

3.9: Postulates of Quantum Mechanics

We now summarize the postulates of Quantum Mechanics that have been introduced. The application of these postulates will be illustrated in subsequent chapters.

Postulate 1

The properties of a quantum mechanical system are determined by a wavefunction $\Psi(r,t)$ that depends upon the spatial coordinates of the system and time, r and t . For a single particle system, r is the set of coordinates of that particle $r = (x_1, y_1, z_1)$. For more than one particle, r is used to represent the complete set of coordinates $r = (x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_n, y_n, z_n)$. Since the state of a system is defined by its properties, ψ specifies or identifies the state and sometimes is called the state function rather than the wavefunction.

Postulate 2

The wavefunction is interpreted as probability amplitude with the absolute square of the wavefunction, $\Psi^*(r,t)\Psi(r,t)$ interpreted at the probability density at time t . A probability density times a volume is a probability, so for one particle

$$\psi^*(x_1, y_1, z_1, t)\psi(x_1, y_1, z_1, t)dx_1dy_1dz_1 \quad (3.9.1)$$

is the probability that the particle is in the volume $dx dy dz$ located at x_l, y_l, z_l at time t .

For a many particle system, we write the volume element as $d\tau = dx_1dy_1dz_1 \dots dx_ndy_n dz_n$; and $\Psi^*(r,t)\Psi(r,t)d\tau$ is the probability that particle 1 is in the volume $dx_1dy_1dz_1$ at $x_1y_1z_1$ and particle 2 is in the volume $dx_2dy_2dz_2$ at $x_2y_2z_2$, etc.

Because of this probabilistic interpretation, the wavefunction must be *normalized*.

$$\int_{all\ space} \psi^*(r,t)\psi(r,t)d\tau = 1 \quad (3.9.2)$$

The integral sign here represents a multi-dimensional integral involving all coordinates: $x_l \dots z_n$. For example, integration in three-dimensional space will be an integration over dV , which can be expanded as:

- $dV = dx dy dz$ in Cartesian coordinates or
- $dV = r^2 \sin \phi dr d\theta d\phi$ in spherical coordinates or
- $dV = r dr d\theta dz$ in cylindrical coordinates.

Postulate 3

For every observable property of a system there is a quantum mechanical operator. The operator for position of a particle in three dimensions is just the set of coordinates x, y , and z , which is written as a vector

$$r = (x, y, z) = x\vec{i} + y\vec{j} + z\vec{k} \quad (3.9.3)$$

The operator for a component of momentum is

$$\hat{P}_x = -i\hbar \frac{\partial}{\partial x} \quad (3.9.4)$$

and the operator for kinetic energy in one dimension is

$$\hat{T}_x = -\left(\frac{\hbar^2}{2m}\right) \frac{\partial^2}{\partial x^2} \quad (3.9.5)$$

and in three dimensions

$$\hat{p} = -i\hbar \nabla \quad (3.9.6)$$

and

$$\hat{T} = -\left(\frac{\hbar^2}{2m}\right) \nabla^2 \quad (3.9.7)$$

The Hamiltonian operator \hat{H} is the operator for the total energy. In many cases only the kinetic energy of the particles and the electrostatic or Coulomb potential energy due to their charges are considered, but in general all terms that contribute to the energy appear in the Hamiltonian. These additional terms account for such things as external electric and magnetic fields and magnetic interactions due to magnetic moments of the particles and their motion.

Postulate 4

The time-independent wavefunctions of a time-independent Hamiltonian are found by solving the time-independent Schrödinger equation.

$$\hat{H}(r)\psi(r) = E\psi(r) \quad (3.9.8)$$

These wavefunctions are called stationary-state functions because the properties of a system in such a state, i.e. a system described by the function $\psi(r)$, are time independent.

Postulate 5

The time evolution or time dependence of a state is found by solving the time-dependent Schrödinger equation.

$$\hat{H}(r, t)\psi(r, t) = i\hbar \frac{\partial}{\partial t}\psi(r, t) \quad (3.9.9)$$

For the case where \hat{H} is independent of time, the time dependent part of the wavefunction is $e^{-i\omega t}$ where $\omega = \frac{E}{\hbar}$ or equivalently $\nu = \frac{E}{h}$, which shows that the energy-frequency relation used by Planck, Einstein, and Bohr results from the time-dependent Schrödinger equation. This oscillatory time dependence of the probability amplitude does not affect the probability density or the observable properties because in the calculation of these quantities, the imaginary part cancels in multiplication by the complex conjugate.

Postulate 6

If a system is described by the eigenfunction ψ of an operator \hat{A} then the value measured for the observable property corresponding to \hat{A} will always be the eigenvalue a , which can be calculated from the eigenvalue equation.

$$\hat{A}\psi = a\psi \quad (3.9.10)$$

Postulate 7

If a system is described by a wavefunction ψ , which is not an eigenfunction of an operator \hat{A} , then a distribution of measured values will be obtained, and the average value of the observable property is given by the expectation value integral,

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi d\tau}{\int \psi^* \psi d\tau} \quad (3.9.11)$$

where the integration is over all coordinates involved in the problem. The average value $\langle A \rangle$, also called the expectation value, is the average of many measurements. If the wavefunction is normalized, then the normalization integral in the denominator of Equation (3-47) equals 1.

Problems

- Exercise 3.9.21 What does it mean to say a wavefunction is normalized? Why must wavefunctions be normalized?
- **Exercise 3.9.22** Rewrite Equations(3-42) and (3-43) using the definitions of \hbar , ∇ , and ∇^2 .
- **Exercise 3.9.23** Write a definition for a stationary state. What is the time dependence of the wavefunction for a stationary state?
- **Exercise 3.9.24** Show how the energy-frequency relation used by Planck, Einstein, and Bohr results from the time-dependent Schrödinger equation.
- **Exercise 3.9.25** Show how the de Broglie relation follows from the postulates of Quantum Mechanics using the definition of the momentum operator.
- **Exercise 3.9.26** What quantity in Quantum Mechanics gives you the probability density for finding a particle at some specified position in space? How do you calculate the average position of the particle and the uncertainty in the position of the

particle from the wavefunction?

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