Complete Quantum Mechanics

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Contents

1 Part I: Theory

1.1 Core ideas

Quantum mechanics is built upon a set of postulates that replace the deterministic trajectories of classical mechanics with a probabilistic framework based on Hilbert space.

Postulates of Quantum Mechanics

1. **The State Vector:** The state of a physical system is completely described by a vector $|\psi(t)\rangle$ in a complex Hilbert space.
2. **Observables and Operators:** Every physical observable (e.g., position, momentum, energy) corresponds to a **Hermitian operator** acting on this Hilbert space.
3. **Measurement (Born's Rule):** If an observable A is measured, the outcome must be one of the eigenvalues a_n of the corresponding operator $\hat{A}$. The probability of obtaining a_n is $P(a_n) = |\langle a_n|\psi\rangle|^2$.
4. **State Collapse:** Immediately after a measurement of A that yields a_n, the state of the system "collapses" to the corresponding eigenvector $|a_n\rangle$.
5. **Time Evolution:** Between measurements, the state evolves according to the **Time-Dependent Schrodinger Equation**:

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

where $\hat{H}$ is the Hamiltonian (total energy) operator.

Superposition Principle Because the Schrodinger equation is linear, any linear combination of valid states is also a valid state: $|\psi\rangle = c_1|\psi_1\rangle + c_2|\psi_2\rangle$. This leads to **interference** effects, where amplitudes (not probabilities) add.

Unitary Evolution For a time-independent Hamiltonian, the evolution operator is $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$. Since $\hat{H}$ is Hermitian, $\hat{U}$ is **unitary** ($\hat{U}^\dagger\hat{U} = \hat{I}$), which ensures that the total probability $\langle\psi|\psi\rangle = 1$ is conserved over time.

1.2 Mathematical spine

$$i\hbar\frac{d}{dt}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \qquad \text{(Schrodinger Equation)}$$

$$\hat{A}|a_n\rangle = a_n|a_n\rangle, \quad P(a_n) = |\langle a_n|\psi\rangle|^2 \qquad \text{(Eigenvalues and Probabilities)}$$

$$\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle \qquad \text{(Expectation Value)}$$

Example: The Qubit The simplest quantum system is a two-level system (qubit). A general state is $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$ with $|\alpha|^2 + |\beta|^2 = 1$. Measuring in the $\{|0\rangle, |1\rangle\}$ basis yields 0 with probability $|\alpha|^2$.

Section summary Quantum mechanics describes systems using state vectors in Hilbert space, with Hermitian operators representing observables and unitary operators representing time evolution.

2 The Wave Function

2.1 Core ideas

The state of a quantum particle is completely specified by a complex-valued **wave function** $\psi(\boldsymbol{r}, t)$. It is a probability amplitude; the physical interpretation is given by Born's rule.

Probability Interpretation and Normalization The probability of finding the particle in a volume d^3r is $P(\boldsymbol{r}, t)d^3r = |\psi(\boldsymbol{r}, t)|^2 d^3r$. Since the particle must be somewhere in space, the wave function must be **normalized**:

$$\int_{-\infty}^{\infty} |\psi(\boldsymbol{r}, t)|^2 d^3r = 1.$$

For a wave function to be physically meaningful, it must be square-integrable (belong to the L^2 Hilbert space).

Expectation Values and Operators Observables are represented by Hermitian operators $\hat{A}$. The average result of many measurements of A on identically prepared states is the **expectation value**:

$$\langle A \rangle = \int \psi^* \hat{A} \psi \, d^3r.$$

Key operators in the position representation:

- Position: $\hat{\boldsymbol{r}} = \boldsymbol{r}$
- Momentum: $\hat{\boldsymbol{p}} = -i\hbar\nabla$

Probability Current Local conservation of probability is expressed by the **continuity equation**:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \boldsymbol{j} = 0, \quad \rho = |\psi|^2.$$

The **probability current** $\boldsymbol{j}$ represents the flow of probability density:

$$\boldsymbol{j} = \frac{\hbar}{2mi}(\psi^* \nabla\psi - \psi \nabla\psi^*) = \frac{1}{m}\mathrm{Re}(\psi^* \hat{\boldsymbol{p}} \psi).$$

Momentum Space and Fourier Transforms The state can also be represented in **momentum space** by the function $\phi(\boldsymbol{p}, t)$. The two representations are related by a **Fourier transform**:

$$\psi(\boldsymbol{x}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \phi(\boldsymbol{p}) e^{i\boldsymbol{p}\cdot\boldsymbol{x}/\hbar} d^3p, \quad \phi(\boldsymbol{p}) = \frac{1}{(2\pi\hbar)^{3/2}} \int \psi(\boldsymbol{x}) e^{-i\boldsymbol{p}\cdot\boldsymbol{x}/\hbar} d^3x.$$

This duality is the origin of the **Heisenberg Uncertainty Principle**: $\Delta x \Delta p \geq \hbar/2$. A spatially localized wave packet (small Δx) must be composed of many momentum states (large Δp).

2.2 Mathematical spine

$$\hat{\boldsymbol{p}} = -i\hbar\nabla \qquad \text{(Momentum Operator)}$$

$$\boldsymbol{j} = \frac{\hbar}{m}\mathrm{Im}(\psi^*\nabla\psi) \qquad \text{(Probability Current)}$$

$$\Delta A \Delta B \geq \frac{1}{2}|\langle[\hat{A}, \hat{B}]\rangle| \qquad \text{(General Uncertainty Relation)}$$

Example: Gaussian Wave Packet A particle at rest localized at the origin can be modeled by:

$$\psi(x, 0) = \left(\frac{1}{\pi\sigma^2}\right)^{1/4} e^{-x^2/(2\sigma^2)}.$$

This state minimizes the uncertainty product: $\Delta x = \sigma/\sqrt{2}$ and $\Delta p = \hbar/(\sigma\sqrt{2})$, so $\Delta x \Delta p = \hbar/2$. As the wave packet evolves in time, it spreads (dispersion).

Section summary The wave function is a normalized probability amplitude whose evolution is constrained by probability conservation and whose spread is limited by the uncertainty principle.

3 Time-Independent Schrodinger Equation

3.1 Core ideas

When the potential $V(\boldsymbol{r})$ is independent of time, the TDSE can be solved using **separation of variables**: $\Psi(\boldsymbol{r}, t) = \psi(\boldsymbol{r})e^{-iEt/\hbar}$. This leads to the **Time-Independent Schrodinger Equation (TISE)**:

$$\hat{H}\psi = E\psi, \quad \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})\right]\psi = E\psi.$$

This is an **eigenvalue problem** for the energy E. The solutions ψ_n are **stationary states** because the probability density $|\Psi|^2 = |\psi|^2$ is constant in time.

Standard Solvable Models Undergraduate quantum mechanics focuses on a few exactly solvable 1D potentials:

1. **Infinite Square Well:** $V = 0$ for $0 < x < a$, and ∞ otherwise.

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2}, \quad \psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), \quad n = 1, 2, \ldots$$

   Quantization arises from the boundary condition $\psi(0) = \psi(a) = 0$.

2. **Harmonic Oscillator:** $V(x) = \frac{1}{2}m\omega^2x^2$.

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

   The **zero-point energy** $E_0 = \frac{1}{2}\hbar\omega$ is the minimum possible energy, a direct consequence of the uncertainty principle.

Nodes and Energy The n-th excited state (for a 1D bound system) has n **nodes** (points where $\psi = 0$). Higher energy states have more nodes because more "wiggles" correspond to higher curvature ($\nabla^2\psi$) and thus higher kinetic energy.

Tunneling and Bound States

- **Bound States:** Discrete energy levels ($E < V_\infty$).
- **Scattering States:** Continuous energy spectrum ($E > V_\infty$).
- **Tunneling:** A particle has a non-zero probability of being found in classically forbidden regions ($E < V(x)$), where the wave function decays exponentially rather than oscillating.

3.2 Mathematical spine

$$\hat{H}\psi = E\psi \qquad \text{(TISE)}$$

$$E_n = \frac{n^2\pi^2\hbar^2}{2ma^2} \qquad \text{(Infinite Well Energies)}$$

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad \text{(SHO Energies)}$$

Example: Finite Square Well Unlike the infinite well, the finite well has a finite number of bound states. The wave function "leaks" into the walls, leading to lower energy levels than an infinite well of the same width.

Section summary The TISE converts the search for energy states into an eigenvalue problem, yielding quantized energy levels for bound systems and predicting phenomena like zero-point energy and tunneling.

4 Formalism

4.1 Core ideas

The mathematical language of quantum mechanics is linear algebra in Hilbert space. States are represented by vectors, and observables by Hermitian operators.

Dirac Notation and Hilbert Space

- **Ket** $|\psi\rangle$: A state vector in Hilbert space.
- **Bra** $\langle\psi|$: The dual vector (complex conjugate transpose).
- **Inner Product** $\langle\phi|\psi\rangle$: A complex number representing the amplitude of ψ in state ϕ.
- **Completeness:** For an orthonormal basis $\{|n\rangle\}$, the sum of projection operators equals the identity: $\sum_n |n\rangle\langle n| = \hat{I}$.

Hermitian Operators and Measurement An operator $\hat{A}$ is **Hermitian** if $\hat{A} = \hat{A}^\dagger$. Its eigenvalues are real, and its eigenvectors form a complete basis. Measurement "projects" the state:

$$|\psi\rangle = \sum_n c_n|a_n\rangle, \quad c_n = \langle a_n|\psi\rangle.$$

The probability of measuring a_n is $|c_n|^2$.

Commutators and CSCO Two observables can be measured simultaneously if and only if their operators commute: $[\hat{A}, \hat{B}] = 0$. A **Complete Set of Commuting Observables (CSCO)** is a set of operators whose joint eigenvectors uniquely specify a state. Non-commuting operators satisfy the generalized **uncertainty relation**.

Schrodinger vs. Heisenberg Pictures

- **Schrodinger Picture:** States evolve in time ($|\psi(t)\rangle$), operators are stationary.
- **Heisenberg Picture:** Operators evolve in time ($\hat{A}(t) = \hat{U}^\dagger \hat{A} \hat{U}$), states are stationary. The equations of motion are $\frac{d\hat{A}}{dt} = \frac{i}{\hbar}[\hat{H}, \hat{A}] + \frac{\partial \hat{A}}{\partial t}$.

4.2 Mathematical spine

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle \qquad \text{(Expectation Value)}$$

$$\sum_n |n\rangle\langle n| = \hat{I} \qquad \text{(Completeness/Resolution of Identity)}$$

$$\frac{d\langle A \rangle}{dt} = \frac{i}{\hbar}\langle [\hat{H}, \hat{A}] \rangle + \langle \frac{\partial \hat{A}}{\partial t} \rangle \qquad \text{(Ehrenfest's Theorem)}$$

Example: Spin-1/2 The state of a spin-1/2 particle (e.g., an electron) is a spinor in a 2D Hilbert space. The observables are the Pauli matrices $\sigma_x, \sigma_y, \sigma_z$. They do not commute, e.g., $[\sigma_x, \sigma_y] = 2i\sigma_z$, so spin components along different axes cannot be known simultaneously.

Section summary The formalism provides a representation-independent framework using Dirac notation, Hermitian operators, and completeness relations to describe states and measurements.

5 Quantum Mechanics in Three Dimensions

5.1 Core ideas

Extending quantum mechanics to 3D involves the Laplacian ∇^2. For **central potentials** $V(r)$, the problem separates into radial and angular parts.

Spherical Coordinates and Separation of Variables Using $\psi(r, \theta, \phi) = R(r)Y_{\ell m}(\theta, \phi)$, where $Y_{\ell m}$ are the **spherical harmonics**:

- **Angular Part:** Solutions to the angular momentum eigenvalue problem:
$$\hat{L}^2 Y_{\ell m} = \hbar^2 \ell(\ell+1) Y_{\ell m}, \quad \hat{L}_z Y_{\ell m} = \hbar m Y_{\ell m}.$$
- **Radial Part:** The function $u(r) = rR(r)$ satisfies a 1D-like equation with an **effective potential**:
$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2}\right] u = Eu.$$
The term proportional to $\ell(\ell+1)/r^2$ is the **centrifugal barrier**.

Hydrogen Atom and Quantum Numbers For the Coulomb potential $V(r) = -e^2/(4\pi\epsilon_0 r)$, the energies are quantized:

$$E_n = -\frac{me^4}{32\pi^2\epsilon_0^2\hbar^2}\frac{1}{n^2} \approx -\frac{13.6 \text{ eV}}{n^2}.$$

The state is labeled by three quantum numbers:

1. n (Principal): $n = 1, 2, \ldots$ (Determines energy).
2. ℓ (Azimuthal): $\ell = 0, 1, \ldots, n-1$ (Magnitude of $\boldsymbol{L}$).
3. m (Magnetic): $m = -\ell, \ldots, +\ell$ (z-component of $\boldsymbol{L}$).

Spin and Addition of Angular Momentum **Spin $\boldsymbol{S}$** is intrinsic angular momentum. For an electron ($s = 1/2$), $S_z = \pm\hbar/2$. When combining two angular momenta $\boldsymbol{J}_1$ and $\boldsymbol{J}_2$ (e.g., L and S), the total J can range from $|j_1 - j_2|$ to $j_1 + j_2$. The states in the combined basis are related to the individual bases by **Clebsch–Gordan coefficients**.

5.2 Mathematical spine

$$V_{\text{eff}}(r) = V(r) + \frac{\hbar^2 \ell(\ell+1)}{2mr^2} \qquad \text{(Effective Potential)}$$

$$\hat{S}_i = \frac{\hbar}{2}\sigma_i \qquad \text{(Spin and Pauli Matrices)}$$

$$\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}, \quad [J^2, L^2] = 0 \qquad \text{(Addition of Angular Momentum)}$$

Example: The Stern–Gerlach Experiment This experiment demonstrated the quantization of spin by passing a beam of silver atoms through a non-uniform magnetic field, splitting the beam into two distinct spots corresponding to $s_z = \pm\hbar/2$.

Section summary Three-dimensional systems with central symmetry are solved by separating radial and angular motion, leading to the quantization of orbital and intrinsic (spin) angular momentum.

6 Identical Particles

6.1 Core ideas

Identical quantum particles cannot be labeled in a physically meaningful way. Exchanging two identical particles cannot produce a new observable state. In three dimensions, many-particle wave functions are either symmetric or antisymmetric:

$$\psi(x_1, x_2) = +\psi(x_2, x_1) \quad \text{for bosons,}$$

$$\psi(x_1, x_2) = -\psi(x_2, x_1) \quad \text{for fermions.}$$

Bosons have integer spin and can occupy the same one-particle state. Fermions have half-integer spin and obey the Pauli exclusion principle. The Pauli principle explains shell structure in atoms and the structure of the periodic table.

For two fermions the antisymmetric state can be written as a Slater determinant. For particles with spin, the total wave function includes spatial and spin parts. The product must have the correct exchange symmetry.

6.2 Mathematical spine

$$\psi(x_1, x_2) = \pm\psi(x_2, x_1), \qquad \Psi_{\text{fermion}}(1,2) = \frac{1}{\sqrt{2}}\begin{vmatrix} \phi_a(1) & \phi_b(1) \\ \phi_a(2) & \phi_b(2) \end{vmatrix}.$$

6.3 Working details

Exchange symmetry applies to the complete state, including spin and spatial parts. Two electrons in the same spatial orbital can coexist only if their spin state is antisymmetric, the singlet. If the spin state is symmetric, the spatial state must be antisymmetric, reducing the probability of finding the particles close together.

For many fermions, the Slater determinant automatically changes sign when two particle labels are exchanged and vanishes if two one-particle states are identical. This is the mathematical form of Pauli exclusion. For bosons, symmetrized products allow macroscopic occupation of one state, which underlies Bose–Einstein condensation and coherent fields.

Identical-particle physics is not a small correction. It controls atomic shells, chemical bonding, the Fermi sea in metals, blackbody radiation, phonons, superfluidity, and the structure of matter. The first check in many-body problems is whether the particles are distinguishable, bosons, or fermions.

Worked example: lithium ground state $1s^2\,2s^1$ Pauli exclusion fixes the electron configuration of lithium. Two electrons fill the $1s$ shell with opposite spins, and the third must occupy the next available spin-orbital, $2s$. Writing the spin-orbitals $\chi_1 = \phi_{1s}\alpha$, $\chi_2 = \phi_{1s}\beta$, $\chi_3 = \phi_{2s}\alpha$, the totally antisymmetric three-electron ground state is the Slater determinant

$$\Psi(1,2,3) = \frac{1}{\sqrt{3!}} \begin{vmatrix} \phi_{1s}(1)\alpha(1) & \phi_{1s}(1)\beta(1) & \phi_{2s}(1)\alpha(1) \\ \phi_{1s}(2)\alpha(2) & \phi_{1s}(2)\beta(2) & \phi_{2s}(2)\alpha(2) \\ \phi_{1s}(3)\alpha(3) & \phi_{1s}(3)\beta(3) & \phi_{2s}(3)\alpha(3) \end{vmatrix}.$$

A hypothetical $1s^3$ configuration would place two columns with identical spin-orbitals (e.g. a second $\phi_{1s}\alpha$); the determinant would then vanish identically. This is Pauli exclusion in action: it forces the third electron out of the K-shell and into $2s$, producing the alkali-metal chemistry of lithium.

Worked example: helium singlet vs. triplet For two-electron helium, the antisymmetric total wave function factorises into spatial and spin parts. The ground state has both electrons in $1s$: the spatial part is symmetric, so the spin part must be the antisymmetric singlet $\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$, giving the configuration $1s^2\,{}^1S_0$. Excited states like $1s^1 2s^1$ admit two combinations: the symmetric spatial $\frac{1}{\sqrt{2}}[\phi_{1s}(1)\phi_{2s}(2) + \phi_{2s}(1)\phi_{1s}(2)]$ paired with the singlet (parahelium), and the antisymmetric spatial $\frac{1}{\sqrt{2}}[\phi_{1s}(1)\phi_{2s}(2) - \phi_{2s}(1)\phi_{1s}(2)]$ paired with the symmetric triplet (orthohelium). The triplet lies lower in energy because the antisymmetric spatial part suppresses the probability of the two electrons being close, reducing Coulomb repulsion. This exchange splitting is a direct, measurable consequence of fermion antisymmetry.

Section summary Identical particles force quantum states to be symmetric or antisymmetric under exchange, producing bosons, fermions, and Pauli exclusion.

7 Part II: Applications

7.1 Core ideas

Few quantum systems are exactly solvable. For most realistic problems (multi-electron atoms, atoms in external fields, anharmonic vibrations) we expand around a solvable reference. The standard approach is Rayleigh–Schrödinger perturbation theory: split the Hamiltonian into a solvable part plus a small correction, then expand energies and states in powers of a bookkeeping parameter λ.

Setup Write $\hat{H}(\lambda) = \hat{H}_0 + \lambda\hat{H}'$, with $\hat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle$ the known eigenproblem. The unperturbed kets $\{|n^{(0)}\rangle\}$ are orthonormal and complete. We seek series

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots, \qquad |n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \cdots,$$

and set $\lambda = 1$ at the end. Intermediate normalisation $\langle n^{(0)}|n\rangle = 1$ is conventional, so each $|n^{(k\geq 1)}\rangle$ is orthogonal to $|n^{(0)}\rangle$.

7.2 Non-degenerate corrections

Substituting the series into $\hat{H}|n\rangle = E_n|n\rangle$ and matching powers of λ gives the standard formulas. Define the matrix element $H'_{mn} \equiv \langle m^{(0)}|\hat{H}'|n^{(0)}\rangle$.

- **First-order energy:** $E_n^{(1)} = H'_{nn} = \langle n^{(0)}|\hat{H}'|n^{(0)}\rangle$, the expectation value of the perturbation in the unperturbed state.
- **First-order state:**
$$|n^{(1)}\rangle = \sum_{m\neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} |m^{(0)}\rangle.$$
- **Second-order energy:**
$$E_n^{(2)} = \sum_{m\neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}.$$
For the ground state every denominator is negative, so $E_0^{(2)} \leq 0$: second-order corrections always lower the ground-state energy.

7.3 When does the series converge?

The expansion is sensible only when each successive term is much smaller than the previous one. A practical criterion is that, for every state $|m^{(0)}\rangle$ coupled to $|n^{(0)}\rangle$ by $\hat{H}'$,

$$\left|H'_{mn}\right| \ll \left|E_n^{(0)} - E_m^{(0)}\right|.$$

Practical implications

- The relevant small parameter is the dimensionless ratio of a typical matrix element to the nearest energy gap, not just the strength of $\hat{H}'$ itself.
- Levels close in energy (small denominators) destroy convergence even for a tiny perturbation; this is precisely where degenerate perturbation theory is needed.
- The series is generically asymptotic rather than convergent: in many physical problems (e.g. anharmonic oscillators, QED) terms first decrease, then grow. Truncating at the smallest term gives the best estimate.
- Perturbation theory cannot describe states absent from $\hat{H}_0$. Bound states produced non-perturbatively (tunnelling resonances, bound states in a new potential well) are missed at every finite order.

7.4 Degenerate perturbation theory

If $E_n^{(0)}$ has a g-fold degenerate subspace $\mathcal{D} = \{|n_a^{(0)}\rangle\}_{a=1}^{g}$, the denominators inside $\mathcal{D}$ vanish. The fix is to choose the right basis inside $\mathcal{D}$ before applying the formulas above. Build the $g \times g$ matrix $W_{ab} = \langle n_a^{(0)}|\hat{H}'|n_b^{(0)}\rangle$ and diagonalise it; its eigenvalues are the first-order shifts and its eigenvectors are the "good" zeroth-order states that diagonalise $\hat{H}'$ inside $\mathcal{D}$. Couplings to states outside $\mathcal{D}$ then enter through the standard non-degenerate sums.

Worked example: linear Stark effect for $n = 2$ hydrogen A hydrogen atom in a uniform electric field $\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\boldsymbol{z}}$ sees the perturbation $\hat{H}' = e\mathcal{E}\, z$, where $e > 0$ is the elementary charge and z is the electron coordinate along the field. The $n = 2$ shell is four-fold degenerate with basis

$$|2s\rangle = |200\rangle, \quad |2p_0\rangle = |210\rangle, \quad |2p_{+1}\rangle = |211\rangle, \quad |2p_{-1}\rangle = |21\,{-1}\rangle.$$

Selection rules from parity (z is odd) and from $[\hat{L}_z, z] = 0$ (so $\Delta m = 0$) leave only one independent matrix element,

$$\langle 200|z|210\rangle = -3a_0,$$

with a_0 the Bohr radius. The perturbation matrix in the ordered basis $(|2s\rangle, |2p_0\rangle, |2p_{+1}\rangle, |2p_{-1}\rangle)$ is

$$W = e\mathcal{E}\begin{pmatrix} 0 & -3a_0 & 0 & 0 \\ -3a_0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

Diagonalising the upper 2×2 block gives eigenvalues $\pm 3ea_0\mathcal{E}$ with eigenvectors $\frac{1}{\sqrt{2}}(|2s\rangle \mp |2p_0\rangle)$; the $m = \pm 1$ states are unshifted to first order. The fourfold level therefore splits into three: two shifted by $\pm 3ea_0\mathcal{E}$ and one doubly degenerate level at the original energy. The shift is linear in $\mathcal{E}$, a signature of the accidental ℓ-degeneracy of the Coulomb spectrum.

7.5 Mathematical spine

$$\hat{H} = \hat{H}_0 + \lambda\hat{H}', \qquad H'_{mn} = \langle m^{(0)}|\hat{H}'|n^{(0)}\rangle$$

$$E_n^{(1)} = H'_{nn}, \qquad E_n^{(2)} = \sum_{m\neq n} \frac{|H'_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}$$

$$|n^{(1)}\rangle = \sum_{m\neq n} \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}}\,|m^{(0)}\rangle, \qquad W_{ab} = \langle n_a^{(0)}|\hat{H}'|n_b^{(0)}\rangle \text{ (degenerate block)}$$

Example: the Zeeman effect For a weak external field $\boldsymbol{B}$ the perturbation is $\hat{H}' = -\boldsymbol{\mu}\cdot\boldsymbol{B}$, with $\boldsymbol{\mu}$ the magnetic moment. Choosing $\boldsymbol{B} = B\hat{\boldsymbol{z}}$ makes $\hat{H}'$ diagonal in the standard $|n\ell m\rangle$ basis (already a "good" basis), so first-order theory predicts level splittings linear in the magnetic quantum number m, in agreement with experiment for fields where spin–orbit coupling can be ignored.

Section summary Perturbation theory expresses corrections as power series in a small parameter, with first- and second-order energies built from the matrix elements H'_{mn} divided by unperturbed gaps. Convergence requires every $|H'_{mn}|$ to be much smaller than the corresponding gap $|E_n^{(0)} - E_m^{(0)}|$; when that fails because of degeneracy, diagonalising $\hat{H}'$ inside the degenerate subspace, as in the linear Stark effect of $n = 2$ hydrogen, restores predictive power.

8 Time-Dependent Perturbation Theory

8.1 Core ideas

Time-dependent perturbation theory computes transition probabilities caused by a weak time-dependent interaction:

$$\hat{H}(t) = \hat{H}_0 + \hat{V}(t).$$

Write the state as a superposition of unperturbed energy eigenstates. The perturbation changes the coefficients.

To first order, the transition amplitude from $|i\rangle$ to $|f\rangle$ is proportional to

$$\int_0^t e^{i\omega_{fi}t'} V_{fi}(t')\,dt', \qquad \omega_{fi} = \frac{E_f - E_i}{\hbar}.$$

If the perturbation oscillates at a frequency close to ω_{fi}, transitions are enhanced. This gives selection rules and resonance behavior in light-matter interaction.

For long times and dense final states, the transition rate becomes Fermi's golden rule:

$$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|V_{fi}|^2 \rho(E_f).$$

It is one of the most important formulas in atomic, nuclear, and condensed-matter physics.

8.2 Mathematical spine

$$P_{i\to f}(t) \approx \frac{1}{\hbar^2}\left|\int_0^t e^{i\omega_{fi}t'} V_{fi}(t')\,dt'\right|^2, \qquad \Gamma_{i\to f} = \frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_f).$$

8.3 Working details

The perturbation drives transitions most efficiently when its frequency matches an energy difference. This is the origin of absorption and emission lines. If $\hat{V}(t)$ comes from an electromagnetic wave, the matrix element contains both the field strength and a transition dipole or multipole matrix element.

Selection rules arise when a matrix element vanishes by symmetry. For electric dipole transitions in atoms, common rules are $\Delta\ell = \pm 1$ and $\Delta m = 0, \pm 1$, with details depending on polarization. A forbidden transition is often not absolutely impossible; it may be allowed by a weaker magnetic dipole, electric quadrupole, or symmetry-breaking interaction.

Fermi's golden rule assumes weak coupling, long times compared with microscopic oscillations, and a continuum or dense set of final states. It is a rate formula, not a formula for coherent two-level oscillations. Strong resonant driving instead leads to Rabi oscillations.

Worked example: Rabi oscillations of a resonantly driven two-level atom Consider a two-level atom with ground state $|g\rangle$ and excited state $|e\rangle$ of energies E_g and E_e, so $\omega_0 = (E_e - E_g)/\hbar$. Place it in a classical monochromatic field $\boldsymbol{E}(t) = E_0\hat{\boldsymbol{\epsilon}}\cos\omega t$, giving the dipole interaction $\hat{V}(t) = -\hat{\boldsymbol{d}}\cdot\boldsymbol{E}(t)$. Writing $|\psi(t)\rangle = c_g(t)e^{-iE_g t/\hbar}|g\rangle + c_e(t)e^{-iE_e t/\hbar}|e\rangle$, the Schrödinger equation gives coupled equations for (c_g, c_e). Defining the Rabi frequency

$$\Omega = \frac{d_{eg}E_0}{\hbar}, \qquad d_{eg} = \langle e|\hat{\boldsymbol{d}}\cdot\hat{\boldsymbol{\epsilon}}|g\rangle,$$

and dropping rapidly oscillating $\sim e^{\pm i(\omega+\omega_0)t}$ terms (rotating-wave approximation) leaves only slow terms $\sim e^{\pm i(\omega-\omega_0)t}$. On exact resonance $\omega = \omega_0$ and with $c_g(0) = 1$, $c_e(0) = 0$, the solution is

$$c_g(t) = \cos\frac{\Omega t}{2}, \qquad c_e(t) = -i\sin\frac{\Omega t}{2},$$

so the excited-state population oscillates coherently as

$$P_e(t) = |c_e(t)|^2 = \sin^2\frac{\Omega t}{2}.$$

The population swaps fully between $|g\rangle$ and $|e\rangle$ with period $2\pi/\Omega$; a pulse of area $\Omega t = \pi$ (a "π-pulse") inverts the atom, while $\Omega t = \pi/2$ prepares an equal superposition. Off resonance, the generalised Rabi frequency $\tilde{\Omega} = \sqrt{\Omega^2 + (\omega - \omega_0)^2}$ replaces Ω and the maximum excitation drops to $\Omega^2/\tilde{\Omega}^2 < 1$. This non-perturbative result complements first-order perturbation theory: short times or weak driving ($\Omega t \ll 1$) recover $P_e \approx (\Omega t/2)^2$, the linear-response limit.

Section summary Time-dependent perturbation theory computes transition probabilities and rates caused by weak time-dependent interactions.

9 The Variational Principle

9.1 Core ideas

The variational principle provides a powerful way to estimate the ground-state energy E_0 of a system when an exact solution is impossible.

The Variational Theorem For any normalized trial wave function $|\psi\rangle$, the expectation value of the Hamiltonian is always greater than or equal to the true ground-state energy:

$$E_0 \leq \langle\psi|\hat{H}|\psi\rangle.$$

For an unnormalized trial state ψ_α depending on a parameter α, we minimize the **Rayleigh quotient**:

$$\epsilon(\alpha) = \frac{\langle\psi_\alpha|\hat{H}|\psi_\alpha\rangle}{\langle\psi_\alpha|\psi_\alpha\rangle}.$$

The best estimate for E_0 is the minimum value of $\epsilon(\alpha)$.

Success of the Method The method is highly successful because even a rough guess for the wave function often yields a very accurate upper bound for the energy. This is because the error in energy is of second order in the error of the wave function.

9.2 Mathematical spine

$$E_0 \leq \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \qquad \text{(Variational Bound)}$$

$$\frac{d\epsilon}{d\alpha} = 0 \qquad \text{(Minimization Condition)}$$

Example: Ground State of Helium The Helium atom has two electrons and a nucleus with charge $Z = 2$. The Hamiltonian includes an electron-electron repulsion term that makes it unsolvable. A simple trial wave function is a product of two hydrogenic states with an **effective charge** Z_{eff} as the variational parameter. Minimizing the energy yields $Z_{\text{eff}} = 2-5/16 = 1.6875$, showing how one electron "screens" the nucleus for the other.

Section summary The variational principle allows for estimating ground-state energies by optimizing trial wave functions, always providing a guaranteed upper bound.

10 The WKB Approximation

10.1 Core ideas

The WKB approximation is a semiclassical method for one-dimensional problems where the potential changes slowly compared with the de Broglie wavelength. Define the local classical momentum

$$p(x) = \sqrt{2m(E - V(x))}.$$

In the classically allowed region $E > V(x)$, the wave function is approximately oscillatory:

$$\psi(x) \approx \frac{C}{\sqrt{p(x)}} \exp\left(\pm \frac{i}{\hbar} \int^x p(x')\, dx'\right).$$

In the forbidden region $E < V(x)$, the momentum is imaginary and the wave function grows or decays exponentially. This gives a simple estimate of tunneling probabilities:

$$T \sim \exp\left[-\frac{2}{\hbar} \int_{x_1}^{x_2} |p(x)|\, dx\right].$$

At turning points $E = V(x)$, the naive WKB form fails and connection formulas are needed. For bound motion between two turning points, WKB gives the quantization rule

$$\int_{x_1}^{x_2} p(x)\, dx = \left(n + \frac{1}{2}\right) \pi\hbar.$$

10.2 Mathematical spine

$$\psi(x) \approx \frac{C}{\sqrt{p(x)}} \exp\left(\frac{i}{\hbar} \int^x p(x')\, dx'\right), \qquad p(x) = \sqrt{2m(E - V(x))},$$

$$\int_{x_1}^{x_2} p(x)\, dx = \left(n + \frac{1}{2}\right) \pi\hbar.$$

10.3 Working details

WKB works when the local wavelength changes slowly:

$$\left|\frac{d\lambda_{\mathrm{dB}}}{dx}\right| \ll 1, \qquad \lambda_{\mathrm{dB}} = \frac{h}{p(x)}.$$

It fails near turning points because $p(x) \to 0$ and the amplitude factor diverges. Connection formulas repair the solution by matching to Airy-function behavior near the turning point.

The quantization rule is a semiclassical action condition. It says that the phase accumulated over a classical round trip must be compatible with a standing wave, with a correction from the turning points. It reproduces the exact large-n behavior of many bound systems and gives good intuition for why classical action appears in quantum mechanics.

For tunneling, the exponential factor is usually more important than the prefactor. This makes WKB useful for alpha decay, field emission, scanning tunneling microscopy, and barrier penetration in semiconductor devices. The approximation should be checked by asking whether the barrier varies slowly on the de Broglie-wavelength scale.

Section summary The WKB approximation connects quantum waves to classical action when the potential varies slowly.