Chapter 25

Quantum Mechanics

States evolve where chance and law entwine,
Waves of thought replace the classical line,
Measured truths collapse from what may be,
In silence ruled by probability

25.1 Introduction

Quantum mechanics provides a fundamental description of physical systems at atomic and subatomic scales. Unlike classical physics, it does not describe nature in terms of deterministic trajectories and continuously varying quantities. Instead, it formulates physical reality in terms of states that encode probabilities of possible outcomes, governed by precise mathematical laws.

At microscopic scales, physical systems cannot always be assigned definite values of observable quantities prior to measurement. The act of measurement plays an essential role in determining outcomes, and the theory replaces certainty at the level of individual events with intrinsic probabilistic structure. This departure from classical intuition represents not a limitation of experimental technique, but a fundamental feature of nature.

Quantum mechanics also introduces concepts such as superposition and entanglement, in which systems may exist in multiple mutually exclusive states simultaneously and exhibit correlations that defy classical notions of locality and separability. Despite its conceptual difficulty, the theory has been confirmed to extraordinary precision and forms the foundation of modern physics, chemistry, and materials science. Technologies ranging from semiconductors and lasers to magnetic resonance imaging rely directly on quantum principles, while emerging fields such as quantum computation seek to exploit its most counterintuitive features.

Rather than merely extending classical physics, quantum mechanics forces a reassessment of what it means to describe physical reality. Determinism gives way to probability, objects give way to relations, and observation becomes inseparable from theoretical description.

25.2 Failure of Classical Physics

By the end of the nineteenth century, classical physics—principally Newtonian mechanics, Maxwellian electrodynamics, and classical statistical mechanics—was widely regarded as a complete description of the physical world. Within this framework, matter was composed of particles with well-defined positions and momenta, energy was continuous, and physical processes were governed by deterministic laws. However, a series of precise experiments revealed fundamental contradictions within this classical worldview.

One of the most significant failures occurred in the study of blackbody radiation. Classical theory, based on the equipartition of energy, predicted that a heated object should emit radiation with infinite energy at high frequencies, a result known as the ultraviolet catastrophe. Experimental observations instead showed a finite, well-defined spectral distribution that could not be reconciled with classical assumptions.

A second contradiction arose in the photoelectric effect. Classical wave theory predicted that the energy of emitted electrons should depend on the intensity of incident light. Experiments demonstrated instead that electron emission occurs only above a threshold frequency, and that the kinetic energy of emitted electrons depends on frequency rather than intensity. This behavior could not be explained within classical electromagnetism.

Classical physics also failed to account for atomic stability. According to classical electrodynamics, an electron orbiting a nucleus should continuously radiate energy and rapidly collapse into the nucleus. In reality, atoms are stable and exhibit discrete emission and absorption spectra, indicating the existence of quantized energy levels incompatible with classical predictions.

These discrepancies were not isolated anomalies but systematic failures arising from classical assumptions of continuity, determinism, and observer-independent properties. Resolving them required a fundamentally new theoretical framework in which energy is quantized, measurement plays a central role, and physical systems are described probabilistically. This framework became quantum mechanics.

25.3 WAVE-PARTICLE DUALITY

Quantum mechanics is founded on the dual nature of matter and radiation, a concept that fundamentally departs from classical distinctions between waves and particles. In classical physics, waves and particles are mutually exclusive categories: waves are extended, continuous phenomena characterized by interference and diffraction, while particles are localized entities following well-defined trajectories. Quantum mechanics demonstrates that this dichotomy is incomplete.

Experiments involving light revealed that electromagnetic radiation, long understood as a wave, also exhibits particle-like behavior. Phenomena such as the photoelectric effect and Compton scattering require light to be described as consisting of discrete quanta, or photons, carrying localized packets of energy and momentum. At the same time, light continues to display wave phenomena such as interference and diffraction, indicating that neither description alone is sufficient.

Conversely, material particles such as electrons, protons, and even large molecules exhibit wave-like behavior under appropriate conditions. Electron diffraction experiments show interference patterns identical in form to those produced by classical waves, despite the detection of individual electrons as localized impacts. This behavior cannot be reconciled with a purely particle-based description of matter.

Wave–particle duality does not imply that quantum objects alternately behave as waves or particles depending on circumstance. Rather, it reflects the inadequacy of classical concepts when applied to microscopic systems. Quantum entities are described by wavefunctions that encode the probability amplitudes of possible measurement outcomes. The wave-like evolution of these amplitudes gives rise to interference effects, while particle-like behavior emerges in the discrete outcomes of measurements.

The dual nature of matter and radiation is therefore not a property of the objects themselves, but of the experimental contexts in which they are observed. Wave–particle duality underscores the central role of measurement in quantum mechanics and motivates the formulation of the theory in terms of abstract states rather than classical trajectories. It serves as a foundational principle that guides the interpretation and mathematical structure of quantum theory.

25.3.1 DE BROGLIE HYPOTHESIS

In 1924, Louis de Broglie proposed a unifying principle that extended wave–particle duality to all forms of matter. Motivated by the established dual behavior of light, de Broglie suggested that particles traditionally regarded as point-like objects, such as electrons and atoms, should also exhibit wave-like properties under appropriate conditions. This hypothesis represented a radical departure from classical mechanics, in which particles are assumed to follow well-defined trajectories.

De Broglie postulated that to every particle of momentum p there corresponds a wave of wavelength

$$\boxed{\lambda = \frac{h}{p}, \quad \text{where } h \text{ is Planck's constant.}}$$

This relation directly connects a mechanical quantity, momentum, with a wave property, wavelength, thereby bridging classical and quantum descriptions.

> The de Broglie wavelength becomes appreciable when the particle momentum is sufficiently small, which explains why wave-like behavior is prominent at atomic and subatomic scales but negligible for macroscopic objects. For everyday objects, the associated wavelength is vanishingly small, rendering wave effects unobservable and restoring the validity of classical mechanics as an excellent approximation.

The de Broglie hypothesis provided a conceptual foundation for subsequent developments in quantum theory. It explained the existence of discrete atomic energy levels as standing-wave conditions for electrons bound within atoms and predicted phenomena such as electron diffraction, which was later confirmed experimentally. These confirmations established matter waves as a real physical feature rather than a mathematical abstraction.

More broadly, the de Broglie hypothesis motivated the formulation of quantum mechanics in terms of wave equations governing the evolution of quantum states. It marked a crucial step toward replacing classical trajectories with wavefunctions as the primary descriptors of microscopic systems and remains a cornerstone of the quantum-mechanical framework.

25.4 WAVE FUNCTION AND PROBABILITY INTERPRETATION

25.4.1 WAVE FUNCTION

In quantum mechanics, the complete physical state of a system is described by a complex-valued wave function $\psi(x,t)$. This function contains all experimentally accessible information about the system and evolves in time according to the Schrödinger equation. Unlike classical variables such as position or momentum, **the wave function does not represent a directly observable quantity**.

The complex nature of $\psi(x,t)$ is essential. Its phase plays a crucial role in interference and superposition phenomena, even though it cannot be measured directly. Different wave functions that differ only by a global phase factor represent the same physical state, reflecting the fact that only relative phases have physical significance.

The wave function should therefore be regarded not as a physical wave in space, but as a mathematical object that encodes the statistical structure of measurement outcomes. Attempts to interpret $\psi(x,t)$ as a classical field generally fail to account for its probabilistic role and its behavior under measurement.

25.4.2 BORN INTERPRETATION

The physical meaning of the wave function is provided by the Born interpretation, which relates $\psi(x,t)$ to observable probabilities. The probability density of finding a particle at position x at time t is given by

$$\boxed{P(x,t) = |\psi(x,t)|^2}$$

This quantity is real, non-negative, and experimentally measurable through repeated observations of identically prepared systems.

The probabilistic interpretation implies that quantum mechanics does not predict the exact outcome of an individual measurement, but rather the statistical distribution of outcomes over many trials. This represents a fundamental departure from classical determinism and reflects the intrinsic indeterminacy of quantum phenomena.

For the probabilistic interpretation to be consistent, the wave function must satisfy a normalization condition:

$$\boxed{\int_{-\infty}^{\infty} |\psi(x,t)|^2 \, dx = 1}$$

This condition ensures that the total probability of finding the particle somewhere in space is unity at all times. Preservation of normalization under time evolution imposes strong constraints on the allowed dynamics and leads naturally to the unitary time evolution characteristic of quantum mechanics.

Together, the wave function and its probabilistic interpretation form the core of quantum theory. They replace the classical notion of definite trajectories with a framework in which physical predictions are inherently statistical, yet precisely defined.

25.5 OPERATORS AND OBSERVABLES

In quantum mechanics, measurable physical quantities, referred to as observables, are represented by linear operators acting on the wave function.

This represents a fundamental departure from classical physics, where observables are treated as numerical variables. In the quantum framework, the possible outcomes of a measurement are determined by the spectral properties of the corresponding operator.

To represent physically meaningful observables, operators must satisfy specific mathematical conditions. In particular, observable operators are required to be linear and self-adjoint, ensuring that their eigenvalues, which correspond to possible measurement outcomes, are real.

25.5.1 Position and Momentum Operators

The position observable is represented by the operator

$$\boxed{\hat{x} = x}$$

which acts multiplicatively on the wave function. This reflects the direct association between position measurements and spatial coordinates. The momentum observable in one dimension is represented by the operator

$$\boxed{\hat{p} = -i\hbar \frac{d}{dx}}$$

where $\boxed{\hbar = \frac{h}{2\pi}}$ is the reduced Planck constant. This form follows naturally from the wave-like nature of quantum states and is consistent with the de Broglie relation. The position and momentum operators do not commute, satisfying the canonical commutation relation

$$\boxed{[\hat{x}, \hat{p}] = i\hbar}$$

This non-commutativity has profound physical consequences and underlies the uncertainty principle.

25.6 The Schrödinger Equation

The Schrödinger equation is the fundamental dynamical equation of non-relativistic quantum mechanics. It determines how the quantum state of a system evolves in time. Unlike classical mechanics which describes definite particle trajectories quantum mechanics describes the evolution of a wave function whose squared modulus gives probabilistic information about measurement outcomes

25.6.1 Motivation from Classical Mechanics

In classical mechanics the dynamics of a particle moving in one dimension under a potential $V(x)$ are described by the Hamiltonian

$$H(x, p) = \frac{p^2}{2m} + V(x)$$

Here x is the position coordinate p is the canonical momentum conjugate to x m is the particle mass and $V(x)$ is the potential energy

The Hamiltonian formulation is obtained from the Lagrangian

$$L(x, \dot{x}) = \frac{1}{2}m\dot{x}^2 - V(x)$$

The canonical momentum is defined by

$$p = \frac{\partial L}{\partial \dot{x}}$$

Substituting the Lagrangian gives

$$p = \frac{\partial}{\partial \dot{x}}\left(\frac{1}{2}m\dot{x}^2\right)$$

Evaluating the derivative we obtain

$$p = m\dot{x}$$

Thus for this system the canonical momentum coincides with the mechanical momentum

In more general situations such as in the presence of electromagnetic fields canonical momentum differs from mechanical momentum Nevertheless it is the canonical momentum that plays the fundamental role in Hamiltonian mechanics generating spatial translations and together with position forming the natural phase space variables This structure carries over directly to quantum mechanics

25.6.2 PLANE WAVES AND OPERATOR SUBSTITUTIONS

Experimental evidence shows that particles exhibit wave-like behavior For a free particle de Broglie associated a plane wave

$$\psi(x,t) = Ae^{\boldsymbol{i}(kx-\omega t)}$$

with momentum and energy given by

$$p = \hbar k$$

$$E = \hbar\omega$$

We now examine how derivatives act on this wave function. The time derivative is

$$\frac{\partial\psi}{\partial t} = -\boldsymbol{i}\,\omega\psi$$

Multiplying both sides by $i\hbar$ yields

$$\boldsymbol{i}\,\hbar\frac{\partial\psi}{\partial t} = \hbar\omega\psi$$

which gives

$$\boldsymbol{i}\,\hbar\frac{\partial\psi}{\partial t} = E\psi$$

Next consider spatial derivatives

$$\frac{\partial\psi}{\partial x} = ik\psi$$

and

$$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi$$

Multiplying by $-\hbar^2$ we obtain

$$-\hbar^2\frac{\partial^2\psi}{\partial x^2} = \hbar^2k^2\psi$$

which implies

$$-\hbar^2\frac{\partial^2\psi}{\partial x^2} = p^2\psi$$

These relations motivate the operator substitutions

$$E \to i\hbar\frac{\partial}{\partial t}$$

$$p \to -i\hbar\frac{\partial}{\partial x}$$

25.6.3 TIME-DEPENDENT SCHRÖDINGER EQUATION

We now return to the classical Hamiltonian

$$H = \frac{p^2}{2m} + V(x)$$

Replacing energy and momentum by their corresponding operators and allowing them to act on the wave function gives

$$i\hbar\frac{\partial\psi}{\partial t} = \left[\frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 + V(x)\right]\psi$$

Evaluating the square yields

$$\left(-i\hbar\frac{\partial}{\partial x}\right)^2 = -\hbar^2\frac{\partial^2}{\partial x^2}$$

Substituting this result gives

$$\boxed{i\hbar\frac{\partial\psi(x,t)}{\partial t} = \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)\right)\psi(x,t)}$$

This is the time-dependent Schrödinger equation

25.6.4 STATIONARY STATES

If the potential $V(x)$ is time independent solutions may be separated as

$$\psi(x,t) = \phi(x)T(t)$$

Substituting into the Schrödinger equation and dividing by ϕT gives

$$i\hbar\frac{1}{T}\frac{dT}{dt} = -\frac{\hbar^2}{2m}\frac{1}{\phi}\frac{d^2\phi}{dx^2} + V(x)$$

Since the left-hand side depends only on time and the right-hand side only on position both must be equal to a constant denoted E

The time equation becomes

$$i\hbar\frac{dT}{dt} = ET$$

with solution

$$T(t) = e^{-iEt/\hbar}$$

The spatial equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\phi}{dx^2} + V(x)\phi = E\phi$$

This is the time-independent Schrödinger equation

25.7 QUANTIZATION AND ENERGY EIGENVALUES

Quantization in quantum mechanics arises from the mathematical and physical constraints imposed on admissible wave functions. The quantum state is described by a complex-valued wave function $\psi(x,t)$ whose squared magnitude represents a probability density. For this interpretation to be valid the wave function must satisfy the following conditions

- It must be finite everywhere
- It must be single-valued
- It must be normalizable

The normalization condition is expressed as

$$\int |\psi(x,t)|^2 \, dx < \infty$$

When these conditions are applied to systems subject to confining potentials they restrict the allowable solutions of the Schrödinger equation. As a consequence only a discrete set of energy values is permitted for bound systems This discreteness is the origin of energy quantization

25.7.1 ENERGY EIGENSTATES

For a time-independent potential $V(x)$ the Schrödinger equation admits separable solutions of the form

$$\psi(x,t) = \phi(x)T(t)$$

Substitution into the time-dependent Schrödinger equation yields the time-independent Schrödinger equation

$$\hat{H}\phi(x) = E\phi(x)$$

where the Hamiltonian operator is given by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)$$

This equation constitutes an eigenvalue problem for the operator $\hat{H}$ The functions $\phi_n(x)$ that satisfy the required boundary and normalization conditions are eigenfunctions of the Hamiltonian and the corresponding eigenvalues E_n represent the allowed energies of the system

The full time-dependent solution associated with an energy eigenstate is

$$\psi_n(x,t) = \phi_n(x)e^{-iE_n t/\hbar}$$

An energy eigenstate has the following properties

- The probability density $|\psi_n(x,t)|^2$ is time independent
- An energy measurement yields E_n with certainty
- Time evolution consists only of a global phase factor

The set of energy eigenfunctions forms a complete orthonormal basis allowing any physical state to be expressed as a superposition of energy eigenstates

25.7.2 Discrete and Continuous Spectra

The structure of the energy spectrum depends on whether the system is bound or unbound

For bound systems the potential confines the particle to a finite region of space Normalizability then restricts the energy eigenvalues to a discrete set

$$E = E_1 \quad E_2 \quad E_3 \quad \dots$$

Such systems exhibit stationary states and well-defined energy levels Transitions between these levels are accompanied by the absorption or emission of energy

In atomic systems these transitions produce radiation at specific frequencies resulting in sharp spectral lines

For unbound systems the particle is not spatially confined The corresponding energy eigenfunctions are not square integrable in the usual sense and the energy spectrum is continuous

Examples include free particles and scattering states In these cases energy measurements yield values from a continuous range rather than a discrete set

The distinction between discrete and continuous spectra reflects the fundamental role of confinement and normalizability in quantum mechanics