

## 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  $\delta(x)$ ). Further,  $\psi(\vec{r}, t)$  must be normalizable.

The probability to find the  $\psi$  particle in an element of volume  $dx dy dz$  in the vicinity of  $\vec{r}$  is

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

provided  $\Psi$  is normalized:

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

### Definition 5

Two non-zero wave functions 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 (3) and orthogonal are orthonormal,

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

Postulate 2 The superposition principle is valid for functions representing physically admissible states.

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

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

represents a physically allowed state.

- Postulate 3 The time-evolution of the wave function is described by the Schrödinger equation. (4)

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

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.,

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

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

The  $n$ th particular solution is 5

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

Utilizing the superposition principle, the general sol<sup>n</sup> is

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

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

Postulate 4 Each dynamical

• variable  $g$  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  $\psi \rightarrow \psi_q$ , where  $\hat{Q}\psi_q = q\psi_q$  is an eigenstate.

- Definition An operator  $Q$  is linear if it commutes with constants and obeys the distributive law. Specifically if

$$\hat{Q}(c\psi) = c\hat{Q}(\psi)$$

$$\text{and } \hat{Q}(\psi_1 + \psi_2) = \hat{Q}(\psi_1) + \hat{Q}(\psi_2),$$

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

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

$$\int (\hat{Q}\psi_i)^* \psi_j d^3r = \int \psi_i^* (\hat{Q}\psi_j) d^3r$$

In Dirac notation, the  
● Hermitian property is

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

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 real.

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

Example Suppose

$$\begin{aligned} \Psi(\vec{r}, t) &= c_1 \psi_1(\vec{r}) e^{-iE_1 t / \hbar} + c_2 \psi_2(\vec{r}) e^{-iE_2 t / \hbar} \\ &= c_1 \Psi_1(\vec{r}, t) + c_2 \Psi_2(\vec{r}, t). \end{aligned}$$

● The energy of the system  
corresponds to the linear, Hermitian

- operator  $\hat{H}$ . If the energy (8) is measured, either the result  $E_1$  will be obtained, with probability  $\frac{|c_1|^2}{|c_1|^2 + |c_2|^2}$ , or the result  $E_2$  will be obtained, with probability  $\frac{|c_2|^2}{|c_1|^2 + |c_2|^2}$ .

- Once the energy of the system is known, to be say  $E_i$ , then the wavefunction is collapsed onto the state  $\Psi_i$ . Successive measurements of  $E$  will yield the same value, since  $\Psi_i$  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  $\hat{Q}$ .

Theorem The eigenvalues of a Hermitian operator are real.

- Proof: Given  $\hat{Q}\psi_n = q_n\psi_n$  and

•  $Q = Q^\dagger$ . For convenience, let 10

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

$$= g_n \langle \psi_n | \psi_n \rangle$$

$$= g_n$$

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

$$= g_n^*$$

By the Hermitian property, we have

$$g_n = g_n^*$$

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

• Proof: Given  $\hat{Q} |\psi_i\rangle = g_i |\psi_i\rangle$   
and  $\hat{Q} |\psi_j\rangle = g_j |\psi_j\rangle,$

where  $g_i \neq g_j$  and  $Q = Q^\dagger$ . □

• Then  $\langle \psi_i | Q \psi_j \rangle = g_j \langle \psi_i | \psi_j \rangle$   
 $\stackrel{||}{=} \langle Q \psi_i | \psi_j \rangle = g_i^* \langle \psi_i | \psi_j \rangle$   
 $= g_i \langle \psi_i | \psi_j \rangle$

$$0 = (g_j - g_i) \langle \psi_i | \psi_j \rangle \quad \text{Q.E.D.}$$

• 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  $g$  is given mathematically as  $\langle g \rangle = \langle \psi | \hat{Q} | \psi \rangle$  if the system is in the state  $\psi$ .

By the superposition principle, 12  
we may write  $\psi$  as a  
linear combination of the  
eigenstates  $\psi_n$  of the operator

$$\hat{Q} : \hat{Q} \psi_n = g_n \psi_n,$$

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

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

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

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

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

Note that in Order for  $\psi$  to be normalized, (13)

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

Corollary The probability

of obtaining the result

$g_n$  when the variable  $g$  is measured is

$$P(g_n) = |c_n|^2. \quad \text{This follows}$$

because

$$\langle g^N \rangle = \sum_n |c_n|^2 g_n^N \quad \forall N.$$

# More on bra-ket notation

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

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

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

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

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

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

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

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

• 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).

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

Definition of hermitian conjugate