

15/9/2025 Day 20, Quantum free particle.

(26) can be written as:

$$-\frac{\hbar^2}{2m} \frac{d^2 \psi_E(x)}{dx^2} + (V(x) - E) \psi_E(x) = 0 \quad (27)$$

→ 2nd order differential equation
(highest der. is 2)

→ Linear (power of highest
der. is 1)

→ Homogeneous. (if ψ is solution
then $\lambda\psi$ is also
a solution for $\lambda \in \mathbb{C}$)

2nd order $\Rightarrow$ we need 2 conditions to fix
the solution

Linear $\Rightarrow$ If $\psi(x)$ & $\phi(x)$ are solutions then
+ homogeneous
 $c\psi(x) + d\phi(x)$ also a solution
for $c, d \in \mathbb{C}$

A solution to (27) exists, for a given set of initial conditions ($\psi(x_0) = z_0$ and $\psi'(x_0) = z_1$, for instance), if $(V(x) - E)$ is real, finite, single-valued and piece-wise continuous.

$|\psi_E(x)|^2 dx \propto$ probability of finding particle with energy E around a pt. x . — (28)

$$\Rightarrow \int_{-\infty}^{\infty} |\psi_E(x)|^2 dx \rightarrow \text{finite} \quad \text{--- (29)}$$

(28) & (29) are conditions that arise from Postulate 4 (Born's postulate). They will be ensured if we require that the solutions to (27) be

→ single-valued
→ finite
→ continuous
everywhere

for $\psi_E(x)$

Rewriting (27) as

$$\frac{d^2 \psi_E(x)}{dx^2} = \frac{2m}{\hbar^2} (V(x) - E) \psi_E(x) \quad (30)$$

we note that

a) If $V(x)$ is continuous everywhere, so are $\frac{d^2 \psi}{dx^2}$ and $\frac{d\psi}{dx}$ along with $\psi(x)$

b) If $V(x)$ has finite number of finite discontinuities (piecewise continuous), then $\psi''(x)$ has finite discontinuities.

$\Rightarrow \psi'(x) = \int \psi''(x) dx$ is
still continuous.

c) If $V(x)$ has a discontinuity where it jumps to ∞ , then $\frac{d^2 \psi}{dx^2}$ also jumps to ∞ at that pt $\Rightarrow \psi'(x)$ is discontinuous.

The conditions on $\Psi(x)$ may thus be summarized as:

1. $\Psi(x)$ is always continuous, finite and single-valued everywhere.
2. $\frac{d\Psi}{dx}$ is always continuous except at points where $V(x)$ jumps to ∞ discontinuously.
3. $\frac{d^2\Psi}{dx^2}$ may or may not be continuous depending on $V(x)$.

The same conditions hold also for the overall wavefunction $\Psi(x,t)$.

Note that if our initial preparation starts the system off in an energy eigenstate, say $|E_0\rangle$, then

$$a_E(0) = \delta_{E,E_0} \quad (31)$$

$$\Rightarrow |\Psi(t)\rangle = e^{-i\frac{E_0}{\hbar}t} |E\rangle \quad (32)$$

In such a case the probabilities associated with any observable $\hat{\alpha}$

$$P_{\alpha'}(t) = |\langle \alpha' | \Psi(t) \rangle|^2 = |\langle \alpha' | E \rangle|^2 \quad (33)$$

which is not time-dependent. Hence, states such as (32) are called Stationary states.

Solving TISE is equivalent to looking for stationary states.

Free particle in 1-dimension.

A particle of mass m moves freely along the x -axis.

Here "free" means the potential energy it experiences is uniform in space. i.e. $V(x) = \text{constant}$. Let us set it to zero. The results will not change except for a constant shift in energies.

∴ Hamiltonian of the system is

$$\hat{H} = \frac{\hat{p}_x^2}{2m} \quad \text{--- (34)}$$

In position basis, the time-independent Schrödinger eqn. for the system is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x) \quad \text{--- (35)}$$

$$\text{or } \frac{d^2 \psi(x)}{dx^2} + \underbrace{\left(\frac{2mE}{\hbar^2} \right)}_{\rightarrow k^2 \text{ (ray)}} \psi(x) = 0 \quad - (36)$$

This is a 2nd order LHDE. Additionally, it has constant coefficients. In such a case it becomes easier to look for a solution.

$$\text{Given } a_2 \frac{d^2 y(x)}{dx^2} + a_1 \frac{dy(x)}{dx} + a_0 y(x) = 0$$

where $a_0, a_1, a_2 \in \mathbb{R}$ are constants

we can try $y(x) = e^{\lambda x}$ as a solution.

$$\Rightarrow (a_2 \lambda^2 + a_1 \lambda + a_0) y(x) = 0$$

Non-trivial solution exists when:

$$a_2 \lambda^2 + a_1 \lambda + a_0 = 0 \quad - (37)$$

(37) will give 2 roots λ_1 & λ_2 yielding two possible solutions

$$\left. \begin{aligned} y_1(x) &= e^{\lambda_1 x} \\ y_2(x) &= e^{\lambda_2 x} \end{aligned} \right\} (38)$$

If $\lambda_1 \neq \lambda_2$, then it is easily verified that these 2 are Linearly independent. (Using the Wronskian)

$\therefore$ general solution is written as

$$y(x) = C_1 y_1(x) + C_2 y_2(x) \quad (39)$$

(37) is called an auxiliary equation

The auxiliary equation for (36) is

$$\lambda^2 + k^2 = 0 \quad (40)$$

$$\Rightarrow \lambda = \pm \sqrt{-(k^2)} \quad (41)$$

$$\therefore k^2 = \frac{2mE}{\hbar^2}, \quad k^2 \geq 0 \text{ if } E \geq 0 \quad (41.5)$$

Let us consider this case first.

Case (i), $\underline{E \geq 0} \Rightarrow \lambda = \pm ik = \pm \sqrt{2mE/\hbar^2} \quad (42)$

So the L.I. solutions for a given E are $\psi_E^\pm(x) = \exp\left(\pm i \sqrt{\frac{2mE}{\hbar^2}} x\right) \quad (43)$

And the general solution at an E is

$$\psi_E(x) = A_+ \psi_E^+(x) + A_- \psi_E^-(x) \quad (44)$$

Since the problem does not offer any other constraint, we cannot determine $A_\pm$ by applying any boundary conditions.

However, there is one piece of information that we can use.

First let us define the parameter $k \in (-\infty, \infty)$, such that

$$E(k) = \frac{\hbar^2 k^2}{2m} \quad - (45)$$

Thus, the L.I. solutions to the problem, at any energy, can be written as:

$$\begin{aligned} \psi_k(x) &\equiv e^{ikx} \quad - (46) \\ k &\in (-\infty, \infty) \\ E(k) &= \hbar^2 k^2 / 2m \end{aligned}$$

These functions are the eigenfunctions of the momentum operator

$$\hat{p}_x \psi_k(x) = \hbar \frac{d}{dx} \psi_k(x) = \hbar k \psi_k(x) \quad - (47)$$

$\downarrow$ $\hbar k$ is the eigenvalue

This is also evident from the form of momentum eigenfunction seen before

$$\psi_{p'_x}(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i \frac{p'_x x}{\hbar}} \quad \text{--- (48)}$$

This identification has the following implication:

(i), k measures the momentum of the particle ($p'_x = \hbar k$)

$$\begin{aligned} \text{(ii), } \langle \psi_k | \psi_{k'} \rangle &\propto \langle \psi_{p_x} | \psi_{p'_x} \rangle \\ &= \delta(p_x - p'_x) \\ &= \hbar \delta(k - k') \quad \text{--- (49)} \end{aligned}$$

i.e. they are orthogonal

$$\text{(iii), } \psi_k \text{ can be normalized and written as } \psi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx} \quad \text{--- (50)}$$

(51)

iv, Since $[\hat{H}, \hat{p}_x] = 0$ for the free-particle Hamiltonian, we must be able to simultaneously determine energy and momentum of the particle in any energy eigenstate with arbitrary precision.

Therefore, the desired stationary states can be constructed out $\{\psi_k(x)\}$.

$$\Phi_k(x, t) = \frac{1}{\sqrt{2\pi}} e^{ikx} e^{-i\frac{\hbar k^2}{2m}t}$$

(52)

We could easily have noted (51) first and guessed the energy eigenstates directly!! This is the power of the operator algebra we learned so far.

$k \rightarrow$ quantum number.

Case ii, $E < 0$

$$\Rightarrow k^2 = -\frac{2m|E|}{\hbar^2} \quad - (53)$$

$$\text{or } k = \pm i\kappa \quad - (54)$$

$$\text{where } \kappa = \frac{2m|E|}{\hbar^2} \geq 0. \quad - (55)$$

$\Rightarrow$ L.I solution are.

$$\psi_E^+(x) = \exp(-\kappa x) \quad - (56)$$

$$\psi_E^-(x) = \exp(\kappa x) \quad - (57)$$

Both solutions are inadmissible

because (56) diverges as $x \rightarrow -\infty$
while (57) diverges as $x \rightarrow \infty$.

Therefore, the free particle is not allowed to have negative energies

The formula solution to the TDSE is:

$$\bar{\Psi}(x,t) = \int_{-\infty}^{\infty} dk A(k) \bar{\Phi}_k(x,t)$$

where $\bar{\Phi}_k(x,t)$ is given by (58)

and $k \in (-\infty, \infty)$.

$A(k)$ are coefficients of expansion.

Eigen
energies

$$E(k) = \frac{\hbar^2 k^2}{2m} \geq 0$$

Eigen
momenta

$$p_x(k) = \hbar k$$

(59)

Note that the allowed energies in stationary states are gapless.

$k \rightarrow$ quantum number, $|E\rangle \rightarrow |k\rangle$.