

Quantum Mechanics: Postulates

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I. Physical meaning of the Wavefunction

Postulate 1: The wavefunction attempts to describe a quantum mechanical entity (photon, electron, x-ray, etc.) through its spatial location and time dependence, i.e. the wavefunction is in the most general sense dependent on time and space:

$$\Psi = \Psi(x, t)$$

The *state* of a quantum mechanical system is completely specified by the wavefunction $\Psi(x, t)$.

The Probability that a particle will be found at time t_0 in a spatial interval of width dx centered about x_0 is determined by the wavefunction as:

$$P(x_0, t_0) dx = \Psi^*(x_0, t_0)\Psi(x_0, t_0)dx = |\Psi(x_0, t_0)|^2 dx$$

Note: Unlike for a classical wave, with a well-defined amplitude (as discussed earlier), the $\Psi(x, t)$ amplitude is not ascribed a meaning.

Note: Since the postulate of the probability is defined through the use of a *complex conjugate*, Ψ^* , it is accepted that the wavefunction is a complex-valued entity.

Note: Since the wavefunction is squared to obtain the probability, the wavefunction itself can be complex and/or negative. This still leaves a probability of zero to one.

Note: Ψ^* is the complex conjugate of Ψ . For instance:

$$\begin{aligned}\Psi(x) &= A e^{i k x} \\ \Psi^*(x) &= (A^*) e^{-i k x}\end{aligned}$$

Since the probability of a particle being somewhere in space is unity, the integration of the wavefunction over all space leads to a probability of 1. That is, the wavefunction is **normalized**:

$$\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx = 1$$

In order for $\Psi(x, t)$ to represent a viable physical state, certain conditions are required:

1. The wavefunction must be a **single-valued function** of the spatial coordinates. (single probability for being in a given spatial interval)
2. The first derivative of the wavefunction must be **continuous** so that the second derivative exists in order to satisfy the Schrödinger equation.
3. The wavefunction cannot have an infinite amplitude over a finite interval. This would preclude normalization over the interval.

II. Experimental Observables Correspond to Quantum Mechanical Operators

Postulate 2: For every measurable property of the system in classical mechanics such as position, momentum, and energy, there exists a corresponding operator in quantum mechanics. An experiment in the lab to measure a value for such an observable is simulated in theory by operating on the wavefunction of the system with the corresponding operator.

Note: Quantum mechanical operators are classified as **Hermitian operators** as they are analogs of Hermitian matrices, that are defined as having only *real* eigenvalues. Also, the *eigenfunctions of Hermitian operators are orthogonal*.

Table 14.1 (Engel and Reid): list of classical observables and q.m. operator.

| Observable | Operator | Symbol of Operator |
|------------------|--|---------------------|
| Momentum | $-i\hbar \frac{\partial}{\partial x}$ | \hat{p}_x |
| Kinetic Energy | $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ | $\hat{E}_{kinetic}$ |
| Position | x | \hat{x} |
| Potential Energy | $V(x)$ | \hat{V} |
| Total Energy | $\frac{-\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$ | \hat{H} |

Note: operators act on a wavefunction from the left, and the order of operations is important (much as in the case of multiplying by matrices—commutativity is important).

III. Individual Measurements

Postulate 3: For a single measurement of an observable corresponding to a quantum mechanical operator, only values that are eigenvalues of the operator will be measured.

If measuring energy: one obtains eigenvalues of the time-independent Schrödinger equation:

$$\hat{H}\Psi_n(x, t) = E_n\Psi_n(x, t)$$

Note: The total wavefunction defining a given state of a particle need not be an eigenfunction of the operator (but one can expand the wavefunction in terms of the eigenfunctions of the operator as a complete basis).

IV. Expectation Values and Collapse of the Wavefunction

Postulate 4: The average, or expectation, value of an observable corresponding to a quantum mechanical operator is given by:

$$\langle a \rangle = \frac{\int_{-\infty}^{\infty} \Psi^*(x, t) \hat{A} \Psi(x, t) dx}{\int_{-\infty}^{\infty} \Psi^*(x, t) \Psi(x, t) dx}$$

This is a general form for the expectation value expression. If the wavefunction is normalized, then the denominator is identically 1 (this is assumed to be the case since every valid wavefunction must be normalized).

Consider the following cases:

A. The wavefunction represents an eigenfunction of the operator of interest. The expectation value of a measurable is:

$$\langle a \rangle = \int_{-\infty}^{\infty} \phi_j^*(x, t) \hat{A} \phi_j(x, t) dx = a_j \int_{-\infty}^{\infty} \phi_j^*(x, t) \phi_j(x, t) dx$$

where $\phi_j(x, t)$ is an eigenfunction of the operator \hat{A} .

B. Now consider that the wavefunction itself is not an eigenfunction of the operator \hat{A} . However, since the wavefunction belongs to the space of functions that are eigenfunctions of the operator, we can construct (expand) the wavefunction from the basis of eigenfunctions of \hat{A} . Thus:

$$\Psi(x, t) = \sum b_n \phi_n(x, t)$$

where the $\phi_n(x, t)$ are eigenfunctions of the operator \hat{A} . So let's consider the

$$\begin{aligned} \langle a \rangle &= \int_{-\infty}^{\infty} \phi_j^*(x, t) \hat{A} \phi_j(x, t) dx \\ &= \int_{-\infty}^{\infty} \left[\sum_{m=1}^{\infty} b_m^* \phi_m^*(x, t) \right] \left[\sum_{n=1}^{\infty} b_n a_n \phi_n(x, t) \right] dx \\ &= \int_{-\infty}^{\infty} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} b_m^* \phi_m^*(x, t) b_n a_n \phi_n(x, t) dx \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \int_{-\infty}^{\infty} b_m^* \phi_m^*(x, t) b_n a_n \phi_n(x, t) dx \end{aligned}$$

The only terms that survive are the $m=n$ terms (**orthogonality of eigenfunctions of Hermitian operators!**). Thus,

$$\langle a \rangle = \sum_{n=1}^{\infty} b_n^* b_n a_n$$

$$= \sum_{n=1}^{\infty} |b_n|^2 a_n$$

Note: We see that the average value of the observable is a **weighted average** of the possible eigenvalues (i.e., possible measurement outcomes). The weighting factor is the square of the expansion coefficient, b_n for the n 'th eigenfunction with eigenvalue a_n .

Thus, the expansion coefficients, b_n represent the degree to which the full wavefunction possesses the character of the eigenfunction ϕ_n . By analogy to vector space, the coefficients can be thought of as **projections** of the wavefunction on to the basis functions (i.e., the eigenfunctions of the operator).

Note: Individual measurements of a quantum mechanical system have multiple outcomes. We cannot know which of these will be observed **a priori**. We only know in a **probabilistic** way the relative opportunities to realize any particular value. Furthermore, the probabilities become meaningful in the limit of large numbers of measurements.

Note: identically prepared quantum systems can have different outcomes with regard to measure observables. (super position of states)

Note: Initial measurement of a quantum mechanical system is probabilistic. Subsequent measurements will yield the same value of the observable. This is a transition from a probabilistic to a deterministic outcome. **Collapse of the wavefunction.**

V. Time Evolution

Postulate 5: The time-dependent Schrödinger equation governs the time evolution of a quantum mechanical system:

$$\hat{H}\Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t}$$

Note: The Hamiltonian operator \hat{H} contains the kinetic and potential operators (as discussed above). This equation reflects the deterministic (Newtonian) nature of particles/waves. It appears to be in contrast to Postulate 4 (many observations lead to different measured observables, each weighted differently, i.e., a probabilistic view of the particle/wave). The reconciliation is in the fact that Postulate 4 pertains to the outcomes of measurements at

a *specific* instant in time. Postulate 5 allows us to **propagate** the wavefunction in time (we propagate a probabilistic entity). Then, at some future time, if we make another measurement, we are again faced with the implications of Postulate 4.

Note: In dealing stationary quantum mechanical states, we do not need to have an explicit knowledge of the time dependent wavefunction, particularly if the operator of interest is independent of time. Consider:

$$\hat{A}(x)\Psi_n(x, t) = a_n\Psi_n(x, t)$$

Recalling that the time dependent wavefunction can be written as the product of time-*independent* and time-*dependent* components:

$$\Psi_n(x, t) = \psi_n(x)e^{-i(E_n/\hbar)t}$$

Thus:

$$\hat{A}(x)\psi_n(x)e^{-i(E_n/\hbar)t} = e^{-i(E_n/\hbar)t}\hat{A}(x)\psi_n(x) = e^{-i(E_n/\hbar)t}a_n\psi_n(x)$$

$$\hat{A}(x)\psi_n(x) = a_n\psi_n(x)$$

Thus, for time-independent operators, the eigenvalue equations for $\psi_n(x)$ are all we need to consider.