Quantum Mechanics: Formulation

Postulates of quantum mechanics

Since we have constructed a new theory, quantum mechanics, from scratch, by writing down the Schrödinger equation, we need to have a set of rules to follow. The *postulates of quantum mechanics* constitute these rules. The postulates are as follows.

1. The state of a system is specified, at a time t, by a wave-function (typically denoted by ψ). The wave-function contains all information about the system.
2. All observabe quantities are denoted by Hermitian operators.
3. The measurement of an observable yields one of its possible eigenvalues, as the measured value. The wave-function of the system changes to the corresponding eigenfunction of the measured observable, due to the act of measurement.
4. If the wave-function of the system is given by
$$\psi(x) = \sum_n a_n \phi_n(x),$$
where $\phi_n(x)$ are the eigenfunctions of the observable to be measured, the measurement will result in the system changing to the wave-function $\phi_k(x)$ with the probability $|a_k|^2$.
5. The time evolution of the state of the system is governed by the time-dependent Schrödinger equation
$$i\hbar \frac{\partial \psi(x)}{\partial t} = \hat{H}\psi(x),$$
$\hat{H}$ being the Hamiltonian of the system.

Apart from these postulates, there are also some properties which every physical wave-function must satisfy:

- Wave-function must be continuous and differentiable everywhere.
- Wave-function must be single-valued everywhere. If it could have more than one value at a point, it would mean a particle has more than one probability of being found at that point, which is unacceptable.
- Wave-function should be normalized over all space: $\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1$.
- Wave-function should go to zero in limits $x \to \infty$ and $x \to -\infty$. This basically is a consequence of the previous condition.

Bra-Ket notations

In the modern formulation of quantum mechanics, one need not deal with wave-functions which can become cumbersome. We now introduce new notations, called Dirac notations, or Bra-Ket notations, which will make our expressions more concise. The notations are as follows:

$$\begin{aligned} \psi(x) &\to |\psi\rangle && \text{ket} \\ \psi^*(x) &\to \langle\psi| && \text{bra} \\ \int_{-\infty}^{\infty} \phi^*(x)\psi(x)dx &\to \langle\phi|\psi\rangle && \text{inner product} \end{aligned} \quad (1)$$

One has freedom to choose any label of the wave-function to label the ket. For example $\psi_a(x)$ may be replace by $|\psi_a\rangle$ or just $|a\rangle$. The advantage of this notation can be seen by writing some important relations we have used till now:

$$\begin{aligned}
\hat{H}|\psi\rangle &= E|\psi\rangle && \text{Time-independent Schrodinger eqn.} \\
i\hbar\frac{\partial}{\partial t}|\psi\rangle &= \hat{H}|\psi\rangle && \text{Time-dependent Schrodinger eqn.} \\
\langle\psi|\hat{A}^\dagger|\phi\rangle &= \langle\phi|\hat{A}|\psi\rangle^* && \text{Adjoint of an operator} \\
\langle\psi_m|\psi_n\rangle &= \delta_{mn} && \text{Ortho-normality of eigenstates} \\
\left(\hat{A}|\psi\rangle\right)^* &= \langle\psi|\hat{A}^\dagger
\end{aligned} \tag{2}$$

Instead of the wave-function, now we will talk of the *state* of the system, represented by a *ket*. The state is an abstract entity, and it is meaningless to ask what is the form of the state. Properties of a state will be specified by the effect of various operators on it. In fact, it the modern formulation of quantum mechanics we will see that many problems which were traditionally dealt by solving differential equations, can be solved by dealing only with commutation relations between operators and the effect of operators on various kets.

Eigenstates of Hermitian operators

First let us prove an important theorem about eigenstate of Hermitian operators. **Eigenstates of a Hermitian operator, with different eigenvalues, are orthogonal.** Let us consider a Hermitian operator $\hat{A}$ with two eigenstates with different eigenvalues:

$$\hat{A}|\psi_1\rangle = \alpha_1|\psi_1\rangle, \quad \hat{A}|\psi_2\rangle = \alpha_2|\psi_2\rangle$$

We write the relation for the adjoint of $\hat{A}$ (which is $\hat{A}$ itself):

$$\langle\psi_1|\hat{A}|\psi_2\rangle = \langle\psi_2|\hat{A}|\psi_1\rangle^*$$

Using the fact that these are eigenstates of $\hat{A}$, and also recognizing that eigenvalues of Hermitian operators are real, we get

$$\alpha_2\langle\psi_1|\psi_2\rangle = \alpha_1\langle\psi_2|\psi_1\rangle^*$$

But $\langle\psi_2|\psi_1\rangle^* = \langle\psi_1|\psi_2\rangle$, which leads to

$$\langle\psi_1|\psi_2\rangle(\alpha_2 - \alpha_1) = 0$$

Since $\alpha_1 \neq \alpha_2$, the above is possible only if $\langle\psi_1|\psi_2\rangle = 0$. Hence $|\psi_1\rangle, |\psi_2\rangle$ are orthogonal. But what about two eigenstates of a Hermitian operator which have same eigenvalues (degenerate states)?

$$\hat{A}|\psi_3\rangle = \alpha|\psi_3\rangle, \quad \hat{A}|\psi_4\rangle = \alpha|\psi_4\rangle$$

It is true that $|\psi_3\rangle, |\psi_4\rangle$ may not be orthogonal, and $\langle\psi_3|\psi_4\rangle \neq 0$. However, consider the state

$$|\psi_4'\rangle = C\left(|\psi_3\rangle - \frac{1}{\langle\psi_3|\psi_4\rangle}|\psi_4\rangle\right),$$

where C is a normalization constant, which can be determined. It can be easily checked that $\langle\psi_3|\psi_4'\rangle = 0$, meaning $|\psi_4'\rangle$ is orthogonal to $|\psi_3\rangle$. Also

$$\hat{A}|\psi_4'\rangle = C\left(\alpha|\psi_3\rangle - \frac{1}{\langle\psi_3|\psi_4\rangle}\alpha|\psi_4\rangle\right) = \alpha|\psi_4'\rangle,$$

which means that $|\psi_4'\rangle$ is also an eigenstate of $\hat{A}$ with an eigenvalue α. So, one can use $|\psi_4'\rangle$ in place of $|\psi_4\rangle$ so that all eigenstates of $\hat{A}$ are orthogonal to each other. It is easy to see that even if there are more than two degenerate eigenstates of $\hat{A}$, such a procedure can be used to construct mutually orthogonal eigenstates. One can now assert that **all eigenstates of a Hermitian operator are mutual orthogonal**:

$$\hat{A}|\psi_n\rangle = \alpha|\psi_n\rangle \implies \langle\psi_m|\psi_n\rangle = \delta_{mn}.$$

Thus the eigenstates of a Hermitian operator form an ortho-normal set, each state being normalized, and being orthogonal to all other states. We also noted that such an ortho-normal set describes an abstract space called Hilbert space. The ket states are vectors in the Hilbert states, and any other state of this Hilbert space can be represented in terms of this set:

$$|\phi\rangle = \sum_{n=0}^{\infty} c_n|\psi_n\rangle, \tag{3}$$

c_n being certain constants specific to $|\phi\rangle$. If one wants to know what a particular constant (say) c_k is, one can just multiply the bra state $\langle\psi_k|$ on both side of the above equation.

$$\langle\psi_k|\phi\rangle = \sum_{n=0}^{\infty} c_n\langle\psi_k|\psi_n\rangle = \sum_{n=0}^{\infty} c_n\delta_{mn} = c_k.$$

So c_k is just $\langle\psi_k|\phi\rangle$.

Outer product

If one puts a bra and a ket state as $|\phi\rangle\langle\psi|$, what does it mean? To find that out let us put another to the right of it:

$$(|\phi\rangle\langle\psi|)|\chi\rangle = |\phi\rangle\langle\psi|\chi\rangle$$

The RHS is a state times the inner product (which is a number). The outer product thus acts on a state, and gives another state. But that precisely is the definition of an operator! Thus **outer product is an operator**. Let us rewrite (3) using the fact that $c_k = \langle\psi_k|\phi\rangle$

$$\begin{aligned} |\phi\rangle &= \sum_{n=0}^{\infty} c_n|\psi_n\rangle, \\ &= \sum_{n=0}^{\infty}\langle\psi_n|\phi\rangle|\psi_n\rangle = \sum_{n=0}^{\infty}|\psi_n\rangle\langle\psi_n|\phi\rangle, \\ &= \left(\sum_{n=0}^{\infty}|\psi_n\rangle\langle\psi_n|\right)|\phi\rangle. \end{aligned} \tag{4}$$

Comparing the LHS and RHS of the above, we conclude that term in the brackets is nothing but an *identity operator*

$$\sum_{n=0}^{\infty}|\psi_n\rangle\langle\psi_n| = \hat{1}.$$

This is known as a *completeness relation* and is very useful because it can be inserted in any expression without changing anything. This property can also be described by saying that the set of states $\{|\psi_n\rangle\}$ form a *complete set of states*. One could choose another Hermitian operator $\hat{B}$ with the eigenstates

$$\hat{B}|b_n\rangle = \beta_n|b_n\rangle.$$

The set $\{|b_n\rangle\}$ also form a complete set. They can also be used to describe the same Hilbert space that we described using eigenstates of operator $\hat{A}$. This is similar to the fact that 3-dimensional real space can be described using the cartesian coordinates by $\hat{\imath}, \hat{\jmath}, \hat{k}$, and also by another set of unit vectors $\hat{r}, \hat{\theta}, \hat{\phi}$ if one uses spherical polar coordinates.

Simple exercises using completeness

As a simple exercise, let us find the *trace* of the operator $|\phi\rangle\langle\psi|$. Trace is known to be independent of the basis. So, we can use any complete set of states for the job.

$$\begin{aligned} Tr(|\phi\rangle\langle\psi|) &= \sum_{n=0}^{\infty}\langle b_n|(|\phi\rangle\langle\psi|)|b_n\rangle = \sum_{n=0}^{\infty}\langle b_n|\phi\rangle\langle\psi|b_n\rangle \\ &= \sum_{n=0}^{\infty}\langle\psi|b_n\rangle\langle b_n|\phi\rangle = \langle\psi|\sum_{n=0}^{\infty}|b_n\rangle\langle b_n|\,|\phi\rangle \\ &= \langle\psi|\phi\rangle. \end{aligned} \tag{5}$$

Cyclic property of trace

Let us prove the cyclic property of trace, namely $Tr(\hat{A}\hat{B}\hat{C}) = Tr(\hat{B}\hat{C}\hat{A})$.

$$\begin{aligned} Tr(\hat{A}\hat{B}\hat{C}) &= \sum_{n=0}^{\infty}\langle b_n|\hat{A}\hat{B}\hat{C}|b_n\rangle = \sum_{n,m}\langle b_n|\hat{A}|b_m\rangle\langle b_m|\hat{B}\hat{C}|b_n\rangle \\ &= \sum_{n,m}\langle b_m|\hat{B}\hat{C}|b_n\rangle\langle b_n|\hat{A}|b_m\rangle = \sum_{m}\langle b_m|\hat{B}\hat{C}\sum_{n}|b_n\rangle\langle b_n|\hat{A}|b_m\rangle \\ &= \sum_{m}\langle b_n|\hat{B}\hat{C}\hat{A}|b_n\rangle = Tr(\hat{B}\hat{C}\hat{A}). \end{aligned} \tag{6}$$

Expectation value

Till now we have associated the eigenvalue of an operator with the value of the corresponding observable quantity. But there are situations when the state of the system is not an eigenstate of the operator of one's interest. How does one talk of the value of an observable in such a situation. For this general situation one can use the *expectation value* which is defined as

$$\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle.$$

Physical meaning of the expectation value, in terms of measurements, will discussed later when we discuss measurements in quantum mechanics. However, one can easily see that in case the state *is* an eigenstate of the operator, the expectation value is equal to its eigenvalue:

$$\langle\psi_n|\hat{A}|\psi\rangle_n = \langle\psi_n|\alpha_n|\psi\rangle_n = \alpha_n\langle\psi_n|\psi\rangle_n = \alpha_n.$$