldots \qquad (17)$$

Accordingly, we get 2 solutions

$$\psi_m^{(\text{II})}(x) = \begin{cases} A_m \cos\left(\frac{m\pi x}{L}\right) & m = \pm 1, \pm 3, \pm 5, \dots \\ A_m \sin\left(\frac{m\pi x}{L}\right) & m = 0, \pm 2, \pm 4, \pm 6, \dots \end{cases} \quad \text{— (18)}$$

This makes sense since, given the oscillatory nature of the solution, and the requirement that it must vanish at the boundaries of the well, we must have that the trigonometric functions must have wavelengths λ that satisfy

$$n\lambda/2 = L \longrightarrow (19) \quad n \in \mathbb{Z}^+$$

$$\because \sin(kx) = \sin\left(\frac{2\pi x}{\lambda}\right) \quad \text{— (20)}$$

$$(19) \Rightarrow \boxed{k = \frac{n\pi}{L}} \quad n = 1, 2, 3, \dots \quad \text{— (21)}$$

$\because$ k is connected to the energy, this means that allowed energies of the particle are "quantized" (see 7)

$$\boxed{E_n = \frac{n^2\hbar^2}{2mL^2} = \frac{n^2h^2}{8mL^2}} \quad -(22)$$

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

Note that although 18 allows negative values for n, the corresponding wavefunctions are linearly dependent on the ones for $n > 0$.

$$\psi_{-|n|}(x) = \begin{cases} \psi_{|n|}(x) & \text{odd } n \\ -\psi_{|n|}(x) & \text{even } n. \end{cases} \quad -(23)$$

Additionally, $n=0$ corresponds to the trivial solution $\psi = 0$, which means no particle exists. Hence, we reject these.

The following trignometric integrals are helpful.

$$\int_{-L/2}^{L/2} dx \, \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) = \frac{2}{L} \delta_{m,n} \quad \text{for } m,n = \text{even integers} \qquad (24)$$

$$\int_{-L/2}^{L/2} dx \, \cos\left(\frac{m\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) = \frac{2}{L} \delta_{m,n} \quad \text{for } m,n = \text{even integers} \qquad (25)$$

$$\int_{-L/2}^{L/2} dx \, \sin\left(\frac{m\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) = 0 \qquad (26)$$

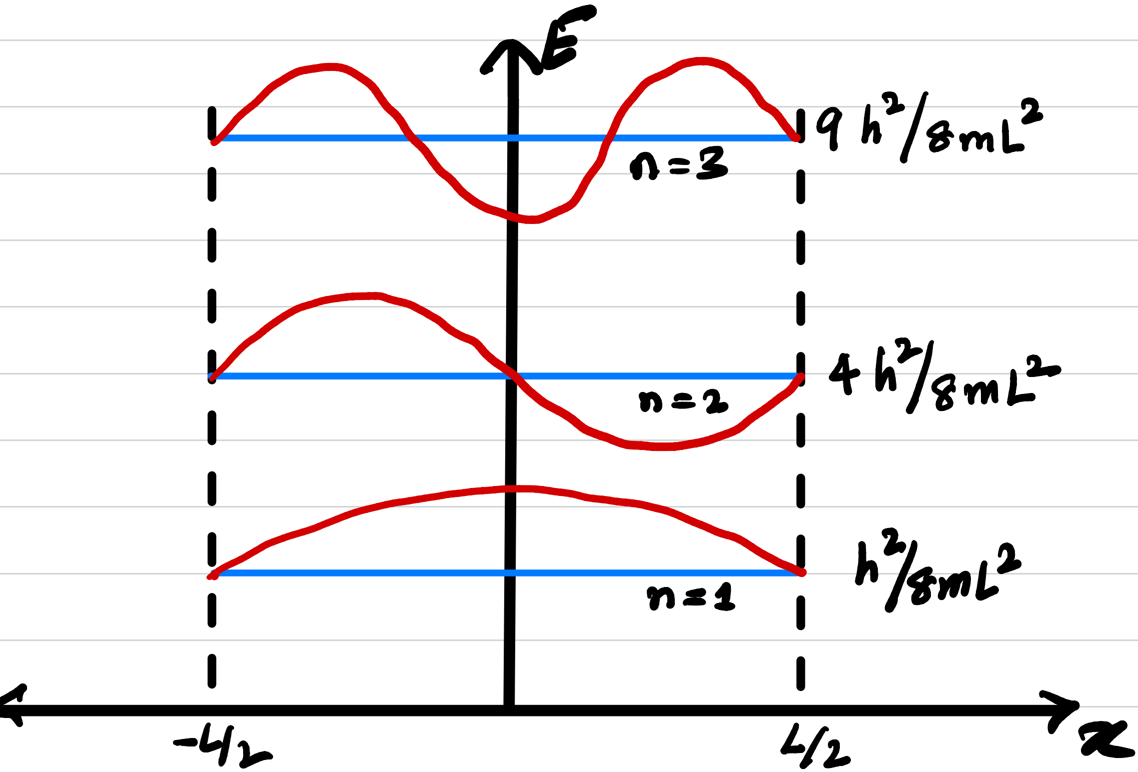
Using these it is straightforward to show that P.T.O

$$\boxed{\psi_n^{(II)}(x) = \begin{cases} \sqrt{\frac{2}{L}}\cos\left(\frac{n\pi x}{L}\right), & n = 1,3,5,\ldots \\ \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), & n = 2,4,6,\ldots \end{cases}} \quad \text{— (27)}$$

and, keeping in mind the piecewise definition of ψ and it being 0 in I & III,

$$\boxed{\langle \psi_m | \psi_n \rangle = \int_{-L/2}^{L/2} dx \; \psi_m^{(II)*}(x)\, \psi_n^{(II)}(x) = \delta_{m,n}} \quad \text{— (28)}$$

That is, as required, the eigenfunctions are orthogonal.



Nodes: pts. where the wavefunction goes to zero.

The probability density also vanishes at these points. These are interference features unique to quantum mechanics

Probability of finding the particle in the region $-L/2 < a < x < b < L/2$

$$= P_{a-b} = \int_a^b dx \, |\psi(x)|^2 \quad — (29)$$

Some question to ponder on

Q1. What is the probability of finding the particle in the left half of the box when it is in the state $n=1$?

Q2. Why is lowest energy not 0 ?

Q3. Are $\psi_n(x)$ are eigenfunctions of $\hat{p}_x$? What is the averages momentum of the particle in any eigenstate ?

Q4. Why are the eigenfunctions real here unlike in the free particle case?