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An Institute of NET-JRF, IIT-JAM, GATE, JEST,
TIFR & CUET in Physics & Physical Sciences

Quantum Mechanics

(NET/JRF, GATE, JEST, TIFR)

Learn Physics in Right Way

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2. POSTULATES OF QUANTUM MECHANICS

The quantum mechanical postulates enable us to understand.

- how a quantum state is described mathematically at a given time t .
- how to calculate the various physical quantities from this quantum state.
- Knowing the system's state at a time t , how to find the state at any later time t . i.e., how to describe the time evolution of a system.

2.1 Postulates of Quantum Mechanics

2.1.1 Postulate 1- State of a Quantum Mechanical System

The state of any physical system is specified, at each time t , by a state vector $|\psi(t)\rangle$ in the Hilbert space. $|\psi(t)\rangle$ contains all the needed information about the system. Any superposition of state vectors is also a state vector.

2.1.2 Postulate 2- Physical Measurement of State: To every measurable quantity A to be called an observable or dynamical variable. There corresponds a linear Hermitian \hat{A} whose eigen vectors form a complete basis. $A|\phi_n\rangle = a_n|\phi_n\rangle$

2.1.3 Postulate 3 (a) Probabilistic Measurement of Eigen Value on State: When the physical quantity A is measured on a system in the state $|\psi\rangle$ the probability $P(a_n)$ of obtaining the non-degenerate eigen value a_n of the corresponding observable A is

$$P(a_n) = \frac{|\langle\phi_n|\psi\rangle|^2}{\langle\psi|\psi\rangle} \quad \text{where } A|\phi_n\rangle = a_n|\phi_n\rangle$$

Postulate 3 (b): When the physical quantity A is measured on a system in the state $|\psi\rangle$. The probability $P(a_n)$ of the obtaining the eigen value a_n of the corresponding observable A is

$$P(a_n) = \frac{\sum_{i=1}^{g_n} |\langle\phi_n^i|\psi\rangle|^2}{\langle\psi|\psi\rangle}$$

Where g_n is the degree of degeneracy of an and $|\phi_n^i\rangle$ ($i = 1, 2, 3, \dots, g_n$) is orthonormal set of vector which forms a basis in the eigen subspace associated with eigen value a_n of A .

2.1.4 Postulate 4: State Just after Measurement

The measurement of an observable A may be represented formally by an action of \hat{A} on a state vector $|\psi(t)\rangle$.

The state of the system immediately after the measurement is the normalized projection

$\frac{P_n|\psi\rangle}{\sqrt{\langle\psi|P_n|\psi\rangle}}$ of $|\psi\rangle$ onto the eigen subspace associated with a_n .

2.1.5 Postulate 5: Time Evolution of State

The time evolution of the state vector $|\psi(t)\rangle$ is governed by Schrodinger equation

$$i\hbar \frac{d}{dt} |\psi(t)\rangle = H(t) |\psi(t)\rangle$$

Where H is Hamiltonian of the system.

The solution of Schrodinger equation must be

- single valued and value must be finite
- continuous
- differentiable
- square integrable.

2.2 Expectation Value of Measurement

The expectation value of operator A is given $\langle A \rangle = \frac{\langle \psi | A | \psi \rangle}{\langle \psi | \psi \rangle} \Rightarrow \langle A \rangle = \sum_n \frac{a_n |\langle \phi_n | \psi \rangle|^2}{\langle \psi | \psi \rangle}$

Where $\langle \psi_m | A | \psi_n \rangle = a_n \delta_{mn} \Rightarrow \langle A \rangle = \sum_n a_n P_n(a_n)$

For continuous variable

$$\bullet \quad \langle A \rangle = \frac{\int_{-\infty}^{\infty} a |\psi(a)|^2 da}{\int_{-\infty}^{\infty} |\psi(a)|^2 da}$$

2.3 The momentum and position representation of wave function.

- The ket $|r\rangle$ is eigen ket at X, Y, Z . which is given as

$$X |r\rangle = x |r\rangle \quad Y |r\rangle = y |r\rangle \quad Z |r\rangle = z |r\rangle$$

- The ket $|p\rangle$ is the eigen ket of p_x, p_y, p_z which is defined as

$$P_x |p\rangle = p_x |p\rangle \quad P_y |p\rangle = p_y |p\rangle \quad P_z |p\rangle = p_z |p\rangle$$

It is given that $\langle r | X | \psi \rangle = x \langle r | \psi \rangle$ $\langle r | Y | \psi \rangle = y \langle r | \psi \rangle$ $\langle r | Z | \psi \rangle = z \langle r | \psi \rangle$

and $\langle r | \psi \rangle = \psi(r)$ and $\langle \psi | r \rangle = \psi^*(r)$.

So $\langle \phi | X | \psi \rangle = \int d^3r \langle \phi | r \rangle \langle r | X | \psi \rangle = \int d^3r \phi^*(r) x \psi(r)$

In momentum space $\langle p | P_x | \psi \rangle = p_x \langle p | \psi \rangle$, $\langle p | P_y | \psi \rangle = p_y \langle p | \psi \rangle$, $\langle p | P_z | \psi \rangle = p_z \langle p | \psi \rangle$

where $\langle p | \psi \rangle = \psi(p)$, $\langle \psi | p \rangle = \psi^*(p)$

$$\langle \phi | p_x | \psi \rangle = \int d^3p \langle \phi | p \rangle \langle p | p_x | \psi \rangle = \int d^3p \phi^*(p) p_x \psi(p)$$

2.4 Fourier transformation and Change in Basis:

Change in basis from one representation to another representation.

$$|p\rangle \text{ is defined as } |p\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{i\hbar p_x}$$

The expansion of $\psi(x)$ in terms of $|p\rangle$ can be written as.

$$\psi(x) = \int_{-\infty}^{\infty} a(p) |p\rangle dp \quad \psi(x) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} a(p) e^{ipx/\hbar} dp$$

where $a(p)$ can be find $a(p) = \frac{1}{\sqrt{2\pi\hbar}} \int_{-\infty}^{\infty} \psi(x) e^{-ipx/\hbar} dx$

$$\text{In 3D} \quad a(p) = \left(\frac{1}{2\pi\hbar} \right)^{3/2} \int_{-\infty}^{\infty} \psi(r) e^{-i\vec{p}\cdot\vec{r}/\hbar} d^3r$$

Where $a(p)$ being expansion coefficient of $|p\rangle$.

- If any function $\psi(x)$ can be expressed as a linear combination of state function ϕ_n

i.e., $\psi(x) = \sum_n c_n \phi_n(x)$ then where $\int \phi_m^* \phi_n dx = \delta_{mn}$ then $c_n = \int \psi_n^*(x) \psi(x) dx$

which is popularly derived from fourier trick.

Delta Dirac: The notation $\langle r | r' \rangle$ defined as $\delta(r - r')$. and $\langle p | p' \rangle$ defined as $d(p - p')$

- The orthonormalisation relation in r representation and p representation respectively

$$\langle r | r' \rangle = \delta(r - r') \quad \langle p | p' \rangle = \delta(p - p')$$

- The closure relation in r representation and p representation respectively.

$$\int d^3r |r\rangle \langle r| = 1 \quad \int d^3p |p\rangle \langle p| = 1$$

2.5 Parity Operator

The parity operator Π defined by its action on the basis.

$$\Pi |r\rangle = |-r\rangle \quad \langle r | \Pi | \psi \rangle = \psi(-r)$$

If $\psi(-r) = \psi(r)$ then state have even parity and

If $\psi(-r) = -\psi(r)$ then state have odd parity.

So parity operator have +1 and -1 eigen value.

Representation of postulate (4) in continuous basis.

When the physical quantity A is measured on a system state $|\psi\rangle$ the probability $dp(\alpha)$ of obtaining a result included α and $\alpha + d\alpha$ is equal to

$$dp(\alpha) = \frac{|V_\alpha | \psi \rangle|^2 d\alpha}{\langle \psi | \psi \rangle}$$

Where $|V_\alpha\rangle$ is the eigen vector corresponding to the eigen value α of the observable A .

Example: A state function is given by

$$|\psi\rangle = |\phi_1\rangle + \frac{1}{\sqrt{2}} |\phi_2\rangle$$

It is given that $\langle \phi_i | \phi_j \rangle = \delta_{ij}$

- check $|\psi\rangle$ is normalized or not
- write down normalized wavefunction $\langle \psi |$.
- It is given $H |\phi_n\rangle = (n+1)\hbar\omega |\phi_n\rangle \quad n = 0, 1, 2, 3, \dots$

If H will measured on $|\psi\rangle$, what will be measurement with what probability.

- Find the expectation value at H i.e., $\langle H \rangle$
- Find the error in the measurement in H .

Solution: (a) To check normalization one should verify.

$$\langle \psi | \psi \rangle = 13$$

$$|\psi\rangle = |\phi_1\rangle + \frac{1}{\sqrt{2}} |\phi_2\rangle$$

$$\langle \psi | \psi \rangle = \langle \phi_1 | \phi_1 \rangle + \langle \phi_1 | \phi_2 \rangle \frac{1}{\sqrt{2}} \langle \phi_2 | \phi_1 \rangle + \frac{1}{\sqrt{2}} \langle \phi_2 + \phi_2 \rangle \left(\frac{1}{\sqrt{2}} \right)^2 = 1 + 0 + 0 + \frac{1}{2} = \frac{3}{2}$$

The value of $\langle \psi | \psi \rangle = \frac{3}{2}$ so $|\psi\rangle$ is not normalized.

- Now we need to find normalized $|\psi\rangle$ let A be normalization constant.

$$|\psi\rangle = A |\phi_1\rangle + \frac{1}{\sqrt{2}} |\phi_2\rangle$$

$$\langle \psi | \psi \rangle = A^2 + \frac{A^2}{2} = 1 \Rightarrow \frac{3A^2}{2} = 1 \Rightarrow A = \sqrt{\frac{2}{3}}$$

$$\text{So } |\psi\rangle = \sqrt{\frac{2}{3}} |\phi_1\rangle + \frac{1}{\sqrt{3}} |\phi_2\rangle$$

$$\langle \psi | = \langle \phi_1 | \frac{2}{\sqrt{3}} + \langle \phi_2 | \frac{1}{\sqrt{2}}$$

- It is given that

$$H |\phi_n\rangle = (n+1)\hbar\omega \quad n = 0, 1, 2, 3, \dots$$

$$H |\phi_1\rangle = 2\hbar\omega \quad H |\phi_2\rangle = 3\hbar\omega$$

When H will measured $|\psi\rangle$ it will measured either $2\hbar\omega$ or $3\hbar\omega$

The probability of measured $2\hbar\omega$ is $P(2\hbar\omega)$ is given by

$$P(2\hbar\omega) = \frac{|\langle \phi_1 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{2}{3} \quad P(3\hbar\omega) = \frac{|\langle \phi_2 | \psi \rangle|^2}{\langle \psi | \psi \rangle} = \frac{1}{3}$$

So when H will measure state $|\psi\rangle$ the following outcome will come.

Measurement of H on state	: $ \phi_1\rangle$	$ \phi_2\rangle$
Measurement	: $2\hbar\omega$	$3\hbar\omega$
Probability	: $2/3$	$1/3$

(d) $\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \sum_n P_n(a_n)a_n$

$$= 2\hbar\omega \times \frac{2}{3} + 3\hbar\omega \times \frac{1}{3} \quad \langle H \rangle = \frac{7\hbar\omega}{3}$$

$$\langle H^2 \rangle = \frac{\langle \psi | H^2 | \psi \rangle}{\langle \psi | \psi \rangle} = \sum P_n(a_n)a_n^2 = \frac{2}{3} \times (2\hbar\omega)^2 + \frac{1}{3} \times (3\hbar\omega)^2 = \frac{8\hbar^2\omega^2}{3} + \frac{9\hbar^2\omega^2}{3} = \frac{17\hbar^2\omega^2}{3}$$

(e) The error in measurement in H is given as

$$\Delta H = \sqrt{\langle H^2 \rangle - \langle H \rangle^2} \quad \langle H^2 \rangle = \frac{17\hbar^2\omega^2}{3}$$

$$\langle H \rangle^2 = \left(\frac{7\hbar\omega}{3}\right)^2 = \frac{49\hbar^2\omega^2}{9} \quad \Delta H = \sqrt{\frac{17}{3} - \frac{49}{9}}\hbar\omega$$

$$\Delta H = \sqrt{\frac{51-49}{9}}\hbar\omega = \frac{\sqrt{2}}{3}\hbar\omega$$

Example: (a) Plot $\psi_I(x) = A_1 e^{-|x|}$ $-\infty < x < \infty$

(b) Plot $\psi_{II}(x) = A_2 e^{-x^2}$ $-\infty < x < \infty$

(c) discuss why ψ_I is not solution of schrodinger wave function rather ψ_{II} is solution of schrodinger wave function.

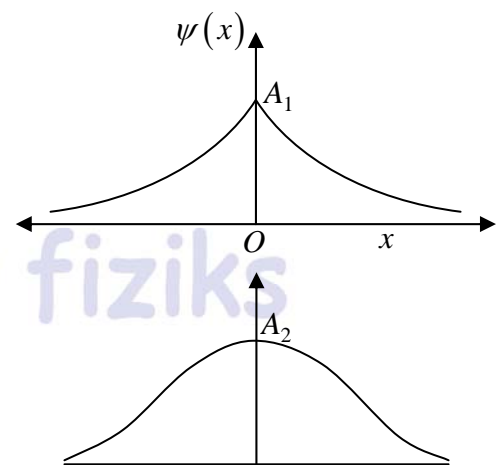
Solution: (a) $\psi_I(x) = A_1 e^{-|x|}$ $x < 0$

$$\psi_{II}(x) = A_2 e^{-x^2} \quad x > 0$$

The plot is given by

(b) $\psi_{II}(x) = A_2 e^{-x^2}$ $-\infty < x < \infty$

The plot is given by



(c) Both the function ψ_I and ψ_{II} are single value, continuous,

square integrable by ψ_I is not differentiable of $x = 0$ rather ψ_{II} is differentiable at $x = 0$

So ψ_{II} can be solution of schrodinger wave function but ψ_I is not solution of schrodinger wave function.

Example: A time $t = 0$ the state vector $|\psi(0)\rangle$

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}}(|\phi_1\rangle + |\phi_2\rangle)$$

It is given as Hamiltonian is defined as $H|\phi_n\rangle = n^2 \epsilon_0 |\phi_n\rangle$

(a) What is wave function $|\psi(t)\rangle$ at later time t .

(b) Write down expression of evolution of $|\psi(x, t)\rangle^2$

(c) Find ΔH

(d) Find the value of $\Delta H \cdot \Delta t$

Solution: (a) $|\psi(t)\rangle = \frac{1}{\sqrt{2}} \left[e^{\frac{-i\epsilon_0 t}{\hbar}} |\phi_1\rangle + e^{\frac{-i4\epsilon_0 t}{\hbar}} |\phi_2\rangle \right]$

$$|\psi(t)\rangle \propto [|\phi_1\rangle + e^{-i\omega_{21}t} |\phi_2\rangle]$$

Where $\omega_{21} = \frac{E_2 - E_1}{\hbar} = \frac{3\epsilon_0}{\hbar}$

(b) Evolution of shape of the wave packet

$$|\psi(x,t)|^2 = \frac{1}{2} |\phi_1(x)|^2 + \frac{1}{2} |\phi_2(x)|^2 + \phi_1 \phi_2 \cos \omega_{21} t$$

(c) $\Delta H = (\langle H^2 \rangle - \langle H \rangle^2)^{1/2}$

$$\langle H \rangle = \frac{1}{2} E_1 + \frac{1}{2} E_2 = \frac{5}{2} E_1 \quad \langle H^2 \rangle = \frac{1}{2} E_1^2 + \frac{1}{2} E_2^2 = \frac{17}{2} E_1^2$$

$$\Delta H = \frac{3}{2} E_1$$

$$\Delta H = \frac{3}{2} \times \epsilon_0$$

(d) $\Delta H = \frac{3}{2} \epsilon_0$

$$\Delta t = \frac{1}{\Delta \omega_{21}}$$

$$\Delta t = \frac{\hbar}{3\epsilon_0}$$

$$\Delta H \cdot \Delta t = \frac{3}{2} \epsilon_0 \times \frac{\hbar}{3\epsilon_0} = \frac{\hbar}{2}$$

$$\Delta H \cdot \Delta t = \frac{\hbar}{2}$$

Example: Consider a one-dimensional particle which is confined within the region $0 \leq x \leq a$ and whose wave function is $\psi(x,t) = \sin\left(\frac{\pi x}{a}\right) e^{i\omega t}$. Find the potential $V(x)$.

Solution: From the fifth postulate.

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

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

$$\frac{\pi^2 \hbar^2}{2ma^2} \sin \frac{\pi x}{a} e^{i\omega t} + V(x) \frac{\sin \pi x}{a} e^{i\omega t} = i\hbar \sin \frac{\pi x}{a} (-i\omega) e^{i\omega t}$$

$$\frac{\pi^2 \hbar^2}{2ma^2} + V(x) = -\hbar \omega \quad V(x) = -\hbar \omega - \frac{\pi^2 \hbar^2}{2ma^2} \quad V(x) = -\left(\hbar \omega + \frac{\pi^2 \hbar^2}{2ma^2} \right)$$

Example: If eigen value of operator A is 0, $2a_0$, $2a_0$ and corresponding normalized eigen vector

is $\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ -i \\ 1 \end{pmatrix}$, $\frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ i \\ 1 \end{pmatrix}$ and $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ respectively t system is in state $\frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix}$ then

(a) When A is measured on system in state $\frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix}$ then what is probability to getting value

0, $2a_0$, respectively.

(b) What is expectation value of A ?

Solution: Let $|\phi_1\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ -i \\ 1 \end{pmatrix}$ $\lambda_1 = 0$, $|\phi_2\rangle = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ i \\ 1 \end{pmatrix}$ $\lambda_2 = 2a_0$

$\lambda_2 = \lambda_3 = 2a_0$ i.e., $\lambda = 2a_0$ is doubly degenerate.

$$P(0) = \frac{|\langle \phi_1 | \psi(t) \rangle|^2}{\langle \psi | \psi \rangle} = \frac{8}{17}$$

$$P(2a_0) = \frac{|\langle \phi_2 | \psi(t) \rangle|^2}{\langle \psi | \psi \rangle} + \frac{|\langle \phi_3 | \psi(t) \rangle|^2}{\langle \psi | \psi \rangle} = \frac{\left[\left(\frac{1}{\sqrt{2}}(0 \ -i \ 1) \frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix} \right)^2 \right]}{\frac{1}{6}(1 \ 0 \ 4) \frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix}} + \frac{\left[(1 \ 0 \ 0) \frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix} \right]^2}{\frac{1}{6}(1 \ 0 \ 4) \frac{1}{6} \begin{pmatrix} 1 \\ 0 \\ 4 \end{pmatrix}}$$

$$= \frac{\frac{1}{2} \times \frac{1}{36} \times 16}{36} + \frac{\frac{1}{36}}{36}$$

$$= \frac{2}{9} + \frac{1}{17} = \frac{9}{17} \Rightarrow \langle A \rangle = 0 \times \frac{8}{17} + 2a_0 \times \frac{9}{17} \Rightarrow \langle A \rangle = \frac{18a_0}{17} \text{ average value.}$$

Example: A free particle which is initially localized in the range $-a < x < a$ is released at time $t = 0$.

$$\psi(x) = \begin{cases} A & \text{if } -a < x < a \\ 0 & \text{otherwise} \end{cases}$$

Find (a) A such that $\psi(x)$ is normalized.

(b) Find $\phi(x)$ i.e., wave function in momentum space.

(c) Find $\psi(x, t)$ i.e., wave function after t time.

Solution: (a) $\int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = A^2 \int_{-a}^a dx = 1 \Rightarrow A = \frac{1}{\sqrt{2a}}$

(b) $\phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-a}^a e^{-ikx} \psi(x) dx = \frac{1}{\sqrt{2\pi}} \frac{1}{\sqrt{2a}} \int_{-a}^a e^{-ikx} dx = \frac{1}{\sqrt{2\pi}} \frac{\sin ka}{k}$

(c) $\psi(x, t) = \frac{1}{\pi\sqrt{2a}} \int_{-\infty}^{\infty} \frac{\sin ka}{k} e^{i\left(kx - \frac{\hbar k^2}{2m}t\right)} dk$