# Lecture Notes on Quantum Mechanics

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# Contents

# 1　Schrödinger Equation

The Schrödinger equation is fundamental to quantum mechanics, describing the time evolution of a quantum state. It exists in two forms: time-dependent and time-independent.

## 1.1　Time-Dependent Schrödinger Equation

The time-dependent Schrödinger equation is given by:

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \hat{H}\Psi(\mathbf{r},t),\tag{1}$$

where:

- $\hbar$ is the reduced Planck's constant.

- $\Psi(\mathbf{r},t)$ is the time-dependent wavefunction, representing the probability amplitude.

- $\hat{H}$ is the Hamiltonian operator, representing the total energy of the system.

The Hamiltonian operator is given by:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\mathbf{r},t),\tag{2}$$

where:

- $m$ is the mass of the particle.

- $\nabla^2$ is the Laplacian operator, representing the spatial second derivatives.

- $\hat{V}(\mathbf{r},t)$ is the potential energy function.

## 1.2　Time-Independent Schrödinger Equation

For stationary states, the wavefunction $\Psi(\mathbf{r},t)$ can be separated as:

$$\Psi(\mathbf{r},t) = \psi(\mathbf{r})e^{-iEt/\hbar},\tag{3}$$

where $\psi(\mathbf{r})$ is the time-independent wavefunction and $E$ is the energy eigenvalue.

The time-independent Schrödinger equation is:

$$\hat{H}\psi(\mathbf{r}) = E\psi(\mathbf{r}),\tag{4}$$

with the Hamiltonian operator:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \hat{V}(\mathbf{r}).\tag{5}$$

# 2    One-Dimensional Potentials

## 2.1    Quantum Tunneling

Quantum tunneling refers to a particle crossing a potential barrier even when its classical energy is insufficient. The one-dimensional Schrödinger equation governing this behavior is:

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \big[E - V(x)\big]\psi(x) = 0. \tag{6}$$

For a rectangular potential barrier of height $V_0$ and width $a$, the transmission probability $T$ is given by:

$$T = \frac{1}{1 + \frac{V_0^2}{4E(V_0-E)}\sinh^2\left(\frac{\sqrt{2m(V_0-E)}}{\hbar}a\right)}, \quad (E < V_0). \tag{7}$$

For $V_0 \gg E$, an approximate expression is:

$$T \approx e^{-2\kappa a}, \quad \text{where } \kappa = \frac{\sqrt{2m(V_0 - E)}}{\hbar}. \tag{8}$$

## 2.2    Quantum Reflection

Quantum reflection occurs when a particle reflects off a potential gradient, even when its energy exceeds the potential $(E - V(x))$. The Schrödinger equation remains:

$$\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + \big[E - V(x)\big]\psi(x) = 0. \tag{9}$$

For a particle incident on a potential step, the reflection coefficient $R$ is:

$$R = \left|\frac{k_1 - k_2}{k_1 + k_2}\right|^2, \tag{10}$$

where:

- $k_1 = \sqrt{2mE}/\hbar$ is the wavevector in the region where $V(x) = 0$.

- $k_2 = \sqrt{2m(E - V_0)}/\hbar$ is the wavevector where $V(x) = V_0$.

If $E < V_0$, total reflection occurs.

## 2.3    Periodic Potentials and Energy Bands

In a periodic potential $V(x)$, the potential satisfies $V(x + a) = V(x)$, where $a$ is the periodicity. Bloch's theorem states that solutions take the form:

$$\psi_k(x) = e^{ikx}u_k(x), \tag{11}$$

where:

- $u_k(x)$ is a periodic function with the same periodicity as $V(x)$.

- $k$ is the wavevector related to momentum.

The energy spectrum forms energy bands, separated by forbidden gaps. For a simple sinusoidal potential $V(x) = V_0 \cos(2\pi x/a)$, the band structure can be approximated using the Kronig-Penney model, leading to the dispersion relation:

$$\cos(ka) = \cos(qa) + \frac{mV_0 a}{\hbar^2 q} \sin(qa), \tag{12}$$

where $q = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$.

# 3 Operators and Commutation Rule

## 3.1 Position Operator

The position operator $\hat{x}$ represents the position of a particle. When acting on a wave-function $\psi(x)$, it is defined as:

$$\hat{x}\psi(x) = x\psi(x), \tag{13}$$

where $x$ is the position variable.

## 3.2 Momentum Operator

The momentum operator $\hat{p}$ is expressed in terms of the spatial derivative. In the position representation, it takes the form:

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}, \tag{14}$$

where $\hbar$ is the reduced Planck's constant, and $i$ is the imaginary unit.

## 3.3 Commutation Rule

The position and momentum operators satisfy the fundamental commutation relation. The commutator $[\hat{x}, \hat{p}]$ is defined as:

$$[\hat{x}, \hat{p}] = \hat{x}\hat{p} - \hat{p}\hat{x}. \tag{15}$$

Substituting the definitions of $\hat{x}$ and $\hat{p}$, we obtain:

$$[\hat{x}, \hat{p}]\psi(x) = \hat{x}\left(-i\hbar\frac{\partial\psi(x)}{\partial x}\right) - \left(-i\hbar\frac{\partial}{\partial x}\right)(x\psi(x)) \tag{16}$$

$$= -i\hbar x\frac{\partial\psi(x)}{\partial x} + i\hbar\left(\psi(x) + x\frac{\partial\psi(x)}{\partial x}\right) \tag{17}$$

$$= i\hbar\psi(x). \tag{18}$$

Thus, the commutation relation is:

$$[\hat{x}, \hat{p}] = i\hbar. \tag{19}$$

# 4 Heisenberg Uncertainty Principle

## 4.1 Heisenberg Uncertainty Principle

The Heisenberg uncertainty principle states that certain pairs of observables cannot be simultaneously measured with arbitrary precision. For position $x$ and momentum $p$, we have:

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \tag{20}$$

where:

- $\Delta x$ is the uncertainty in position.

- $\Delta p$ is the uncertainty in momentum.

- $\hbar$ is the reduced Planck's constant, $\hbar = \frac{h}{2\pi}$.

## 4.2 Derivation from the Commutation Relation

The uncertainty principle can be derived from the commutation relation between the position operator $\hat{x}$ and the momentum operator $\hat{p}$:

$$[\hat{x}, \hat{p}] = i\hbar. \tag{21}$$

For any two operators $\hat{A}$ and $\hat{B}$, the general uncertainty relation is:

$$\Delta A \Delta B \geq \frac{1}{2} \left| \left\langle [\hat{A}, \hat{B}] \right\rangle \right|. \tag{22}$$

Setting $\hat{A} = \hat{x}$ and $\hat{B} = \hat{p}$, we obtain:

$$\Delta x \Delta p \geq \frac{1}{2} |\langle i\hbar \rangle| = \frac{\hbar}{2}. \tag{23}$$

# 5 Harmonic Oscillator and Ladder Operators

## 5.1 Harmonic Oscillator

The quantum harmonic oscillator is a cornerstone of quantum mechanics, describing a particle subjected to a restoring force proportional to its displacement. The Hamiltonian for a one-dimensional harmonic oscillator is given by:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2} m \omega^2 \hat{x}^2, \tag{24}$$

where:

- $\hat{p}$ is the momentum operator.

- $\hat{x}$ is the position operator.

- $m$ is the mass of the particle.

- $\omega$ is the angular frequency of the oscillator.

The energy eigenvalues and eigenfunctions are derived from the Schrödinger equation:

$$\hat{H} \psi_n(x) = E_n \psi_n(x), \tag{25}$$

with solutions:

$$E_n = \hbar \omega \left( n + \frac{1}{2} \right), \quad n = 0, 1, 2, \ldots \tag{26}$$

$$\psi_n(x) = \sqrt{\frac{1}{2^n n!}} \left( \frac{m\omega}{\pi \hbar} \right)^{1/4} e^{-\frac{m\omega x^2}{2\hbar}} H_n \left( \sqrt{\frac{m\omega}{\hbar}} x \right), \tag{27}$$

where $H_n(x)$ are the Hermite polynomials.

## 5.2 Ladder Operators

Ladder operators $\hat{a}$ (annihilation operator) and $\hat{a}^\dagger$ (creation operator) simplify the analysis of the harmonic oscillator. They are defined as:

$$\hat{a} = \sqrt{\frac{m\omega}{2\hbar}} \left( \hat{x} + \frac{i}{m\omega} \hat{p} \right), \tag{28}$$

$$\hat{a}^\dagger = \sqrt{\frac{m\omega}{2\hbar}} \left( \hat{x} - \frac{i}{m\omega} \hat{p} \right). \tag{29}$$

These operators satisfy the commutation relation:

$$[\hat{a}, \hat{a}^\dagger] = 1. \tag{30}$$

The Hamiltonian can be expressed in terms of these operators as:

$$\hat{H} = \hbar \omega \left( \hat{a}^\dagger \hat{a} + \frac{1}{2} \right), \tag{31}$$

where $\hat{a}^\dagger \hat{a}$ is the number operator.

## 5.3   Action of Ladder Operators

The ladder operators act on the eigenstates $|n\rangle$ as:

$$\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle, \tag{32}$$

$$\hat{a}^{\dagger}\,|n\rangle = \sqrt{n+1}\,|n+1\rangle, \tag{33}$$

where $|n\rangle$ represents the $n$-th quantum state.

# 6 Heisenberg Equation

## 6.1 Heisenberg Equation of Motion

The Heisenberg equation describes the time evolution of operators in the Heisenberg picture of quantum mechanics. It provides an alternative perspective to the time-dependent Schrödinger picture. The general form of the Heisenberg equation of motion is given by:

$$\frac{d\hat{A}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t}, \tag{34}$$

where:

- $\hat{A}$ is an operator in the Heisenberg picture.

- $\hat{H}$ is the Hamiltonian operator of the system.

- $[\hat{H}, \hat{A}]$ denotes the commutator of $\hat{H}$ and $\hat{A}$.

- $\frac{\partial \hat{A}}{\partial t}$ represents the explicit time dependence of $\hat{A}$, if any.

## 6.2 Derivation

The Heisenberg equation can be derived from the Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\left|\psi(t)\right\rangle = \hat{H}\left|\psi(t)\right\rangle. \tag{35}$$

In the Heisenberg picture, the time dependence is transferred from the state $|\psi\rangle$ to the operators $\hat{A}_H$:

$$\hat{A}_H(t) = e^{i\hat{H}t/\hbar}\hat{A}_S e^{-i\hat{H}t/\hbar}, \tag{36}$$

where $\hat{A}_S$ is the corresponding operator in the Schrödinger picture. Differentiating $\hat{A}_H(t)$ with respect to time leads to the Heisenberg equation.

## 6.3 Example: Position and Momentum Operators

For the position operator $\hat{x}$ and momentum operator $\hat{p}$, the Heisenberg equation yields:

$$\frac{d\hat{x}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{x}] = \frac{\hat{p}}{m}, \tag{37}$$

$$\frac{d\hat{p}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{p}] = -\frac{\partial V(\hat{x})}{\partial \hat{x}}, \tag{38}$$

where $V(\hat{x})$ is the potential energy.

# 7 Central Potentials

## 7.1 Schrödinger Equation for Central Potentials

A central potential depends only on the radial distance $r$, i.e., $V(\vec{r}) = V(r)$. For a particle of mass $m$ moving under a central potential $V(r)$, the time-independent Schrödinger equation is:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) \right] \Psi(r) = E\Psi(r). \tag{39}$$

In spherical coordinates $(r, \theta, \phi)$, the Laplacian operator is:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left( \sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2}{\partial \phi^2}. \tag{40}$$

## 7.2 Separation of Variables

For central potentials $V(r)$, the Schrödinger equation separates into radial and angular components:

$$\Psi_{n,l,m}(r, \theta, \phi) = R_{n,l}(r) Y_{l,m}(\theta, \phi), \tag{41}$$

where:

- $n$ is the principal quantum number.

- $\ell$ is the angular momentum quantum number.

- $m$ is the magnetic quantum number.

The angular part $Y_{l,m}(\theta, \phi)$, known as the spherical harmonics, satisfies:

$$\nabla^2_{\text{angular}} Y_{l,m}(\theta, \phi) = -\ell(\ell+1) Y_{l,m}(\theta, \phi). \tag{42}$$

The radial part $R(r)$ satisfies:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + V_{\text{eff}}(r) \right] u(r) = Eu(r), \tag{43}$$

where $V_{\text{eff}}(r) = V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}$ is the effective potential, and $u(r) = rR(r)$ is the reduced radial wavefunction.

# 8 Angular Momentum

## 8.1 Orbital Angular Momentum

In quantum mechanics, the orbital angular momentum operator is defined as:

$$\hat{L} = \hat{L}_x \hat{i} + \hat{L}_y \hat{j} + \hat{L}_z \hat{k}, \tag{44}$$

where the components are given by:

$$\hat{L}_x = -i\hbar \left( y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right), \tag{45}$$

$$\hat{L}_y = -i\hbar \left( z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z} \right), \tag{46}$$

$$\hat{L}_z = -i\hbar \left( x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x} \right). \tag{47}$$

## 8.2 Spin Angular Momentum

Spin angular momentum is an intrinsic property of particles, represented by the spin operator $\hat{S}$:

$$\hat{S}^2 \left| s, m_s \right\rangle = \hbar^2 s(s+1) \left| s, m_s \right\rangle, \tag{48}$$

where $s$ is the spin quantum number and $m_s$ is the spin projection.

For spin-$\frac{1}{2}$ particles, the spin operators are represented using the Pauli matrices:

$$\hat{S}_i = \frac{\hbar}{2}\sigma_i, \quad i = x, y, z, \tag{49}$$

where $\sigma_i$ are the Pauli matrices. They are given by:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{50}$$

## 8.3 Total Angular Momentum

The total angular momentum operator is defined as:

$$\hat{J} = \hat{L} + \hat{S}. \tag{51}$$

The total angular momentum satisfies the commutation relations:

$$[\hat{J}_i, \hat{J}_j] = i\hbar \epsilon_{ijk} \hat{J}_k, \tag{52}$$

$$\hat{J}^2 \left| j, m \right\rangle = \hbar^2 j(j+1) \left| j, m \right\rangle, \tag{53}$$

$$\hat{J}_z \left| j, m \right\rangle = \hbar m \left| j, m \right\rangle. \tag{54}$$

The allowed values of total angular momentum $j$ result from adding orbital and spin angular momentum:

$$j = |\ell - s|, \ldots, (\ell + s). \tag{55}$$

Clebsch-Gordan coefficients describe the expansion of total angular momentum states in terms of individual angular momentum states.

# 9  Time-Independent Perturbation Theory

Perturbation theory is a powerful method used to find approximate solutions to the Schrödinger equation when the Hamiltonian can be written as:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}', \tag{56}$$

where $\hat{H}_0$ is the unperturbed Hamiltonian, and $\lambda \hat{H}'$ represents a small perturbation.

## 9.1  First-Order Perturbation Theory

The first-order energy correction is given by:

$$E_n^{(1)} = \left\langle n^{(0)} \middle| \hat{H}' \middle| n^{(0)} \right\rangle. \tag{57}$$

The first-order correction to the wavefunction is:

$$\left| n^{(1)} \right\rangle = \sum_{m \neq n} \frac{\left\langle m^{(0)} \middle| \hat{H}' \middle| n^{(0)} \right\rangle}{E_n^{(0)} - E_m^{(0)}} \left| m^{(0)} \right\rangle. \tag{58}$$

## 9.2  Second-Order Perturbation Theory

The second-order energy correction is given by:

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\left\langle m^{(0)} \middle| \hat{H}' \middle| n^{(0)} \right\rangle|^2}{E_n^{(0)} - E_m^{(0)}}. \tag{59}$$

The second-order correction to the wavefunction is:

$$\left| n^{(2)} \right\rangle = \sum_{m \neq n} \sum_{k \neq n} \frac{\left\langle m^{(0)} \middle| \hat{H}' \middle| k^{(0)} \right\rangle \left\langle k^{(0)} \middle| \hat{H}' \middle| n^{(0)} \right\rangle}{(E_n^{(0)} - E_m^{(0)})(E_n^{(0)} - E_k^{(0)})} \left| m^{(0)} \right\rangle. \tag{60}$$

# 10 Energy Structure of the Hydrogen Atom

The total Hamiltonian of the hydrogen atom consists of three main contributions:

$$H = H_{\text{Coulomb}} + H_{\text{Fine}} + H_{\text{Hyperfine}}. \tag{61}$$

## 10.1 Coulomb Potential

The dominant term in the hydrogen atom Hamiltonian is the Coulomb interaction between the electron and the proton:

$$H_{\text{Coulomb}} = \frac{\mathbf{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r}, \tag{62}$$

where:

- $\mathbf{p} = -i\hbar\nabla$ is the momentum operator,

- $m$ is the reduced mass of the system,

- $r$ is the radial distance between the electron and proton.

Solving the Schrödinger equation for this Hamiltonian gives the well-known hydrogen energy levels:

$$E_n = -\frac{13.6 \text{ eV}}{n^2}, \quad n = 1, 2, 3, \ldots. \tag{63}$$

## 10.2 Fine Structure Corrections

The fine structure corrections include relativistic correction, spin-orbit coupling, and the Darwin term:

### Relativistic Correction to Kinetic Energy

A relativistic expansion of the kinetic energy gives a correction term:

$$H_{\text{rel}} = -\frac{\mathbf{p}^4}{8m^3c^2}. \tag{64}$$

Applying first-order perturbation theory, this leads to an energy correction:

$$\Delta E_{\text{rel}} = -\frac{E_n^2}{2mc^2}\left(\frac{4n}{l+1/2} - 3\right). \tag{65}$$

### Spin-Orbit Coupling

The spin-orbit interaction comes from the coupling between the electron's spin and the effective magnetic field due to orbital motion:

$$H_{\text{SO}} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV}{dr}\mathbf{L} \cdot \mathbf{S}. \tag{66}$$

For the Coulomb potential $V(r) = -e^2/4\pi\epsilon_0 r$, this results in the energy correction:

$$\Delta E_{\text{SO}} = \frac{\alpha^2}{2n^3} \left( \frac{j(j+1) - l(l+1) - \frac{3}{4}}{l(l+1/2)(l+1)} \right) E_n, \tag{67}$$

where $\alpha$ is the fine-structure constant and $j$ is the total angular momentum quantum number.

## Darwin Term

For $s$-orbitals ($l = 0$), there is an additional quantum fluctuation correction called the Darwin term:

$$H_{\text{D}} = \frac{\hbar^2}{8m^2c^2} \nabla^2 V. \tag{68}$$

For a Coulomb potential, this results in:

$$\Delta E_{\text{D}} = \frac{\alpha^4}{4n^3} E_n \delta_{l,0}. \tag{69}$$

## Total Fine Structure Correction

Combining all terms, the total fine structure correction is:

$$H_{\text{Fine}} = H_{\text{rel}} + H_{\text{SO}} + H_{\text{D}}. \tag{70}$$

## 10.3 Hyperfine Structure

The hyperfine structure arises due to the interaction between the electron's magnetic moment and the proton's nuclear spin.

## Magnetic Dipole Interaction

The dominant hyperfine interaction comes from the dipole-dipole interaction between the electron and proton magnetic moments:

$$H_{\text{Hyperfine}} = \frac{8}{3} \frac{\mu_0}{4\pi} \frac{g_e g_p \mu_B \mu_N}{r^3} \mathbf{S}_e \cdot \mathbf{S}_p. \tag{71}$$

where $\mathbf{S}_e$ and $\mathbf{S}_p$ are the electron and proton spin operators.

The energy shift due to hyperfine interaction is:

$$\Delta E_{\text{Hyperfine}} = \frac{8}{3} \alpha^4 \left( \frac{m_e}{m_p} \right) \frac{E_1}{n^3} \left( \mathbf{S}_e \cdot \mathbf{S}_p \right). \tag{72}$$

For the ground state ($n = 1$), this hyperfine splitting gives rise to the famous 21 cm line observed in astrophysics.

# References

1. Schwabl, F. (2007). *Quantum Mechanics.* Springer Science & Business Media.

2. Zettili, N. (2009). *Quantum Mechanics: Concepts and Applications.*