Basic postulates of Quantum Mechanics:

Postulate 1: Wave function

The state of a system having n degrees of freedom is specified by a wavefunction $\psi(q_1, q_2, \ldots q_n, t)$. The wavefunction is a complex function that contains all the information about a quantum mechanical system and from which all the dynamical physical quantities such as momentum and energy of the system can be computed.

* Since the magnitude of ψ oscillates b/w positive and negative values, the wavefunction ψ has no physical significance.

However $|\psi|^2$ is always positive and thus physically significant. It gives the probability density of finding the particle at time t in a volume element $d\tau$

$$|\psi(\vec{r}, t)|^2 d\tau = \text{probability density in a volume element } d\tau$$

Normalization: Since the particle is found somewhere

$$\int_{-\infty}^{\infty} |\psi(\vec{r}, t)|^2 \, d\tau = 1$$

(Normalization condition)

Physically acceptable wavefunctions:

(i) $\psi(\vec{r}, t)$ must be finite, single valued and continuous

(ii) The first order derivative $\frac{\partial \psi}{\partial x}, \frac{\partial \psi}{\partial y}, \frac{\partial \psi}{\partial z}$ must be finite, single valued and continuous

* In some model situations, the first order derivative may be discontinuous such as

(a) If the potential under which the particle has an infinite discontinuity at some points

(b) If the potential is of dirac delta nature

(iii) $\psi(\vec{r}, t)$ must be square integrable

$$\int_{-\infty}^{\infty} |\psi(\vec{r}, t)|^2 \, d\tau = \text{Finite}$$

$\psi \to 0$, $x \to \pm\infty$, $y \to \pm\infty$, $z \to \pm\infty$

Postulate 2: Observables and operators

To every physically measureable quantity A to be called dynamical variable or observable, there corresponds to a linear Hermitian operator $\hat{A}$

$$\boxed{\begin{aligned} &\hat{x} \to x \\ &\hat{p}_x \to -i\hbar\frac{\partial}{\partial x}, \quad p_y \to -i\hbar\frac{\partial}{\partial y}, \quad p_z \to -i\hbar\frac{\partial}{\partial z} \\ &\hat{p} \to -i\hbar\vec{\nabla} \\ &\hat{K} \to \frac{p^2}{2m} \to -\frac{\hbar^2}{2m}\nabla^2 \\ &\hat{V}(\vec{r},t) \to V(\vec{r},t) \\ &\hat{E} \to i\hbar\frac{\partial}{\partial t} \end{aligned}}$$

Total energy $\frac{p^2}{2m} + V(\vec{r},t) \to -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r},t)$

(Hamiltonian operator)

Postulate 3: Expectation Value

When a system is in a state described by a wavefunction ψ, the expectation value of any observable A is given by

$$\langle A \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, d\tau$$

If the wavefunction is not normalized

$$\langle A \rangle = \frac{\int_{-\infty}^{\infty} \psi^* \hat{A} \psi \, d\tau}{\int_{-\infty}^{\infty} \psi^* \psi \, d\tau} \quad \text{(average value)}$$

Postulate 4: Eigenvalues and eigen-value equation

The possible values of the measurement of an observable A is given by the equation

$$\hat{A} \psi_i = a_i \psi_i \quad , \quad i = 1, 2, \ldots n$$

(eigenvalue equation)

a_i = eigenvalues

ψ_i = eigenfunctions

* eigenvalues are independent of the variables on which ψ depends

* An important eigenvalue equation corresponding to Hamiltonian operator is given by

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

$$-\frac{\hbar^2}{2m}\nabla^2\psi_i(\vec{r}) + V(\vec{r})\psi_i(\vec{r}) = E_i\psi_i(\vec{r})$$

(Time-independent Schrödinger equation)

The wavefunction of a freely moving particle in the $+x$ direction can be given as

$$\psi(x,t) = A e^{i(kx-\omega t)}$$

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

$$\omega = 2\pi\nu = \frac{2\pi E}{h} = \frac{E}{\hbar}$$

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

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

$$-i\hbar\frac{\partial}{\partial x} = p\psi, \quad \boxed{\hat{p} \to -i\hbar\frac{\partial}{\partial x}}$$

$$\frac{\partial\psi}{\partial t} = -\frac{i}{\hbar}E A e^{-\frac{i}{\hbar}(Et-px)} = -\frac{i}{\hbar}E\psi$$

$$i\hbar\frac{\partial\psi}{\partial t} = E\psi, \quad \boxed{\hat{E} \to i\hbar\frac{\partial}{\partial t}}$$

Postulate 5: Time evolution of a quantum system

The time evolution of a quantum system is given by time-dependent Schrödinger equation

$$i\hbar \frac{\partial \psi(\vec{r},t)}{\partial t} = \hat{H}\psi(\vec{r},t)$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r},t) + V(\vec{r},t)\psi(\vec{r},t) = i\hbar\frac{\partial \psi(\vec{r},t)}{\partial t}$$

(Time-dependent Schrödinger equation)

Q1. Which of the following wave functions cannot be solutions of Schrödinger's equation for all values of x? Why not? (a) y =A sec x; (b) y= A tan x; (c) y= A exp(x^2); (d) y = A exp($-x^2$).

[Ans: (a), (b) and (c)]

Q2. The time-independent wave function of a particle of mass m moving in a potential $V(x) = \alpha^2x^2$ is $\psi(x) = \exp\left[-\sqrt{\frac{m\alpha^2}{2\hbar^2}}\,x^2\right]$, α being a constant. Find the energy of the system.

[Ans: $E = \frac{\hbar\alpha}{\sqrt{2m}}$**]**

Q3. A partcicle constrained to move along x-axis in the domain $0 \leqslant x \leqslant L$ has a wave function $\psi(x) = \sin(n\pi x/L)$, where n is an integer. Normalize the wave function and evaluate the expectation value of its momentum.

[Ans: $\psi(x) = \sqrt{\frac{2}{l}}\,\sin\frac{n\pi x}{l}$**]**

Q4: Find the eigenfunctions and nature of eigenvalues of the operator $\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}$

[Ans: $\psi(x) = c\,\frac{\sin\beta x}{x}$**]**

Q.2: $V(x) = \alpha^2 x^2$

$$\psi(x) = \exp\left[-\sqrt{\frac{m\alpha^2}{2\hbar^2}}\, x^2\right]$$

Using time-independent Schrodinger equation

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

$$\frac{d\psi}{dx} = -\sqrt{\frac{2m\alpha^2}{\hbar^2}}\, x \exp\left[-\sqrt{\frac{m\alpha^2}{2\hbar^2}}\, x^2\right]$$

$$\frac{d\psi}{dx} = -\sqrt{\frac{2m\alpha^2}{\hbar^2}}\, x\, \psi$$

$$\frac{d^2\psi}{dx^2} = -\sqrt{\frac{2m\alpha^2}{\hbar^2}}\left[x\frac{d\psi}{dx} + \psi\right]$$

$$= -\sqrt{\frac{2m\alpha^2}{\hbar^2}}\left[-\sqrt{\frac{2m\alpha^2}{\hbar^2}}\, x^2\psi + \psi\right]$$

Using eq. (1)

$$\frac{\hbar^2}{2m} \times \sqrt{\frac{2m\alpha^2}{\hbar^2}}\left[1 - \sqrt{\frac{2m\alpha^2}{\hbar^2}}\, x^2\right] + \alpha^2 x^2 = E$$

$$\sqrt{\frac{\hbar^2\alpha^2}{2m}} - \alpha^2 x^2 + \alpha^2 x^2 = E$$

$$\boxed{E = \frac{\hbar\alpha}{\sqrt{2m}}}$$

Q.4:
$$\left[\frac{d^2}{dx^2} + \frac{2}{x}\frac{d}{dx}\right]\psi = \lambda\psi$$

let $u = x\psi$

$$\frac{du}{dx} = \psi + x\frac{d\psi}{dx}$$

$$\frac{d^2u}{dx^2} = \frac{d\psi}{dx} + x\frac{d^2\psi}{dx^2} + \frac{d\psi}{dx}$$

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

$$\frac{1}{x}\frac{d^2u}{dx^2} = \frac{d^2\psi}{dx^2} + \frac{2}{x}\frac{d\psi}{dx}$$

$$\frac{1}{x}\frac{d^2u}{dx^2} = \lambda\psi$$

$$\frac{d^2u}{dx^2} = \lambda x\psi = \lambda u$$

$u(x) = c_1 e^{\sqrt{\lambda}x} + c_2 e^{-\sqrt{\lambda}x}$. c_1 and c_2 are Constants

For $u(x)$ to be physically acceptable, $\sqrt{\lambda}$ must be imaginary. Also at $x=0$, $u=0$

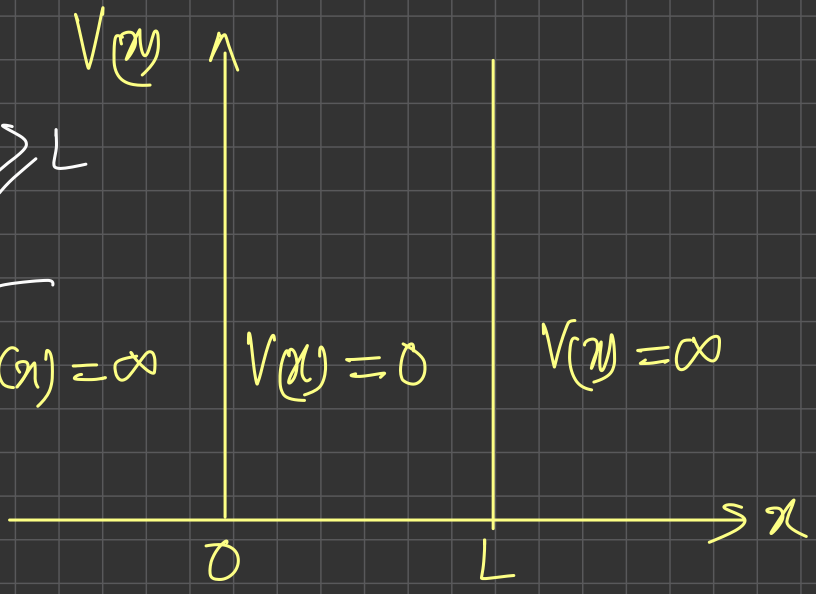
$$c_1 + c_2 = 0, \quad c_1 = -c_2$$

$$u(x) = c_1\left[e^{i\beta x} - e^{-i\beta x}\right]$$

$$\boxed{\psi = c\,\frac{\sin\beta x}{x}}$$

Particle in a 1-dimensional box (with infinitely hard walls)

$$V(x) = 0 \, , \quad 0 < x < L$$
$$= \infty \, , \quad x \leq 0 \text{ and } x \geq L$$



Using time independent Schrodinger eq.

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

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

$$k^2 = \frac{2mE}{\hbar^2} \quad \text{——— (1)}$$

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

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

A and B are constants

Using boundary conditions

$$\psi = 0 \, , \quad x = 0$$
$$\psi = 0 \, , \quad x = L$$

For $x = 0$, $\psi = 0$

$B = 0$

$\psi = A \sin kx$

$\psi_n(x) = A \sin \frac{n\pi x}{L}$

For $x = L$, $\psi = 0$

$\sin kL = 0$, $A \neq 0$

$\boxed{kL = n\pi}$, $n = 1, 2, 3 \ldots$

$n \neq 0$, That would mean $\psi = 0$ everywhere

Using eq. (1) $\frac{2mE}{\hbar^2} = \frac{n^2\pi^2}{L^2}$

$$\boxed{E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}}$$

(discrete energy eigen values)

* Since $E_n \propto n^2$, energy levels are not equally spaced

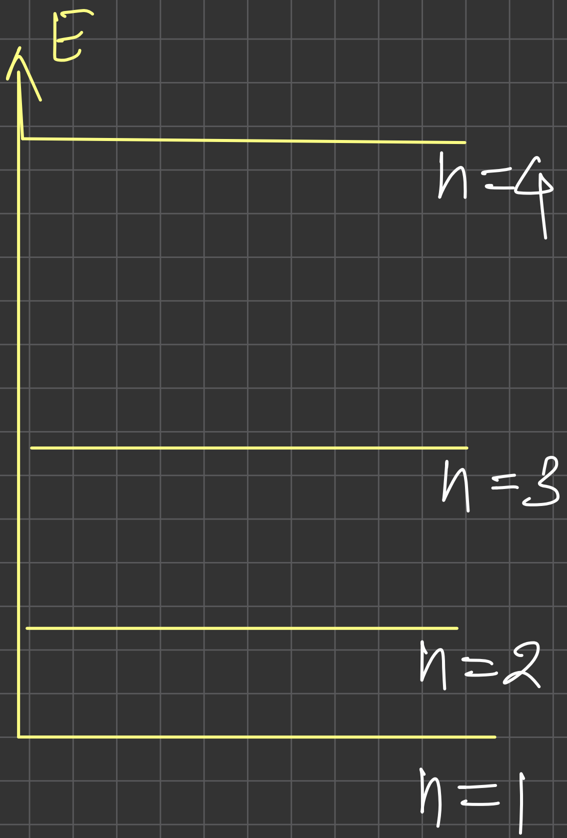
Using normalization condition:

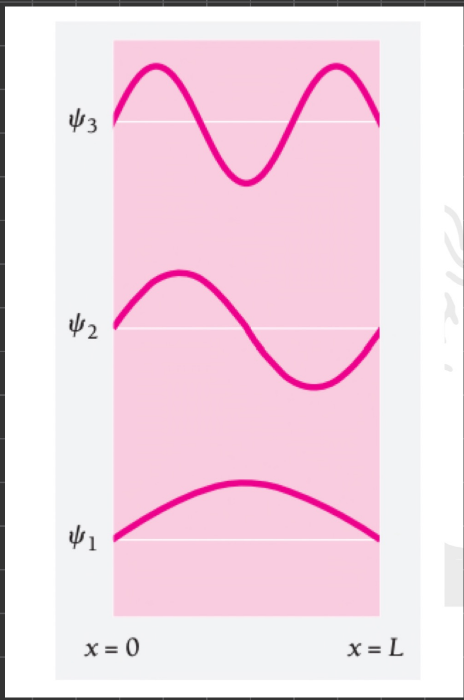
$$\int_0^L \psi^* \psi \, dx = 1$$

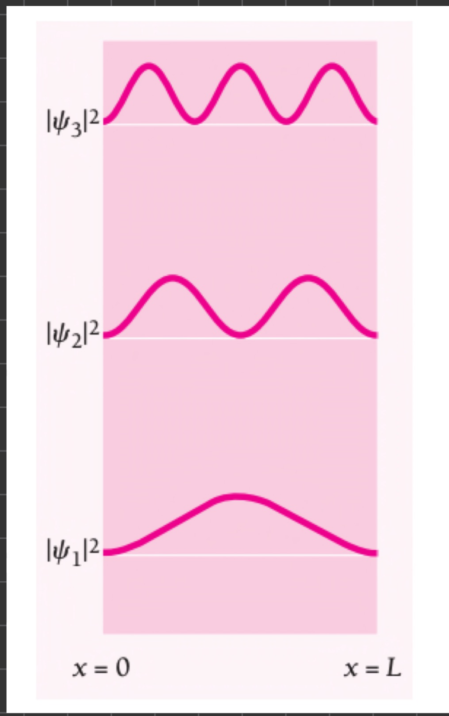
$$A^2 \int_0^L \sin^2\left(\frac{n\pi x}{L}\right) dx = 1$$

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

$$A=\sqrt{\frac{2}{L}}\,, \quad \boxed{\psi_n(x)=\sqrt{\frac{2}{L}}\,\sin\frac{n\pi x}{L}}$$







Expectation values:

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

$$\langle p\rangle = \int_0^L \psi^*\left(-i\hbar\frac{\partial\psi}{\partial x}\right)dx = 0 \quad \text{(Try!)}$$

* The uncertainty (ΔA) in a dynamical variable A is defined as the root mean square deviation from the mean.

$$\Delta A = \sqrt{\langle (A - \langle A \rangle)^2 \rangle}$$
$$= \sqrt{\langle A^2 \rangle + \langle A \rangle^2 - 2\langle A \rangle \langle A \rangle}$$
$$= \sqrt{\langle A^2 \rangle - \langle A \rangle^2}$$

For particle in 1-dim box

$$\langle x \rangle = \frac{L}{2} \quad , \quad \langle p_x \rangle = 0$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = L\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}$$

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} = \frac{n\pi\hbar}{L}$$

Uncertainty relation

$$\Delta x \, \Delta p_x = n\pi\hbar\sqrt{\frac{1}{12} - \frac{1}{2n^2\pi^2}}$$

* For Gaussian wavepacket

$$\Delta x \, \Delta p_x = \frac{\hbar}{2}$$

* Hermitian operator:

The eigenvalues of Hermitian operator are real and the eigenfunctions corresponding to different eigenvalues are orthogonal.

$$\boxed{\int \psi_1^* \hat{A} \psi_2 \, d\tau = \int (A\psi_1)^* \psi_2 \, d\tau}$$

* Representation of wavepacket in 1-dim

$$\psi(x,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \phi(\vec{p},t)\, e^{\frac{i}{\hbar}(px-Et)}\, dp$$

$$\phi(p,t) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x,t)\, e^{-\frac{i}{\hbar}(px-Et)}\, dx$$

* Gaussian type wavefunctions

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-\left(\frac{x-\langle x\rangle}{2\sigma^2}\right)^2}$$

$\langle x\rangle$ = expectation value

σ = standard deviation

* Let us revisit conditions for physically acceptable wavefunction in the context of Schrodinger eq.

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

* Since the momentum of the system is found using momentum operator, which is a first order derivative. If ψ is not continuous, the first order derivative of ψ will become infinite. This would imply an infinite momentum, which is not possible in a physically realistic system.

* Similarly, a discontinuous first order derivative of the wavefunction would imply an infinite second order derivative. Since the energy of the system is found using the second order derivative, a discontinuous first derivative would mean an infinite energy, which is again not physically realistic.