Chapter 1: Quantum Formalism and the Schrödinger Equation

Axioms, derivations, and examples

Abstract

We present the foundational postulates of non-relativistic quantum mechanics in Hilbert space language, develop the operator formalism, and derive the time-dependent and time-independent Schrödinger equations. Conservation laws, unitarity, and explicit one-dimensional examples are included, along with proofs of key theorems such as Ehrenfest's theorem.

Contents

1 Postulates of Quantum Mechanics

1.1 Postulate I: State space

The state of a system is represented by a unit vector $|\psi\rangle$ in a complex Hilbert space $\mathcal{H}$. In position representation,

$$\psi(\mathbf{r},t) = \langle \mathbf{r}|\psi(t)\rangle, \quad \int_{\mathbb{R}^3} |\psi(\mathbf{r},t)|^2 \, d^3r = 1.$$

1.2 Postulate II: Observables

Every observable quantity A is represented by a self-adjoint (Hermitian) linear operator $\hat{A}$ on $\mathcal{H}$. Measurement outcomes are eigenvalues of $\hat{A}$.

1.3 Postulate III: Measurement outcomes

If $\hat{A}\,|a\rangle = a\,|a\rangle$ with $\{|a\rangle\}$ an orthonormal eigenbasis, then measurement of A yields a with probability

$$P(a) = |\langle a|\psi\rangle|^2.$$

Post-measurement state collapses to $|a\rangle$.

1.4 Postulate IV: Time evolution

The time evolution of a closed system is governed by a unitary operator $U(t,t_0)$:

$$|\psi(t)\rangle = U(t,t_0)\,|\psi(t_0)\rangle\,, \quad U^\dagger U = I.$$

For infinitesimal evolution, there exists a Hermitian operator $\hat{H}$ (Hamiltonian) such that

$$\mathrm{i}\hbar \frac{d}{dt}\,|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle\,.$$

2 Derivation of the Schrödinger Equation

2.1 From the postulates

From Postulate IV and unitarity, Stone's theorem ensures the generator of continuous time translations is Hermitian: $\hat{H}$. In position representation:

$$\mathrm{i}\hbar \frac{\partial}{\partial t}\psi(\mathbf{r},t) = \langle \mathbf{r}|\hat{H}|\psi(t)\rangle.$$

For a single particle with kinetic plus potential energy:

$$\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x},t), \quad \hat{p} = -\mathrm{i}\hbar\nabla.$$

Thus, the *time-dependent Schrödinger equation* (TDSE) is

$$\mathrm{i}\hbar \frac{\partial \psi(\mathbf{r},t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r},t)\right]\psi(\mathbf{r},t). \tag{1}$$

2.2 Properties

- Linearity: superpositions remain solutions.
- Norm conservation: $\frac{d}{dt}\langle\psi|\psi\rangle = 0$.
- Probability continuity equation:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot\mathbf{j} = 0, \quad \rho = |\psi|^2, \quad \mathbf{j} = \frac{\hbar}{2mi}(\psi^*\nabla\psi - \psi\nabla\psi^*).$$

3 Stationary States and TISE

3.1 Separation of variables

If $V(\mathbf{r},t) = V(\mathbf{r})$ is time-independent, we try

$$\psi(\mathbf{r},t) = \phi(\mathbf{r})T(t).$$

Substitution into TDSE and separation yields:

$$\frac{1}{T}\frac{dT}{dt} = -\frac{\mathrm{i}E}{\hbar}, \quad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\phi(\mathbf{r}) = E\phi(\mathbf{r}).$$

The latter is the *time-independent Schrödinger equation* (TISE).

3.2 Eigenfunction expansion

The set $\{\phi_n\}$ solving TISE form an orthonormal basis; general solutions are

$$\psi(\mathbf{r},t) = \sum_n c_n\phi_n(\mathbf{r})e^{-\mathrm{i}E_nt/\hbar}.$$

4 Operator Formalism and Commutators

4.1 Canonical commutation relations

For position and momentum operators:

$$[\hat{x}_i, \hat{p}_j] = \mathrm{i}\hbar\delta_{ij}.$$

These imply the Heisenberg uncertainty relation:

$$\Delta x_i\,\Delta p_i \geq \frac{\hbar}{2}.$$

4.2 Ehrenfest theorem

For any $\hat{A}$ without explicit t-dependence:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{A}\rangle = \frac{1}{\mathrm{i}\hbar}\langle[\hat{A},\hat{H}]\rangle.$$

For $\hat{x}$ and $\hat{p}$, this yields:

$$m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle\hat{x}\rangle = -\langle\nabla V(\hat{x})\rangle.$$

5 Examples

5.1 Free particle

$V = 0$, TISE: $-\frac{\hbar^2}{2m}\nabla^2\phi = E\phi$, solutions are plane waves $\phi_{\mathbf{k}} \propto e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}}$ with $E = \frac{\hbar^2 k^2}{2m}$.

5.2 Infinite square well

$V(x) = 0$ for $0 < x < L$, $V = \infty$ otherwise. Solutions:

$$\phi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), \quad E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}.$$

5.3 Harmonic oscillator: full derivation

Hamiltonian: $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2$. Define ladder operators:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} + \frac{\mathrm{i}\hat{p}}{m\omega}\right), \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}}\left(\hat{x} - \frac{\mathrm{i}\hat{p}}{m\omega}\right),$$

with $[a, a^\dagger] = 1$. Then:

$$\hat{H} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right).$$

Eigenvalues: $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$, $n = 0, 1, 2, \ldots$.

Ground state solves $a\left|0\right\rangle = 0$, giving:

$$\phi_0(x) = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega x^2/2\hbar}.$$

Excited states: $\phi_n(x) \propto H_n(\xi)e^{-\xi^2/2}$, $\xi = \sqrt{\frac{m\omega}{\hbar}}x$.

6 Exercises

Exercise 6.1. *Derive the continuity equation from the TDSE for a real potential $V(\mathbf{r})$.*

Exercise 6.2. *Normalize the n-th harmonic oscillator eigenfunction and compute $\langle x^2\rangle$.*

Exercise 6.3. *For the infinite square well, compute the time-dependent probability density for a superposition of the first two eigenstates.*

References

- L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory.*
- J. J. Sakurai and J. Napolitano, *Modern Quantum Mechanics.*
- R. Shankar, *Principles of Quantum Mechanics.*