The Formal Rules of Quantum Mechanics

THE WAVE FUNCTION

- POSTULATE 1: The quantum state of a particle, or system of particles, can be described by means of a **wave function**, Ψ. The wave function carries all the information that can be known about the system.
  - In general, Ψ will be complex.
- POSTULATE 2: The time dependence of Ψ is governed by the Schrodinger wave equation
$$H\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$
where $H = T+V$ is the energy operator.
  - Since the wave equation is linear, the superposition principle holds. If Ψ_1, Ψ_2, Ψ_3, *etc.* are physically acceptable wave functions, then
$$\Psi = \sum_n a_n \Psi_n$$
is also physically acceptable, and thus represents a possible quantum state of the system.
  - Solutions to the wave equation can be found by solving the energy eigenvalue equation
$$H\psi_n = E_n\psi_n.$$
If ψ_n satisfies this equation then
$$\Psi = \psi_n e^{-iE_nt/\hbar}$$
solves the wave equation. More generally we can construct solutions of the form
$$\Psi = \sum_n a_n\psi_n e^{-iE_nt/\hbar}.$$
- POSTULATE 3: Quantum mechanics is a theory of probabilities. Measurements carried out in identical systems described by the same wave function Ψ do not necessarily yield identical results.
  - Nature only allows us to know the probability of various outcomes.
  - The probability distribution for measurements of position is
$$P(\vec{r},t) = \Psi^*(\vec{r},t)\Psi(\vec{r},t).$$

OPERATORS

- POSTULATE 4: Associated with each measurable quantity, q, there is an operator Q. The operators corresponding to physical observables must be **linear** and **Hermitian**. The **expectation value** of q is given by

$$\langle q \rangle = \langle \Psi | Q | \Psi \rangle = \int_{-\infty}^{+\infty} \Psi^*(x,t)\, Q\, \Psi(x,t)\, dx,$$

  assuming that $\langle \Psi | \Psi \rangle = 1$.

  - An operator is linear if it satisfies $Q[\Psi_1 + \Psi_2] = Q\Psi_1 + Q\Psi_2$ and $Q\, a\Psi = a\, Q\Psi$ for all Ψ.

  - An operator is Hermitian if its expectation value is **real** for all physically acceptable wave functions.

- THEOREM: If Q is Hermitian then $\langle \Psi_1 | Q\Psi_2 \rangle = \langle Q\Psi_1 | \Psi_2 \rangle$ for all physically acceptable wave functions, Ψ_1 and Ψ_2.

EIGENFUNCTIONS AND EIGENVALUES

For any given operator Q it may be possible to find a set of functions ψ_n for which

$$Q\psi_n = q_n\, \psi_n$$

where q_n is a number. If this is the case we say ψ_n is an eigenfunction of Q with eigenvalue q_n.

- THEOREM: The eigenvalues of a Hermitian operator are real, provided that we accept only physically meaningful eigenfunctions.

  - Proof: The expectation value of Q in the state ψ_n is $\langle q \rangle = \langle \psi_n | Q | \psi_n \rangle = \langle \psi_n | Q\psi_n \rangle = \langle \psi_n | q_n \psi_n \rangle = q_n \langle \psi_n | \psi_n \rangle = q_n$. But the expectation value is always real for Hermitian operators, so q_n must be real.

- POSTULATE 5: The outcome of any individual measurement of q is always one of the eigenvalues of Q.

- THEOREM: If the wave function of a system at time t is one of the eigenfunctions of Q then a measurement of q at that time gives the result $q = q_n$ with probability 1.

  - Proof: As shown above, the expectation value of q in state ψ_n is q_n. To show that the measurement **always** yields the mean value we calculate the the uncertainty in q. The mean-square deviation from the average is given by $\langle (q-\langle q\rangle)^2\rangle = \langle (q-q_n)^2\rangle = \langle q^2\rangle - q_n^2$. But $\langle q^2\rangle = \langle\psi_n|Q^2|\psi_n\rangle = \langle\psi_n|Q^2\psi_n\rangle = \langle\psi_n|Qq_n\psi_n\rangle = \langle\psi_n|q_nQ\psi_n\rangle = \langle\psi_n|q_n^2\psi_n\rangle = q_n^2$. So $\sigma_q = 0$, which means that the measurement of q always yields the mean value q_n.

- THEOREM: Eigenfunctions of any Hermitian operator corresponding to different eigenvalues are orthogonal.

  - Proof: We have $Q\psi_n = q_n\psi_n$ and $Q\psi_m = q_m\psi_m$ with $q_n \neq q_m$. To prove the theorem we focus on the quantity $\langle\psi_n|Q|\psi_m\rangle$. By the usual rules we have $\langle\psi_n|Q|\psi_m\rangle = \langle\psi_n|Q\psi_m\rangle = \langle\psi_n|q_m\psi_m\rangle = q_m\langle\psi_n|\psi_m\rangle$. But since Q is Hermitian we can also write $\langle\psi_n|Q|\psi_m\rangle = \langle Q\psi_n|\psi_m\rangle = \langle q_n\psi_n|\psi_m\rangle = q_n\langle\psi_n|\psi_m\rangle$, where in the last step we used the fact that q_n is real. Comparing the two results, we have $q_m\langle\psi_n|\psi_m\rangle = q_n\langle\psi_n|\psi_m\rangle$ or equivalently $(q_m - q_n)\langle\psi_n|\psi_m\rangle = 0$. But $q_n \neq q_m$, and so we conclude that $\langle\psi_n|\psi_m\rangle = 0$.

DEGENERATE EIGENFUNCTIONS

This last theorem raises the question of whether we can draw any conclusions about orthogonality in situations where we have two or more eigenfunctions with the same eigenvalue. Suppose we have two eigenfunctions, ψ_1 and ψ_2 with eigenvalue q. If we construct the function $\psi_3 = c_1\psi_1 + c_2\psi_2$ and operate on this function with Q, we see immediately that ψ_3 is also an eigenfunction of Q with the same eigenvalue: $Q\psi_3 = Q[c_1\psi + c_2\psi_2] = c_1Q\psi_1 + c_2Q\psi_2 = c_1q\psi_1 + c_2q\psi_2 = q[c_1\psi_1 + c_2\psi_2] = q\psi_3$. Of course, we do not consider ψ_3 to be a **separate** eigenfunction since it is simply a linear combination of the first two. When counting the number of degenerate eigenfunctions, we will count ψ_{n+1} as a separate eigenfunction only if it is **linearly independent** of ψ_1, ψ_2 . . . ψ_n.

- THEOREM: Given a set of n linearly independent, degenerate eigenfunctions, $\{\psi_k\}$, it is possible to construct a new set of n eigenfunctions, $\{\hat{\psi}_k\}$, which are both linearly independent and mutually orthogonal.

  - Proof: The proof is by construction.

    Step 1 : Choose $\hat{\psi}_1 = N_1\psi_1$ where N_1 is chosen to give $\langle\hat{\psi}_1|\hat{\psi}_1\rangle = 1$.

Step 2 : Take $\hat{\psi}_2 = N_2 \, [\, \psi_2 - \langle \hat{\psi}_1 | \psi_2 \rangle \, \hat{\psi}_1 \,]$, and as before choose N_2 to give $\langle \hat{\psi}_2 | \hat{\psi}_2 \rangle = 1$. It is then easily shown that $\hat{\psi}_1$ and $\hat{\psi}_2$ are orthogonal: $\langle \hat{\psi}_1 | \hat{\psi}_2 \rangle = N_2 \, [\, \langle \hat{\psi}_1 | \psi_2 \rangle - \langle \hat{\psi}_1 | \psi_2 \rangle \, \langle \hat{\psi}_1 | \hat{\psi}_1 \rangle \,] = N_2 \, [\, \langle \hat{\psi}_1 | \psi_2 \rangle - \langle \hat{\psi}_1 | \psi_2 \rangle \cdot 1 \,] = 0$.

Step 3 : Take $\hat{\psi}_3 = N_3 \, [\, \psi_3 - \langle \hat{\psi}_1 | \psi_3 \rangle \, \hat{\psi}_1 - \langle \hat{\psi}_2 | \psi_3 \rangle \, \hat{\psi}_2 \,]$. Once again it is easy to show that $\hat{\psi}_3$ is orthogonal to both $\hat{\psi}_1$ and $\hat{\psi}_2$. For example, $\langle \hat{\psi}_1 | \hat{\psi}_3 \rangle = N_3 \, [\langle \hat{\psi}_1 | \psi_3 \rangle - \langle \hat{\psi}_1 | \psi_3 \rangle \, \langle \hat{\psi}_1 | \hat{\psi}_1 \rangle - \langle \hat{\psi}_2 | \hat{\psi}_3 \rangle \, \langle \hat{\psi}_1 | \hat{\psi}_2 \rangle \,] = N_3 \, [\langle \hat{\psi}_1 | \psi_3 \rangle - \langle \hat{\psi}_1 | \psi_3 \rangle \cdot 1 - \langle \hat{\psi}_2 | \hat{\psi}_3 \rangle \cdot 0 \,] = 0$

To complete the construction of the set $\{\hat{\psi}_k\}$ we simply continue in the same manner, defining

$$\hat{\psi}_k = N_k \, [\, \psi_k - \sum_{j=1}^{k-1} \langle \hat{\psi}_j | \psi_k \rangle \, \hat{\psi}_j \,].$$

Since our original functions are linearly independent, it is clear that $\hat{\psi}_k$ will never be zero. Furthermore, it is clear from the construction that each $\hat{\psi}_k$ will be orthogonal to all the $\hat{\psi}_j$ with $j < k$. Thus we have achieved the goal of constructing a set of functions $\{\hat{\psi}_k\}$ with the property $\langle \hat{\psi}_i | \hat{\psi}_j \rangle = \delta_{ij}$.

By virtue of this theorem, we are now free to assume that **all** the eigenfunctions of any Hermitian operator, whether degenerate or not, are mutually orthogonal. We simply agree that our "basis" eigenfunctions will always be chosen in such a way that $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ for all i, j.

EXPANSION OF Ψ IN TERMS OF BASIS FUNCTIONS

When we work with ordinary vectors we often find that it is useful to introduce vector components and write

$$\vec{A} = A_x \, \hat{x} + A_y \, \hat{y} + A_z \, \hat{z}$$

where the "basis vectors" employed in the expansion, $\hat{x}$, $\hat{y}$ and $\hat{z}$ in this example, are normalized and mutually orthogonal. The same general concept is useful in quantum mechanics. In this case, we often find that it is useful to expand the wave function of the system, Ψ, in terms of a set of "basis functions" $\{\psi_n\}$:

$$\Psi = \sum_n a_n \psi_n.$$

If the basis set we have chosen is sufficiently complete, expansions of this form may be possible for all physically reasonable wave functions, and if this condition is met we say that the basis functions "span the space", or that they constitute a "complete set of functions".

The math involved in expansions of this kind is greatly simplified if the basis functions we select are normalized and mutually orthogonal – i.e. if $\langle\psi_i|\psi_j\rangle = \delta_{ij}$. In particular, if we assume that the expansion exists, then the expansion coefficients are easily found as follows: $\langle\psi_k|\Psi\rangle = \langle\psi_k|\sum_n a_n\psi_n\rangle = \sum_n a_n\langle\psi_k|\psi_n\rangle = \sum_n a_n\delta_{kn} = a_k$. So the conclusion is that $a_k = \langle\psi_k|\Psi\rangle$.

Suppose we use as our basis functions the eigenfunctions of some operator Q, so that $Q\psi_n = q_n\psi_n$. The expectation value of q in the state Ψ is then given by $\langle q\rangle = \langle\Psi|Q|\Psi\rangle = \langle\sum_n a_n\psi_n|Q|\sum_m a_m\psi_m\rangle = \sum_{n,m} a_n^* a_m\langle\psi_n|Q|\psi_m\rangle = \sum_{n,m} a_n^* a_m\langle\psi_n|q_m\psi_m\rangle = \sum_{n,m} a_n^* a_m q_m\delta_{nm} = \sum_n |a_n|^2 q_n$. Since we have postulated that the q_n's are the only possible outcomes of any individual measurement of q, we are led to interpret $|a_n|^2$ as the **probability** of obtaining the result q_n. Thus we have $P_n = |a_n|^2 = |\langle\psi_n|\Psi\rangle|^2$.

What we have learned in the preceding paragraphs is that we can predict the probability distribution for measurements of q provided that the wave function of the system can be expanded in terms of the eigenfunctions of the associated operator. This raises the question of whether eigenfunction expansions are possible in all situations, or in other words, whether the eigenfunctions span the space. The question is obviously important the probability distribution is directly measurable and since quantum theory is supposed to describe what we observe in nature. This leads us to the following:

- <u>POSTULATE 6</u>: The eigenfunctions of the operator Q corresponding to any measurable quantity constitute a complete set of functions.

- <u>SUMMARY</u>: Let's now summarize what we have learned about the issue of how to predict the outcome of measurements:

  1) The expectation value of any measurable quantity q for a system in quantum state Ψ is given by $\langle q\rangle = \langle\Psi|Q|\Psi\rangle$. Remember that the expectation value represents the average of a large number of measurements carried out on identical systems.

  2) The outcome of any individual measurement of q will always be one of the eigenvalues of Q.

  3) The probability of obtaining the result q_n is found by expanding the wave function Ψ in terms of the eigenfunctions of Q. Postulate 6 asserts that this will always be possible. The result is that $P_n = |\langle\psi_n|\Psi\rangle|^2$, where ψ_n is the eigenfunction corresponding to eigenvalue q_n.

CONTINUOUS EIGENFUNCTIONS

The above formulas need to be modified somewhat when the eigenvalues of Q are continuous rather than discrete. In this case we write the eigenvalue equation in the form $Q\psi_\alpha = \alpha\psi_\alpha$, and assume that valid solutions exist for all α's within a certain range. For Hermitian operators it is still true that the eigenvalues must be real, and also that eigenfunctions with different eigenvalues are orthogonal: $\langle\psi_\alpha|\psi_{\alpha'}\rangle = 0$ if $\alpha \neq \alpha'$. The change for continuous eigenvalues is that $\langle\psi_\alpha|\psi_\alpha\rangle$ is no longer 1. Instead we want

$$\langle\psi_\alpha|\psi_{\alpha'}\rangle = \delta(\alpha - \alpha'),$$

where $\delta(x - x_0)$ is the "Dirac delta function". This function is defined as follows: $\delta(x - x_0) = 0$ for $x \neq x_0$ and $\delta(x - x_0) = \infty$ for $x = x_0$, subject to the condition $\int \delta(x - x_0)\, dx = 1$ whenever the range of integration includes x_0. One of the important properties of the delta function is

$$\int_{-\infty}^{+\infty} f(x)\, \delta(x - x_0)\, dx = f(x_0).$$

The rule for the expansion of the wave function in terms of the eigenfunctions is now

$$\Psi(x) = \int C(\alpha)\, \psi_\alpha(x)\, d\alpha,$$

where the integral extends over the full range of eigenvalues. Assuming (on the basis of Postulate 6) that the expansion exists for all physically allowable Ψ we can easily demonstrate that the expansion function C is given by

$$C(\alpha) = \langle\psi_\alpha|\Psi\rangle = \int_{-\infty}^{+\infty} \psi_\alpha^*(x)\, \Psi(x)\, dx.$$

Finally, the probability formula $P_n = |a_n|^2$ is modified as well, with $|C(\alpha)|^2\, d\alpha$ now interpreted as the probability that a measurement of q would result in a value in the interval $d\alpha$.

MOMENTUM SPACE AND COORDINATE SPACE

The results summarized above can be applied directly to measurements of the momentum. We take the momentum eigenfunctions to be

$$\psi_p(x) = \tfrac{1}{\sqrt{2\pi\hbar}}\, e^{ipx/\hbar}.$$

The normalization constant in this definition is chosen to give $\langle\psi_p|\psi_{p'}\rangle = \delta(p - p')$, a result

that follows easily from the Fourier transform theorem. Application of the above formulas with the substitution $C(\alpha) \rightarrow \Phi(p)$ then leads to the familiar relationships between the momentum space and coordinate space wave functions:

$$\Psi(x) = \int \Phi(p)\, \psi_p(x)\, dp \qquad \leftrightarrow \qquad \Phi(p) = \int \psi_p^*(x)\, \Psi(x)\, dx.$$

When we work with the momentum space wave functions, we are really just using mathematics that allows us to expand of the state vector Ψ in terms of the eigenfunctions of the momentum, with $\Phi(p) = \langle \psi_p | \Psi \rangle = \langle p | \Psi \rangle$. We should notice that the momentum space wave function carries all the information about Ψ [since we can reconstruct $\Psi(x)$ given $\Phi(p)$], and also that the main usefulness of the momentum expansion is that it gives us the momentum distribution $P(p)\, dp = |\Phi(p)|^2\, dp$. By analogy we may conclude that the coordinate space wave function, $\Psi(x)$, is really also just an expansion of the state vector, in this case in terms of the eigenfunctions of the "position operator", $\Psi(x) = \langle x | \Psi \rangle$. As with all eigenfunction expansions, the expansion function [$\Psi(x)$ in this case] carries all information, and the most readily accessible information is the position distribution $P(x)\, dx = |\Psi(x)|^2\, dx$.