

PHY 301

QUANTUM MECHANICS LECTURE II NOTES

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TABLE OF CONTENTS

| | | |
|-------|--|---|
| 0.1 | Mathematical Axioms of Quantum Mechanics | 3 |
| 0.1.1 | The Basic Postulates of Quantum Mechanics | 3 |
| 0.1.2 | Wave Packet | 4 |
| 0.1.3 | Born's Interpretation of the Wave function | 4 |
| 0.1.4 | Conditions of Admissibility of the Wave Function | 6 |
| 0.1.5 | Time-Dependent Schrodinger Equation | 6 |
| 0.1.6 | Time- Independent Schrodinger Equation | 8 |
| 0.1.7 | Heisenberg's Uncertainty Principle | 8 |
| 0.1.8 | Expectation Values | 8 |

0.1 Mathematical Axioms of Quantum Mechanics

0.1.1 The Basic Postulates of Quantum Mechanics

Postulates are not unknown in physics. They often serve as a basis of physical theories. Though they cannot be proved, one can prove the conclusions derived on the basis of the postulates. The success or failure of the postulates depends on the strength of the experimental results. There are different ways of stating the basic postulates of quantum mechanics, but the following formulation seems satisfactory:-

Postulate 1: Wavefunctions

The state of a physical system is completely described by a complex mathematical object, called the wavefunction ψ (psi, pronounced "sigh"). At any time, the wavefunction $\psi(x)$ is single-valued, continuous, and normalized.

The wave function $\psi(x)$ is not "the particle", or "the position of the particle", it is a mathematical function which carries information about the particle.

In this course, we will mostly be restricting ourselves to systems that contain a single particle (like one electron). In such a case, the wavefunction can be written as a function of the position coordinate \vec{r} of the particle, and the time: $\Psi = \Psi(\vec{r}, t)$

Often, we will simplify our lives by considering the (rather artificial) case of a particle restricted to motion in 1D, in which case we can write $\Psi = \Psi(x, t)$. We may also consider a particular moment in time, and focus on just $\Psi(x)$.

In general, $\Psi(x)$ is a complex function of x ; it has a real and an imaginary parts.

Postulate 2 : Operators and Observables

To every observable physical quantity there corresponds a Hermitian operator or matrix. Some of the important operators associated with observables in the co-ordinate representation:-

| Observables | Classical form | Operator |
|----------------------------|----------------|---|
| Co-ordinates | x, y, z | x, y, z |
| Momentum (x-component) | p_x | $-i\hbar \frac{\partial}{\partial x}$ |
| Momentum | \mathbf{p} | $-i\hbar \nabla$ |
| Energy | E | $-i\hbar \frac{\partial}{\partial t}$ |
| Kinetic energy | T | $-\frac{\hbar^2}{2m} \nabla^2$ |
| Hamiltonian (Total Energy) | H | $-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$ |

Postulate 3: Expectation Value

When a system is in a state described by a wave function Ψ , the expectation value of any observable A is given by:

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi d\tau}{\int \psi^* \psi d\tau}$$

If the wavefunction is normalized then we simply get the expectation value as

$$\langle A \rangle = \int \psi^* A_{op} \psi d\tau$$

Postulate 4 : Eigenvalues

The possible values which a measurement of an observable, whose operator is A , can give are the eigenvalues a_i of the equation

$$A\psi_i = a_i\psi_i$$

The eigenfunctions ψ_i form a complete set of n independent functions. The expectation value of the observable A when it is in the state ψ_n is given by

$$\langle A \rangle = \int \psi_n^* A \psi_n d\tau = \int \psi_n^* a_n \psi_n d\tau = a_n \int \psi_n^* \psi_n d\tau = a_n$$

The meaning here is that when an experiment is performed to determine the value of an observable A in a particular state, the value we expect in the measurement is its eigenvalue. In other words, the eigenvalues of an operator are the only experimentally measurable quantities.

Postulate 5 : Time Evolution of a Quantum System

The wavefunction of an isolated system evolves in time according to the Schrodinger Equation:

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

where $V = V(x)$ is (classical) potential energy of the particle, which depends on the physical system under discussion.

0.1.2 Wave Packet

Matter exhibits wave-like nature under suitable conditions according to the de Broglie's hypothesis. When the momentum of a particle is well defined, the wave can be of infinite extent. Therefore a free particle moving along x-axis with well defined momentum is described by an infinite plane wave $\psi(x, t)$ given by:

$$\psi(x, t) = A_0 \exp[i(kx - \omega t)] \quad (1)$$

where the wave vector $k = \frac{2\pi}{\lambda}$ and ω is the angular frequency. To describe matter waves associated with particles in motion, we need a quantity that varies in space and time. This variable quantity, called the wavefunction, $\psi(x, t)$ must be large in regions where the particles is likely to be found and small in the region where it is less likely to be found. That is, the wavefunction of a particle in conformity with the uncertainty principle must be localized in a small region around it. The wavefunction of the matter wave which is confined to a small region of space is termed as a wavepacket or wavegroup.

Mathematically, a wave packet can be constructed by the superposition of an infinite number of plane waves with slightly differing k-values as

$$\psi(x, t) = \int_{-\infty}^{\infty} A(k) \exp[ikx - i\omega(k)t] dk \quad (2)$$

0.1.3 Born's Interpretation of the Wave function

A particle by its nature is localized at a point, whereas the wavefunction is spread out in space. How can such an object represent the state of a particle? The answer is provided by the Born's statistical interpretation of the wavefunction, which says that in 1D case $|\psi(x, t)|^2$ gives the probability of finding the particle at point x , at time t , or more precisely

$$\int_a^b |\psi(x, t)|^2 dx = \{ \text{Probability of finding the particle between } a \text{ and } b, \text{ at time } t \} \quad (3)$$

Born interpreted the product $|\psi(x, t)|^2 = \psi^*(x, t)\psi(x, t)$ as the position **probability density**.

When $|\psi(x, t)|^2$ is integrated over the entire x dimension, one should get the total probability which is unity. i.e.

$$|N|^2 \int_{-\infty}^{\infty} |\psi(x, t)|^2 dx = 1 \quad (4)$$

where N is called the *normalization constant* and Eq.[4] is sometimes referred to as the *normalization condition*.

Example 1

Normalize the wavefunction $\psi(x) = A\exp(-ax^2)$ A and a are constants over the domain $-\infty \leq x \leq \infty$.

Solution:

Taking A as the normalization constant, we have

$$A^2 \int_{-\infty}^{\infty} \psi^* \psi dx = A^2 \int_{-\infty}^{\infty} \exp(-2ax^2) dx = 1$$

$$\text{Using the standard integral } \int_{-\infty}^{\infty} \exp(-2ax^2) dx = \sqrt{\frac{\pi}{2a}}$$

$$\text{we get } A = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}}$$

and hence the normalized wavefunction becomes

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \exp(-ax^2)$$

Example 2

Normalize the one-dimensional wavefunction given by $\psi(x) = A\sin(\frac{\pi x}{l})$ where $0 < x < l$.

Solution:

The wavefunction ψ is said to be normalized if it satisfies the relation:

$$\int_{-\infty}^{\infty} \psi^* \psi dx = 1$$

$$\int_0^l A^* \sin(\frac{\pi x}{l}) A \sin(\frac{\pi x}{l}) dx = 1$$

$$A^* A \int_0^l \sin^2(\frac{\pi x}{l}) dx = 1$$

$$|A|^2 \int_0^l \frac{1}{2} [1 - \cos(\frac{2\pi x}{l})] dx = 1$$

giving $A = \sqrt{\frac{1}{2}}$ and hence the normalized wavefunction is:

$$\psi(x) = \sqrt{\frac{2}{l}} \sin(\frac{\pi x}{l})$$

Example 3

The wavefunction of a particle is given by $\psi(x) = A\exp(-ax^2)$, A and a are constants over the domain $-\infty \leq x \leq \infty$. Calculate the probability of finding the particle in the region $-\infty \leq x \leq \infty$.

Solution:

From example 0.1.3 the normalization constant $A = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}}$ and hence the normalized wavefunction is

$$\psi(x) = \left(\frac{2a}{\pi}\right)^{\frac{1}{4}} \exp(-ax^2)$$

The probability of finding the particle in the region $0 < x < \infty$ is

$$P = \int_0^{\infty} \psi^* \psi dx$$

$$= \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} \int_0^{\infty} \exp(-2ax^2) dx$$

$$= \left(\frac{2a}{\pi}\right)^{\frac{1}{2}} \frac{1}{2} \sqrt{\frac{\pi}{2a}}$$

$$= \frac{1}{2}$$

0.1.4 Conditions of Admissibility of the Wave Function

In this section we need to answer the question: What are the characteristics of acceptable wavefunctions in quantum mechanics?

The admissibility conditions on the wavefunctions (well-behaved wavefunctions) are as follows:

- i. $\psi(x, t)$ must be finite everywhere in space. This is because $|\psi(x, t)|^2 dx$ for an infinitesimal length dx should be between 0 and 1.
- ii. $\psi(x, t)$ must be single valued everywhere. This is necessary because at any given x , $\psi(x, t)$ should have a unique value and then only the probability $|\psi(x, t)|^2$ may be uniquely defined.
- iii. $\psi(x, t)$ and its first partial derivatives with respect to its variables are continuous. This implies, there must not exist any sudden change in $\psi(x, t)$ when its variables undergo a change.
- iv. $\psi(x, t)$ must be square integrable so that the integral of its modulus squared is finite. This is necessary as the probability $P = \int_{-\infty}^{\infty} |\psi(x, t)|^2 = \text{finite value or Zero}$.
- v. $\psi(x, t)$ must vanish at infinity. A wavefunction is taken to represent the position of a particle and intuitively no particle is taken to exist at infinity.
- vi. $\psi(x, t)$ is zero at any surface at which there is an infinite potential step.

0.1.5 Time-Dependent Schrodinger Equation

We derive below the one-dimensional time dependent Schrodinger equation for a free particle. The wave function of a localized free particle is given by Eq.[4] as

$$\psi(x, t) = \int_{-\infty}^{\infty} A(k) \exp[ikx - i\omega(k)t] dk \quad (5)$$

For a free particle, the classical expression for energy is

$$E = \frac{p_x^2}{2m} \quad (6)$$

Replacing p_x by $\hbar k$ and E by $\hbar\omega$, we get

$$\omega = \frac{\hbar k^2}{2m} \quad (7)$$

Substituting this value of ω in Eq.[5] gives

$$\psi(x, t) = \int_{-\infty}^{\infty} A(k) \exp[i(kx - \frac{\hbar k^2}{2m}t)] dk \quad (8)$$

Differentiating $\psi(x, t)$ with respect to t , we get

$$\frac{\partial \psi}{\partial t} = -\frac{i\hbar}{2m} \int_{-\infty}^{\infty} k^2 A(k) \exp[i(kx - \frac{\hbar k^2}{2m}t)] dk \quad (9)$$

Differentiating $\psi(x, t)$ twice with respect to x , we get

$$\frac{\partial^2 \psi}{\partial x^2} = - \int_{-\infty}^{\infty} k^2 A(k) \exp[i(kx - \frac{\hbar k^2}{2m}t)] dk \quad (10)$$

Comparing Eqs.[9] and Eqs.[10] we have

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} = i\hbar \frac{\partial \psi}{\partial t} \quad (11)$$

which is the one-dimensional Schrodinger equation for a free particle.

Modification of the free particle equation to a system moving in a one-dimensional potential $V(x)$ can easily be done. The classical energy expression for such a system is given by

$$E = \frac{p^2}{2m} + V(x, t) \quad (12)$$

Now we can simply substitute E and p by their respective operators:

$$E \longrightarrow i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad (13)$$

$$p \longrightarrow i\hbar \frac{\partial}{\partial x} \quad (14)$$

So we have

$$i\hbar \frac{\partial}{\partial t} = (-i\hbar \frac{\partial}{\partial x})^2 \frac{1}{2m} + V(x, t) \quad (15)$$

and by letting each operator term act on $\psi(x, t)$ we get the time-dependent Schrodinger equation for a particle of mass m moving in a potential $V(x, t)$ as

$$[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x, t)]\psi(x, t) = i\hbar \frac{\partial \psi(x, t)}{\partial t} \quad (16)$$

The quantity in the bracket of Eq.[16] is the Hamiltonian Operator of the system.

Extension to Three Dimensions

The one-dimensional treatment given above can easily be extended to three dimensions. The three dimensional wave packet can be written as

$$\psi(\mathbf{r}, t) = \int_{-\infty}^{\infty} A(\mathbf{k}) \exp[i((\mathbf{k} \cdot \mathbf{r}) - \omega t)] d\mathbf{k}_x d\mathbf{k}_y d\mathbf{k}_z \quad (17)$$

Proceeding on similar lines as in the one-dimensional case we get the three dimensional Schrodinger equation for a free particles as

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (18)$$

giving the energy and momentum operators as

$$E \longrightarrow i\hbar \frac{\partial}{\partial t} \quad \text{and} \quad (19)$$

$$\mathbf{p} \longrightarrow -i\hbar \nabla \quad (20)$$

Similarly in three dimensions Eq.[16], when involving a three dimensional potential $V(\mathbf{r}, t)$ is simply re-written as

$$[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}, t)]\psi(\mathbf{r}, t) = i\hbar \frac{\partial \psi(\mathbf{r}, t)}{\partial t} \quad (21)$$

0.1.6 Time- Independent Schrodinger Equation

The time –dependent Schrodinger equation, Eq. [16] describes the evolution of quantum systems using time-dependent wavefunction $\psi(\mathbf{r}, t)$. It completely neglects the time dependence of the operators. If the Hamiltonian operator does not depend on time, the variables \mathbf{r} and t of the wavefunction $\psi(\mathbf{r}, t)$ can be separated into two functions $\varphi(\mathbf{r})$ and $\Phi(t)$ as

$$\psi(\mathbf{r}, t) = \varphi(\mathbf{r})\Phi(t) \quad (22)$$

Substituting this value in Eq.[21] and dividing throughout by $\varphi(\mathbf{r})\Phi(t)$ we get

$$i\hbar \frac{1}{\Phi(t)} \frac{d\Phi(t)}{dt} = \frac{1}{\varphi(\mathbf{r})} \left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right) \varphi(\mathbf{r}) \quad (23)$$

The left hand-side of Eq.[23] is a function of time and the right hand side a function of space co-ordinates . Since t and \mathbf{r} are independent variables, each side must be equal to a constant, say E (the total energy which is conserved). This gives rise to the equations

$$\frac{1}{\Phi(t)} \frac{d\Phi(t)}{dt} = -\frac{iE}{\hbar} \quad (24)$$

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] \psi(\mathbf{r}) = E\psi(\mathbf{r}) \quad (25)$$

Eq.[25] is the *time-independent Schrodinger equation*.

0.1.7 Heisenberg's Uncertainty Principle

Heisenberg's Uncertainty Principle should more appropriately be called Heisenberg's Indeterminacy Principle since we can measure either x or p_x with very low 'uncertainty' but we cannot measure both. If one is certain, the other is indeterminate! Heisenberg's Uncertainty Principle is stated as

$$\Delta x \Delta p_x \geq \frac{h}{4\pi} \quad (26)$$

where Δx is the uncertainty in the position, Δp_x is the uncertainty in the component of the momentum in the x direction and h is Planck's constant.

(The symbol \geq means greater than or equal to.)

Quantum mechanics can show that there are other pairs of quantities that have this indeterminacy, for example energy and time

$$\Delta E \Delta t \geq \frac{h}{4\pi} \quad (27)$$

where ΔE is the uncertainty in energy and Δt is the uncertainty in time.

0.1.8 Expectation Values

For a particle in state $\psi(x, t)$ the **expectation** or **mean** or **average** value of x is

$$\langle x \rangle = \int_{-\infty}^{\infty} \psi^*(x, t) x \psi(x, t) dx \quad (28)$$

if $\psi(x, t)$ is normalized.

In general, the expectation value of any dynamical variable A whose operator is A_{op} is expressed as

$$\langle A \rangle = \frac{\int \psi^* A_{op} \psi d\tau}{\int \psi^* \psi d\tau} \quad (29)$$

However, it is important to note that if ψ is normalized already then the denominator in Eq.[29] will be equal to 1 (by normalization condition) and therefore the expectation value is simply evaluated as

$$\langle A \rangle = \int \psi^* A_{op} \psi d\tau \quad (30)$$

The expectation value is the average of repeated measurements on an ensemble of identically prepared systems and not the average of repeated measurements on one and the same system.

Closely related to the expectation values are the **standard deviations** associated with a measurement of a dynamical variable A and this is written as

$$\Delta A = \sqrt{\langle A^2 \rangle - \langle A \rangle^2} \quad (31)$$

Note that Eq.[30] would be important in evaluating quantities such as Δx , Δp_x e.t.c.

Example 1

Show that the expectation value of Hamiltonian operator H is the total energy of the system.

Solution:

We have the expectation value of H as

$$\begin{aligned} \langle H \rangle &= \int \psi^* H \psi d\tau \\ &= \int \psi^* E \psi d\tau \\ &= E \int \psi^* \psi d\tau \\ &= E, \text{ the total energy of the system.} \end{aligned}$$

Example 2

Calculate the value of $\langle r \rangle$ related to the wavefunction $\psi(r) = \sqrt{\frac{1}{\pi a^3}} e^{-\frac{r}{a}}$ where a is a constant.

Solution:

Since this is a radial wavefunction it is better to work in spherical co-ordinates.

$$\begin{aligned} \langle r \rangle &= \int \psi^* r \psi d\tau \\ &= \int_0^\infty r^2 dr \int_0^\pi \sin \vartheta d\vartheta \int_0^{2\pi} d\Phi (\psi^* r \psi) \quad [\text{Remember } d\tau = r^2 \sin \vartheta dr d\vartheta d\Phi] \\ &= \frac{1}{\pi a^3} 4\pi \int_0^\infty r^3 e^{-\frac{2r}{a}} dr \quad [\text{Use standard integral } \int_0^\infty x^n e^{-ax} dx = \frac{n!}{a^{n+1}}] \\ &= \frac{1}{\pi a^3} 4\pi \times \frac{3}{8} a^4 \\ &= \frac{3}{2} a \end{aligned}$$

Example 3

Calculate $\langle p \rangle$, $\langle p^2 \rangle$ and Δp for the normalized wavefunction $\psi(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$ for $0 < |x| < L$

Solution:

$$\begin{aligned} \langle p \rangle &= \int_{-\infty}^\infty \psi^* p \psi dx \\ &= \frac{1}{2} \int_{-L}^L \left(\frac{2}{L} \right) \sin \frac{\pi x}{L} \left(-i\hbar \frac{d}{dx} \right) \sin \frac{\pi x}{L} dx \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} \int_{-L}^L \left(\frac{2}{L} \right) \sin \frac{\pi x}{L} (-i\hbar) \frac{\pi}{L} \cos \frac{\pi x}{L} dx \\
&= \frac{\pi\hbar}{2iL^2} \int_{-L}^L 2 \sin \frac{\pi x}{L} \cos \frac{\pi x}{L} dx \\
&= \frac{\pi\hbar}{2iL^2} \int_{-L}^L \sin \frac{2\pi x}{L} dx \\
&= \mathbf{0}
\end{aligned}$$

$$\begin{aligned}
\langle p^2 \rangle &= \int_{-\infty}^{\infty} \psi^* p \psi dx \\
&= \int_{-L}^L \psi^* \left(-\hbar^2 \frac{d^2}{dx^2} \right) \psi dx \\
&= \frac{\hbar^2}{2} \frac{2}{L} \left(\frac{\pi}{L} \right)^2 \int_{-L}^L \sin \frac{\pi x}{L} \sin \frac{\pi x}{L} dx \\
&= \frac{\pi^2 \hbar^2}{2L^3} \int_{-L}^L 2 \sin^2 \frac{\pi x}{L} dx \\
&= \frac{\pi^2 \hbar^2}{L^2}
\end{aligned}$$

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