Review of Quantum Mechanics

Postulates of quantum mechanics
The Wavefunction
Probability
Operators
Averaging

Postulates of quantum mechanics are assumptions found to be consistent with observation

The first postulate states that the state of a system can be represented by a wavefunction $\Psi(q_1, q_2,.. q_{3n}, t)$. The q_i are coordinates of the particles in the system and t is time.

The wavefunction can also be time-independent or stationary, $\psi(q_1, q_2,.. q_{3n})$.

Postulate 2. The probability of finding a particle in a region of space is given by

$$P(a) = \int_0^a \Psi^* \Psi \, d\tau$$

Postulate 2. Assumptions

1. $\Psi^*\Psi$ is real (Ψ is Hermitian).
2. The wavefunction is normalized.
3. We integrate over all relevant space.

Normalization is needed so that probabilities are meaningful.

Normalization means that the integral of the square of the wavefunction (probability density) over all space is equal to one.

$$\int_{all\ space} \Psi^* \Psi \, d\tau = 1$$

The significance of this equation is that the probability of finding the particle somewhere in the universe is one.

Normalization is needed so that probabilities are meaningful.

Normalization means that the integral of the square of the wavefunction (probability density) over all space is equal to one.

$$<\Psi|\Psi> = 1$$

The braket representation is equivalent to writing the integral over all space. The bra signifies the complex conjugate.

The wavefunctions form an orthonormal set

Orthogonal wavefunctions have zero overlap

$$\int_{all\ space} \Psi_i^* \Psi_j \, d\tau = 0$$

Normalized wavefunctions integrate to 1.

$$\int_{all\ space} \Psi_i^* \Psi_i \, d\tau = 1$$

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$$<\Psi_i|\Psi_j> = 0$$

Normalized wavefunctions integrate to 1.

$$<\Psi_i|\Psi_i> = 1$$

Postulate 3. Every physical observable is associated with a linear Hermitian operator

Observables are energy, momentum, position, dipole moment, etc.

$$operator\ \hat{P} \rightarrow observable\ P$$

The fact that the operator is Hermitian ensures that the observable will be real.

Postulate 4. The average value of a physical property can be calculated by

$$\langle \mathrm{P} \rangle = \frac{\int \Psi^* \hat{\mathrm{P}} \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

Normalization

Postulate 4. The calculation of a physical observable can be written as an eigenvalue equation

$$\hat{P}\Psi = P\Psi$$

This is an operator equation that returns the same wavefunction multiplied by the constant P. P is an eigenvalue. An eigenvalue is a number.

The form of the operators is

Position	$\hat{q}$	q
Momentum	$\hat{P}$	$i\hbar\dfrac{\partial}{\partial q}$
Time	$\hat{t}$	t
Energy	$\hat{H}$	$i\hbar\dfrac{\partial}{\partial t}$

Stationary State Wave Equation
Quantum Mechanical Description

Hamiltonian
Energy Operator

Eigenvalue
Energy value

$$\hat{H}_0 \Psi = E_0 \Psi$$

Wavefunction

The Hamiltonian and wavefunction are time-independent

The wavefunction is composed of electronic and nuclear parts

$$\Psi = \psi_{electronic}\chi_{nuclear}$$

$\uparrow$ Total

$\uparrow$ Electronic

$\uparrow$ Nuclear

The wavefunction represents the probability amplitude of electrons and nuclei.

The wave equation can be separated into electronic and nuclear parts

Hamiltonian
Energy Operator

Eigenvalue
Energy value

$$\hat{H}_{elec}\psi = E_{elec}\psi$$

$$\hat{H}_{nucl}\chi = E_{nucl}\chi$$

Wavefunctions

The Hamiltonian contains both kinetic and potential energy terms

Kinetic Energy Potential Energy

$$\hat{H}_{elec} = \hat{T}_{elec} + \hat{V}_{elec} = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial q^2} + \frac{e}{4\pi\varepsilon_0 q}$$

$$\hat{H}_{nucl} = \hat{T}_{nucl} + \hat{V}_{nucl} = -\frac{\hbar^2}{2M}\frac{\partial^2}{\partial Q^2} + \frac{1}{2}kQ^2$$