Physics 570A Lecture 9

The Postulates of QM

Postulate 1 The dynamical state of a quantum system can be described by a complex wavefunction that contains all that can be known about the system.

In order to be physically admissible, $\psi(\vec{r},t)$ must be continuous and finite. The same holds for its first derivative (except for the case of singular potentials, such as hard walls or $\lambda\delta(x)$). Further, $\psi(\vec{r},t)$ must be normalizable.

The probability to find the particle in an element of volume $dxdydz$ in the vicinity of $\vec{r}$ is

$$dP(x,y,z,t) = |\Psi(\vec{r},t)|^2 \, dx\,dy\,dz,$$

provided Ψ is normalized:

$$1 = \int |\Psi(\vec{r},t)|^2 \, dx\,dy\,dz.$$

Definitions

Two non-zero wavefunctions are said to be orthogonal if their scalar product is zero,

$$\langle i|j\rangle = \int \psi_i^* \, \psi_j \, dx\,dy\,dz = 0$$

wavefunctions that are normalized and orthogonal are <u>orthonormal</u>,

$$\langle i|j\rangle = \int \psi_i^* \psi_j \, d^3r = \delta_{ij} = \begin{cases} 1, & i=j \\ 0, & i\neq j \end{cases}$$

<u>Postulate 2</u> The superposition principle is valid for functions representing physically admissible states.

That is, if ψ_i, $i=1,2,\dots,n$ are wavefunctions representing possible physical states, then

$$\psi = \sum_{i=1}^{n} c_i \psi_i$$

also represents a physically allowed state.

Postulate 3 The time-evolution of the wave function is described by the Schrödinger equation.

$$i\hbar \frac{\partial}{\partial t} \Psi(\vec{r},t) = \hat{H}\, \Psi(\vec{r},t) \quad (1)$$

e.g. $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r},t)$.

For the particular case of a time-indep. potential $V = V(\vec{r})$, Eq. (1) is separable, leading to the time-indep. Sch. eq.,

$$H\, \psi_n(\vec{r}) = E_n\, \psi_n(\vec{r})$$

$\psi_n(\vec{r})$ = stationary states or energy eigenstates

The nth particular solution is

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}.$$

Utilizing the superposition principle, the general sol'n is

$$(2) \quad \Psi(\vec{r},t) = \sum_n c_n \psi_n(\vec{r})\, e^{\frac{-iE_n t}{\hbar}}.$$

The sufficient condition for Eq. (2) to be a valid expansion for a general wavefunction $\Psi(\vec{r},t)$ is that the functions $\psi_n(\vec{r})$ form a complete, orthonormal set of functions (more on this later.)

<u>Postulate 4</u> Each dynamical variable q can be directly associated with a linear, Hermitian operator

$\hat{Q}$. The only possible result of a measurement of the observable q is one of the eigenvalues of $\hat{Q}$. After the measurement $\Psi \to \Psi_q$, is an eigenstate where $\hat{Q}\Psi_q = q\Psi_q$

Definition An operator Q is linear if it commutes with constants and obeys the distributive law: specifically if

$$\hat{Q}(c\Psi) = c\,\hat{Q}(\Psi)$$

and $\hat{Q}(\Psi_1 + \Psi_2) = \hat{Q}(\Psi_1) + \hat{Q}(\Psi_2)$,

then $\hat{Q}$ is a linear operator.

Definition An operator is Hermitian if it satisfies the following equality,

$$\int (\hat{Q}\Psi_i)^* \Psi_j \, d^3r = \int \Psi_i^* (\hat{Q}\Psi_j) \, d^3r$$

$\hat{Q} = \hat{Q}^\dagger$

In Dirac notation, the Hermitian property is

$$\langle \hat{Q}\psi_i | \psi_j \rangle = \langle \psi_i | \hat{Q}\psi_j \rangle .$$

It follows that

$$\langle \psi | \hat{Q}\psi \rangle^* = \langle \hat{Q}\psi | \psi \rangle = \langle \psi | \hat{Q}\psi \rangle .$$

Thus $\langle \psi | \hat{Q}\psi \rangle$ is <u>real</u>.

One writes, simply $\langle \psi | \hat{Q} | \psi \rangle$, indicating $\hat{Q}$ acts the same to the right or the left.

<u>Example</u> Suppose

$$\Psi(\vec{r},t) = c_1 \psi_1(\vec{r}) e^{-\frac{iE_1 t}{\hbar}} + c_2 \psi_2(\vec{r}) e^{-\frac{iE_2 t}{\hbar}}$$

$$= c_1 \Psi_1(\vec{r},t) + c_2 \Psi_2(\vec{r},t) .$$

The energy of the system corresponds to the linear, Hermitian

operator $\hat{H}$. If the energy
is measured, either the result
E_1 will be obtained, with
probability $\dfrac{|C_1|^2}{|C_1|^2+|C_2|^2}$, or the
result E_2 will be obtained,
with probability $\dfrac{|C_2|^2}{|C_1|^2+|C_2|^2}$.

Once the energy of the
system is known, to be say
E_i, then the wavefunction
is collapsed onto the state
Ψ_i. Successive measurements
of E will yield the
same value, since Ψ_i is

a stationary state. For general operators $\hat{Q}$, the measured value may change after some time, but if the measurement is repeated right away, the same value q must be obtained. This is only possible if the wavefunction after the measurement is an eigenstate of the operator $\hat{Q}$.

<u>Theorem</u> The eigenvalues of a Hermitian operator are real.

<u>Proof</u>: Given $\hat{Q}\psi_n = q_n \psi_n$ and

$Q = Q^\dagger$. For convenience, let

$\langle \psi_n | \psi_n \rangle = 1$. $\quad \langle \psi_n | Q \psi_n \rangle = \langle \psi_n | q_n | \psi_n \rangle$

$$= q_n \langle \psi_n | \psi_n \rangle$$
$$= q_n$$

But $\langle Q \psi_n | \psi_n \rangle = \langle \psi_n | q_n^* | \psi_n \rangle = q_n^* \langle \psi_n | \psi_n \rangle$

$$= q_n^*$$

By the Hermitian property, we have

$$q_n = q_n^*$$

<u>Theorem</u> The eigenfunctions of a Hermitian operator are orthogonal if they correspond to distinct eigenvalues.

<u>Proof</u>: Given $\hat{Q} |\psi_i\rangle = q_i |\psi_i\rangle$
and $\hat{Q} |\psi_j\rangle = q_j |\psi_j\rangle$,

where $q_i \neq q_j$ and $Q = Q^\dagger$.

Then $\langle \psi_i | Q \psi_j \rangle = q_j \langle \psi_i | \psi_j \rangle$

$$\begin{aligned} &\parallel \\ \langle Q \psi_i | \psi_j \rangle &= q_i^* \langle \psi_i | \psi_j \rangle \\ &= q_i \langle \psi_i | \psi_j \rangle \end{aligned}$$

$$0 = (q_j - q_i) \langle \psi_i | \psi_j \rangle \qquad \text{Q.E.D.}$$

If there are degenerate eigenfunctions, we will see that they too can be orthogonalized.

Postulate 5 The expectation value of a measurement of an observable q is given mathematically as $\langle q \rangle = \langle \psi | \hat{Q} | \psi \rangle$ if the system is in the state ψ.

By the superposition principle, we may write ψ as a linear combination of the eigenstates ψ_n of the operator $\hat{Q}$: $\hat{Q}\psi_n = q_n \psi_n$,

$$\psi = \sum_n c_n \psi_n$$

$$\langle q \rangle = \langle \psi | \hat{Q} | \psi \rangle$$

$$= \sum_n c_n^* \sum_{n'} c_{n'} \int \psi_n^* \hat{Q} \psi_{n'} \, d^3r$$

$$= \sum_n \sum_{n'} c_n^* c_{n'} q_{n'} \underbrace{\int \psi_n^* \psi_{n'} \, d^3r}_{\delta_{nn'}}$$

$$= \sum_n |c_n|^2 q_n .$$

Note that in order for ψ to be normalized,

$$\langle \psi | \psi \rangle = \sum_n |c_n|^2 = 1.$$

<u>Corollary</u> The probability of obtaining the result q_n when the variable q is measured is

$$P(q_n) = |c_n|^2.$$

This follows because

$$\langle q^N \rangle = \sum_n |c_n|^2 q_n^N \quad \forall N.$$

More on bra-ket notation

Suppose $\hat{Q}$ is not a hermitian operator.

$$\langle \phi | \hat{Q} \psi \rangle = \int dx\, \phi^*(x)\, \hat{Q}\, \psi(x)$$

$$\langle \phi | \hat{Q} \psi \rangle^* = \int dx\, \phi(x)\, \hat{Q}^*\, \psi^*(x)$$

$$= \int dx \left[\hat{Q}^* \psi^*(x)\right] \phi(x)$$

$$= \int dx \left[\hat{Q}\, \psi(x)\right]^* \phi(x) = \langle \hat{Q} \psi | \phi \rangle$$

$$\langle \hat{Q} \rangle = \langle \psi | \hat{Q} \psi \rangle = \int dx\, \psi^*(x)\, \hat{Q}\, \psi(x)$$

$$\langle \hat{Q} \rangle^* = \langle \hat{Q} \psi | \psi \rangle = \int dx \left[\hat{Q}^* \psi^*(x)\right] \psi(x)$$

$$\equiv \int dx\, \psi^*(x) \left(\hat{Q}^*\right)^T \psi(x)$$

But $(\hat{Q}^*)^T \equiv \hat{Q}^\dagger$

$$\Rightarrow \langle \hat{Q} \rangle^* = \int dx\, \psi^*(x)\, \hat{Q}^\dagger\, \psi(x)$$

$$= \langle \hat{Q}^\dagger \rangle.$$

Thus, if $\hat{Q} = \hat{Q}^\dagger$, then

$\langle \hat{Q} \rangle \in \mathbb{R}$ (as we showed previously).

$$\boxed{\langle \hat{Q}\phi | \psi \rangle \equiv \langle \phi | \hat{Q}^\dagger \psi \rangle}$$

Definition of hermitian conjugate