Brief summary

- This is just a brief summary of important points in this course. You certainly need to read the textbook and/or other materials to fully understand these topics.
- Textbook: D.J. Griffiths, "Introduction to Quantum Mechanics", 3rd ed.
  Chapter "Ch." and Section "§" numbers refer to this book.
- Other references: J.J. Sakurai, "Modern Quantum Mechanics".
- Note: Einstein convention of implicit summation over repeated indices.

Contents

I. FUNDAMENTALS AND FORMALISM (∼ CH.1 & CH.3)

- Wavefunction: complex function $\psi(\boldsymbol{r}, t)$.
  - Here $\boldsymbol{r}$ labels the classical configuration of the system, *e.g.* position of a particle.
  - Normalization: $\int \mathrm{d}\boldsymbol{r}|\psi(\boldsymbol{r}, t)|^2 = 1$.
  - Statistical interpretation (by Max Born):
    $|\psi(\boldsymbol{r}, t)|^2$ is the *a priori* probability density for the particle to be at $\boldsymbol{r}$, at time t.
- Hilbert space: ≈ complex linear space of wavefunctions, with an "inner product".
  - Inner product: $(\phi, \psi) \equiv \int \mathrm{d}\boldsymbol{r}\,(\phi(\boldsymbol{r}))^*\psi(\boldsymbol{r})$, also called "overlap between ϕ and ψ".
    - Hermitivity: $(\phi, \psi) = (\psi, \phi)^*$.
    - Linear with respect to(w.r.t) the 2nd argument: $(\phi, \sum_i c_i\psi_i) = \sum_i c_i \cdot (\phi, \psi_i)$.
      Then anti-linear w.r.t. the 1st argument: $(\sum_i c_i\phi_i, \psi) = \sum_i c_i^* \cdot (\phi_i, \psi)$.
    - Positive semi-definiteness: $(\psi, \psi) \geq 0$.
    - Cauchy-Schwarz inequality (can be derived from the above three facts):
      $(\psi, \psi) \cdot (\phi, \phi) \geq (\psi, \phi) \cdot (\phi, \psi) = |(\psi, \phi)|^2$.
- Dirac symbols: 'kets' $|\psi\rangle$, and 'bras' $\langle\psi|$;
  - 'kets': abstract notation for a (pure) quantum state, a 'vector' in Hilbert space.
  - 'bras': a 'dual vector' in the 'dual space' (linear space of linear functionals).
    $\langle\psi|$ maps a quantum state to a complex number, $|\phi\rangle \mapsto (\psi, \phi)$.
  - $\langle\psi|\phi\rangle$ is a complex number, the inner product $(\psi, \phi) = \int \mathrm{d}\boldsymbol{r}\,\psi^*\phi$.
  - $|\phi\rangle\langle\psi|$ is a linear operator, maps one quantum state to another, $|\varphi\rangle \mapsto |\phi\rangle \cdot \langle\psi|\varphi\rangle$.
- Linear operators: linear mapping of wavefunctions, $\hat{O}: \ \psi \mapsto \hat{O}\psi$
  - Products of operators, $\hat{O}_1\hat{O}_2: \ \psi \mapsto (\hat{O}_1\hat{O}_2)\psi \equiv \hat{O}_1(\hat{O}_2\psi)$.
  - Hermitian conjugate $\hat{O}^\dagger$ of an operator $\hat{O}$: $\langle\hat{O}^\dagger\psi|\phi\rangle = \langle\psi|\hat{O}\phi\rangle$, for any states ψ, ϕ.
  - $(\hat{O}^\dagger)^\dagger = \hat{O}$. $(\hat{O}_1\hat{O}_2)^\dagger = \hat{O}_2^\dagger\hat{O}_1^\dagger$. If $\hat{O}^\dagger = \hat{O}$ then $\hat{O}$ is a *hermitian operator*.
  - Commutator: $[\hat{O}_1, \hat{O}_2] \equiv \hat{O}_1\hat{O}_2 - \hat{O}_2\hat{O}_1$.
    Anti-commutator $\{\hat{O}_1, \hat{O}_2\} \equiv \hat{O}_1\hat{O}_2 + \hat{O}_2\hat{O}_1$.

- (1D) Position operator, $\hat{x}$: $\psi(x) \mapsto x \cdot \psi(x)$. Hermitian.
- (1D) Momentum operator, $\hat{p}_x$: $\psi(x) \mapsto -\mathbb{i}\hbar\partial_x\psi(x)$. Hermitian.
- Canonical commutation relation: $[\hat{x}, \hat{p}_x] = \mathbb{i}\hbar$.

- Eigenbasis:
  - Eigenstates & eigenvalues: if $\hat{O}|\psi\rangle = \lambda|\psi\rangle$, where λ is a complex number, then the state $|\psi\rangle$ is an eigenstate of $\hat{O}$ with eigenvalue λ (also denoted by $|\hat{O} = \lambda\rangle$)
    - If $[\hat{O}, \hat{B}] = c \cdot \hat{B}$, then $\hat{B}|\hat{O} = \lambda\rangle \propto |\hat{O} = \lambda + c\rangle$ (this state may vanish).
  - For "observable"(hermitian operator) $\hat{O}$: eigenvalues must be real, eigenstates for different eigenvalues are orthogonal to each other (have zero inner product).
  - Label the eigenstates $|\psi_k\rangle$ of a hermitian operator by a real number index k (may not be the eigenvalue itself, may be discrete, *e.g.* integers), without "degeneracy" (given k, there is a unique eigenstate, upto overall phase factor), the normalization of these states are, $\langle\psi_k|\psi_{k'}\rangle = \begin{cases} \delta_{k,k'}, & \text{discrete eigenvalues \& indices,} \\ \delta(k-k'), & \text{continuous eigenvalues \& indices.} \end{cases}$
  - Completeness of the eigenbasis: any state $|\psi\rangle$ can be expanded into a linear superposition of the eigenbasis $|\psi_k\rangle$, $|\psi\rangle = \text{“}\sum_k\text{”} c_k|\psi_k\rangle$, $c_k = \langle\psi_k|\psi\rangle$. Here “$\sum_k$” may contain integral over continuous index k.
    - “Resolution of identity”: $\hat{\mathbb{1}} = \text{“}\sum_k\text{”}|\psi_k\rangle\langle\psi_k|$.
  - (1D) Position eigenbasis $|x\rangle$: $\hat{x}|x\rangle = x|x\rangle$, $\langle x|x'\rangle = \delta(x - x')$.
    $|\psi\rangle = \int \mathrm{d}x\, |x\rangle\langle x|\psi\rangle$, and $\langle x|\psi\rangle = \psi(x)$ is the wavefunction.
  - (1D) Momentum eigenbasis $|p\rangle$: $\hat{p}|p\rangle = p|p\rangle$, $\langle p|p'\rangle = \delta(p - p')$, $\langle x|p\rangle = \frac{e^{\mathbb{i}px/\hbar}}{\sqrt{2\pi\hbar}}$.
    $|\psi\rangle = \int \mathrm{d}p\, |p\rangle\langle p|\psi\rangle$, $\langle p|\psi\rangle = \tilde{\psi}(p)$ is “wavefunction in momentum representation”.
    - In momentum representation: $\hat{x}: \tilde{\psi}(p) \mapsto \mathbb{i}\hbar\partial_p\tilde{\psi}(p)$, and $\hat{p}: \tilde{\psi}(p) \mapsto p\cdot\tilde{\psi}(p)$.
  - Under *complete orthonormal basis* $|\psi_k\rangle$, state $|\psi\rangle$ is a column vector $\langle\psi_k|\psi\rangle$, operator $\hat{O}$ is a matrix $O_{k',k} \equiv \langle\psi_{k'}|\hat{O}|\psi_k\rangle$, and $\langle\psi_{k'}|\hat{O}\psi\rangle = \text{“}\sum_k\text{”}O_{k',k}\langle\psi_k|\psi\rangle$ (matrix-vector product). The indices k, k' may be continuous.

- Measurement ‘postulate’ & generalized statistical interpretation:
  - Each measurement of an observable $\hat{O}$ under state $|\psi\rangle$, will produce one of the eigenvalues (say, λ) of $\hat{O}$, with *a priori* probability $|\langle\hat{O} = \lambda|\psi\rangle|^2$. $|\hat{O} = \lambda\rangle$ is the ‘normalized’ eigenstate of $\hat{O}$.

- If λ is continuous, $|\langle \hat{O} = \lambda|\psi\rangle|^2$ is the probability density.
- "Collapse postulate": after this measurement, the state becomes $|\hat{O} = \lambda\rangle$.
- If the eigenstates $|\hat{O} = \lambda,\ k\rangle$ are degenerate, and labeled by another index k, then the probability (density) is "$\sum_k$"$|\langle \hat{O} = \lambda,\ k|\psi\rangle|^2$, the "collapsed" state is $\left(\text{"}\sum_k\text{"}|\langle \hat{O} = \lambda,\ k|\psi\rangle|^2\right)^{-1/2}$ "$\sum_k$"$|\hat{O} = \lambda,\ k\rangle\langle \hat{O} = \lambda,\ k|\psi\rangle$.
- Expectation value $\langle \hat{O}\rangle_\psi$: *a priori* average of measurement results, $\langle\psi|\hat{O}|\psi\rangle$.
- Uncertainty principle: $\sigma_{\hat{A}}^2 \cdot \sigma_{\hat{B}}^2 \geq \frac{1}{4}|\langle[\hat{A}, \hat{B}]\rangle|^2$. See §3.5 for proof.
  The variance is $\sigma_{\hat{A}}^2 \equiv \langle(\hat{A} - \langle\hat{A}\rangle)^2\rangle = \langle\hat{A}^2\rangle - \langle\hat{A}\rangle^2$.

- Schrödinger equation: $\mathbb{i}\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r}, t) = \hat{H}\psi(\boldsymbol{r}, t)$.
  - Hamiltonian $\hat{H}$ is a (bosonic) hermitian operator.
  - For classical Hamiltonian $H(\boldsymbol{r}, \boldsymbol{p})$, the quantum Hamiltonian is $\hat{H} = H(\hat{\boldsymbol{r}}, \hat{\boldsymbol{p}})$, and $\hat{H}\psi(\boldsymbol{r}, t) = H(\boldsymbol{r}, -\mathbb{i}\hbar\partial_{\boldsymbol{r}})\psi(\boldsymbol{r}, t)$. For example: for non-relativistic particle, $H = \frac{\boldsymbol{p}^2}{2m} + V(\boldsymbol{r})$, then $\hat{H}\psi(\boldsymbol{r}, t) = [-\frac{\hbar^2}{2m}\nabla^2 + V(\boldsymbol{r})]\psi(\boldsymbol{r}, t)$
    - Probability current: $\boldsymbol{J}(\boldsymbol{r}) \equiv \mathrm{Re}[\psi^*(\boldsymbol{r})\frac{-\mathbb{i}\hbar\nabla}{m}\psi(\boldsymbol{r})]$ for non-relativistic particle.
      It satisfies the *continuity equation* for probability: $\frac{\partial}{\partial t}(|\psi(\boldsymbol{r})|^2) + \mathrm{div}\boldsymbol{J} = 0$.
  - Stationary states: eigenstates for time-independent $\hat{H}$.
    Stationary Schrödinger equation: $\hat{H}\psi(\boldsymbol{r}, t) = E\psi(\boldsymbol{r}, t)$,
    then $\psi(\boldsymbol{r}, t) = \exp(-\mathbb{i}\frac{E\cdot t}{\hbar})\psi(\boldsymbol{r}, t = 0)$. The expectation value of any observable (not explicitly involving t) under a stationary state, does not change over time.
  - If $\hat{H}$ is independent of time t, generic solutions of Schrödinger equation are linear superpositions of stationary states, $\psi(\boldsymbol{r}, t) = \text{"}\sum_n\text{"}c_n e^{-\mathbb{i}E_n t/\hbar}\psi_n(\boldsymbol{r})$.
    Here n labels energy eigenvalues (may be continuous), c_n are complex coefficients, E_n are energy eigenvalues (eigenvalues of $\hat{H}$), ψ_n are eigenstate wavefunctions of $\hat{H}$ for eigenvalue E_n.
  - Heisenberg equations of motion (Equation 6.78 in §6.8): $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{Q}\rangle = \frac{\mathbb{i}}{\hbar}\langle[\hat{H}, \hat{Q}]\rangle + \langle\frac{\partial\hat{Q}}{\partial t}\rangle$.
    The expectation values are taken under a solution $\psi(t)$ of Schrödinger equation.
  - If $\frac{\partial\hat{Q}}{\partial t} = 0$ and $[\hat{H}, \hat{Q}] = 0$, then observable $\hat{Q}$ is *conserved*, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{Q}\rangle = 0$.

II. ONE-DIMENSIONAL EIGENVALUE PROBLEMS (∼ CH.2)

- $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x})$. Namely, $\hat{H}\psi(x) = [-\frac{\hbar^2}{2m}\partial_x^2 + V(x)]\psi(x)$.
- Qualitative features (*c.f.* Sturm-Liouville theory):
  - The "energy spectrum" (collection of energy eigenvalues) contains discrete "bound states", between $\min_x V(x)$ and $\min\{V(+\infty), V(-\infty)\}$; and continuous "scattering states", above $\min\{V(+\infty), V(-\infty)\}$.
  - Bound states are non-degenerate, bound state wavefunctions $\psi_n(x)$, labeled by integer n, are orthonormal, $\langle\psi_n|\psi_{n'}\rangle = \delta_{n,n'}$. And $\psi_n(x)$ can be chosen real.
  - If $V(x)$ is finite in a neighborhood of x, the eigenstate $\psi_n(x)$ is smooth at x. If $V(x) = +\infty$ in a neighborhood of x, the eigenstate $\psi_n(x)$ vanishes at x.
  - Node: where $\psi_n(x) = 0$. (excluding the trivial case above at $V(x) = +\infty$) Nodes are "simple", where $\psi_n(x) = 0$, $\partial_x\psi_n(x) \neq 0$.
  - For bound states, ground state (lowest energy state) wavefunction has no node; n-th excited state wavefunction has n nodes, $x_i^{(n)}$, $i = 1, \ldots, n$; nodes of adjacent levels are interpenetrating, $x_1^{(n)} < x_1^{(n-1)} < x_2^{(n)} < x_2^{(n-1)} < \cdots < x_{n-1}^{(n-1)} < x_n^{(n)}$. NOTE: the n here may not be exactly the label(quantum number) of ψ_n.
  - Inversion symmetry: if $V(x) = V(-x)$, for bound states, the ground state is even function, the n-th excited state has $\psi_n(-x) = (-1)^n\psi_n(x)$. (see NOTE above) NOTE: the inversion center may be at $x_0 \neq 0$, $V(x_0 + x) = V(x_0 - x)$.
- (§2.4) Free particle: $V(x) = V_0$ =const.
  - System has "translation symmetry": if $\psi(x)$ is eigenstate of $\hat{H}$, then $\psi(x + a)$ is also eigenstate with the same eigenvalue. Here a is an arbitrary real constant.
  - Eigenstates: plane waves, $\psi_p(x) = \frac{e^{\frac{i}{\hbar}px/\hbar}}{\sqrt{2\pi\hbar}}$, $E_p = \frac{p^2}{2m} + V_0$. $p \in \mathbb{R}$.
  - Wave packet: $\Psi(x,t) = \int_{-\infty}^{\infty} \phi(p - p_0) \cdot e^{\frac{i}{\hbar}[(p-p_0)\cdot x - (E_p - E_{p_0})\cdot t]}\, \mathrm{d}p \cdot \frac{\exp(\frac{i}{\hbar}(p_0\cdot x - E_{p_0}\cdot t))}{\sqrt{2\pi\hbar}}$ $= f(x,t)\cdot\frac{\exp(\frac{i}{\hbar}(p_0\cdot x - E_{p_0}\cdot t))}{\sqrt{2\pi\hbar}}$. Here $\phi(p-p_0)$ has a "narrow" peak around $p = p_0$ (peak width $\ll p_0$), $f(x,t)$ is a "broad" envelope function (relevant length scale $\gg \frac{\hbar}{p_0}$). The peak of the envelop function moves with the "group velocity" $v_g \equiv \frac{\partial E_p}{\partial p}$.

- (§2.2) Infinite square potential well: $V(x) = \begin{cases} +\infty, & x - x_0 < 0 \text{ or } x - x_0 > a; \\ 0, & 0 < x - x_0 < a. \end{cases}$
  - Eigenstates: standing waves, $\psi_n(x) = \sqrt{\frac{2}{a}} \sin(\frac{n\pi}{a}(x - x_0))$, $E_n = \frac{\hbar^2 n^2 \pi^2}{2ma^2}$. $n \in \mathbb{Z}^+$
- (§2.5) δ-function potential: $V(x) = \alpha \cdot \delta(x - x_0)$. NOTE: α has unit of (energy·length).
  - Boundary condition for eigenstates $\psi_n(x)$ at the δ-function potential position: integrate the stationary Schrödinger equation over an infinitesimal region $-\delta < x - x_0 < \delta$, and take limit $\delta \to +0$, $\left[-\frac{\hbar^2}{2m}\partial_x \psi_n\right]_{x=x_0-0}^{x=x_0+0} + \alpha\psi_n(x_0) = 0$.
    If the potential contains an additional smooth part, this is still true.
  - The eigenstate wavefunction is continuous, but its 1st derivative may not be continuous, at the δ-function potential position.
- (§2.6) Finite square potential well: $V(x) = \begin{cases} 0, & x - x_0 < -a \text{ or } x - x_0 > a; \\ -V_0, & -a < x - x_0 < a. \end{cases}$
  - For any positive V_0 and a, there is at least one "even-parity" bound state.
  - Resonant tunneling for scattering states: when $E = \frac{\hbar^2 n^2 \pi^2}{2m(2a)^2} - V_0 > 0$, the would-be bound state energy for infinite square well, the "transmission coefficient"$= 1$.
- (§2.3) Harmonic oscillator: $V(x) = \frac{m\omega^2}{2}x^2$.
  - Ladder operators: $\hat{a}_\pm = \sqrt{\frac{m\omega}{2\hbar}}(\hat{x} \mp \frac{\mathrm{i}}{m\omega}\hat{p}) = \sqrt{\frac{m\omega}{2\hbar}}(x \mp \frac{\hbar}{m\omega}\partial_x)$. $[\hat{a}_-, \hat{a}_+] = 1$. $(\hat{a}_\pm)^\dagger = \hat{a}_\mp$. $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2} = \hbar\omega \cdot (\hat{a}_+\hat{a}_- + \frac{1}{2})$.
  - $\hat{a}_+\hat{a}_-$ is positive semi-definite: $\langle\psi|\hat{a}_+\hat{a}_-|\psi\rangle = \langle(\hat{a}_+)^\dagger\psi|\hat{a}_-\psi\rangle = \langle\hat{a}_-\psi|\hat{a}_-\psi\rangle \geq 0$, for any ψ. Therefore hermitian operator $\hat{a}_+\hat{a}_-$ has non-negative eigenvalues.
  - Commutators $[\hat{a}_+\hat{a}_-, \hat{a}_\pm] = (\pm 1) \cdot \hat{a}_\pm$. Then $\hat{a}_\pm|\hat{a}_+\hat{a}_- = n\rangle \propto |\hat{a}_+\hat{a}_- = n \pm 1\rangle$.
  - Therefore $\hat{a}_+\hat{a}_-$ eigenvalues n are non-negative integers.
  - $\psi_0(x) = (\frac{m\omega}{\hbar\pi})^{1/4} \exp(-\frac{m\omega}{2\hbar}x^2)$, and $\psi_n(x) = \frac{1}{\sqrt{n!}}(\hat{a}_+)^n\psi_0(x)$. $E_n = \hbar\omega \cdot (n + \frac{1}{2})$.
    $\hat{a}_+\psi_n = \sqrt{n+1}\,\psi_{n+1}$; $\hat{a}_-\psi_n = \sqrt{n}\,\psi_{n-1}$, in particular $\hat{a}_-\psi_0 = 0$.
  - See §2.3.2 for "Analytic Method" (solving differential equations):
    $\psi_n(x) = (\frac{m\omega}{\hbar\pi})^{1/4}\frac{1}{\sqrt{2^n n!}}H_n(\frac{x}{\sqrt{\hbar/m\omega}})\exp(-\frac{m\omega}{2\hbar}x^2)$. $\hat{H}_n$ are Hermite polynomials.
    - $e^{-(x-t)^2} = \sum_{n=0}^{\infty}\frac{t^n}{n!}H_n(x)e^{-x^2}$. [Related to the "coherent state".]
    - $H_{n+1}(x) = 2x \cdot H_n(x) - 2n \cdot H_{n-1}(x)$. [Check $\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_- + \hat{a}_+)$.]

III. THREE-DIMENSIONAL PROBLEMS (∼ CH.4)

- Central potential problem: $\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(r)$. Potential V depends only on radius r.
  - Separation of variables in polar coordinates (r, θ, ϕ):
    $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(r) = -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\partial_r(r^2\partial_r) - \frac{1}{r^2}\frac{\hat{\boldsymbol{L}}^2}{\hbar^2}\right] + V(r)$.
    $\hat{\boldsymbol{L}}^2 = -\hbar^2 \cdot \left[\frac{1}{\sin\theta}\partial_\theta(\sin\theta\partial_\theta) + \frac{1}{(\sin\theta)^2}\partial_\phi^2\right]$.
  - Eigenstates are of the form $\psi(r, \theta, \phi) = R(r) \cdot Y_\ell^m(\theta, \phi)$.
  - "spherical harmonics": $Y_\ell^m(\theta, \phi) = \begin{cases} (-1)^m\sqrt{\frac{2\ell+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_\ell^m(\cos\theta)e^{\mathbb{i}m\phi}, & m \geq 0; \\ \sqrt{\frac{2\ell+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}P_\ell^m(\cos\theta)e^{\mathbb{i}m\phi}, & m < 0. \end{cases}$
    - "associated Legendre polynomial": $P_\ell^m(x) = (1-x^2)^{|m|/2}(\frac{\mathrm{d}}{\mathrm{d}x})^{|m|}P_\ell(x)$.
    - "Legendre polynomial": $P_\ell(x) = \frac{1}{2^\ell \ell!}(\frac{\mathrm{d}}{\mathrm{d}x})^\ell[(x^2-1)^\ell]$.
    - "orbital angular momentum quantum number" ℓ is a non-negative integer.
    - "magnetic quantum number" $m = -\ell, -\ell+1, \ldots, \ell$, is integer.
    - Orthonormal property: $\int_0^\pi \sin\theta \mathrm{d}\theta \int_0^{2\pi} \mathrm{d}\phi\, [Y_\ell^m(\theta,\phi)]^* Y_{\ell'}^{m'}(\theta,\phi) = \delta_{\ell,\ell'}\delta_{m,m'}$.
  - Radial equation: define $u(r) \equiv r \cdot R(r)$, it satisfies a 1D Schrödinger equation,
    $\left[-\frac{\hbar^2}{2m}\partial_r^2 + V(r) + \frac{\hbar^2\ell(\ell+1)}{2mr^2}\right]u(r) = E \cdot u(r)$.
    Here $\frac{\hbar^2\ell(\ell+1)}{2mr^2}$ is the "centrifugal potential". E is the energy eigenvalue.
    - $R(r) \sim r^\ell$ when $r \to 0$, for normalizable eigenfunction.
    - Energy eigenvalues depend on ℓ and another "principal quantum number", but will be independent of m, so at least $(2\ell+1)$-fold degenerate.

- Example: free particle, $V(r) = V_0$=const.
  - Spherical waves: $\psi_k(r, \theta, \phi) \propto j_\ell(kr)Y_\ell^m(\theta, \phi)$, $E = V_0 + \frac{\hbar^2k^2}{2m}$.
  - "spherical Bessel function": $j_\ell(x) = (-x)^\ell(\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x})^\ell(\frac{\sin x}{x})$.
    $j_\ell(x) \sim x^\ell$ when $x \to 0$, $\sim \frac{\sin(x-\frac{\ell}{2}\pi)}{x}$ when $x \to +\infty$.
  - "spherical Neumann function": $n_\ell(x) = -(-x)^\ell(\frac{1}{x}\frac{\mathrm{d}}{\mathrm{d}x})^\ell(\frac{\cos x}{x})$.
    $n_\ell(x) \sim x^{-\ell-1}$ when $x \to 0$, $\sim -\frac{\cos(x-\frac{\ell}{2}\pi)}{x}$ when $x \to +\infty$.

- Example: finite spherical potential well: $V(r) = \begin{cases} -V_0, & r < a; \\ 0, & r > a. \end{cases}$
  - If V_0 or a is too small, there will be NO bound state. See Textbook Problem 4.11.

- Example: 3D harmonic oscillator (Textbook Problem 4.46, 4.47), $V(r) = \frac{m\omega^2 r^2}{2}$.
  - $E_{n\ell m} = \hbar\omega \cdot (n + \frac{3}{2})$. Here $(n - \ell)$ is an even non-negative integer.
  - Side remark: the degeneracy $\frac{(n+1)(n+2)}{2}$ is higher than $(2\ell + 1)$, due to a hidden $SU(3)$ symmetry, higher than just 3D rotation symmetry $SO(3)$. There are more conserved observables than the orbital angular momentum $\hat{\boldsymbol{L}}$, including $\hat{x}\hat{y} + \frac{\hat{p}_x\hat{p}_y}{m^2\omega^2}$, $\hat{y}\hat{z} + \frac{\hat{p}_y\hat{p}_z}{m^2\omega^2}$, $\hat{z}\hat{x} + \frac{\hat{p}_z\hat{p}_x}{m^2\omega^2}$, $\hat{x}^2 - \hat{y}^2 + \frac{\hat{p}_x^2 - \hat{p}_y^2}{m^2\omega^2}$, $\hat{x}^2 + \hat{y}^2 - 2z^2 + \frac{\hat{p}_x^2 + \hat{p}_y^2 - 2\hat{p}_z^2}{m^2\omega^2}$,
- (§4.2) Example: "hydrogen atom", $V(r) = -\frac{\mathrm{e}^2}{4\pi\epsilon_0}\frac{1}{r}$, here e is elementary charge.
  - $E_{n\ell m} = E_1 \cdot \frac{1}{n^2}$. Here $(n - \ell)$ is a positive integer.
  - The "Rydberg energy" $E_1 = -\frac{m}{2\hbar^2}(\frac{\mathrm{e}^2}{4\pi\epsilon_0})^2 = -\frac{\hbar^2}{2m}(\frac{1}{a_0})^2 = -\frac{1}{2}\frac{\mathrm{e}^2}{4\pi\epsilon_0}\frac{1}{a_0} \approx -13.6\mathrm{eV}$. The "Bohr radius" $a_0 = \frac{\hbar^2}{m}\frac{4\pi\epsilon_0}{\mathrm{e}^2} \approx 0.53\mathring{A}$.
  - Ground state wavefunction $\psi_{100} = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$.
  - $\psi_{n\ell m} = \sqrt{(\frac{2}{na_0})^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/na_0} (\frac{2r}{na_0})^\ell L_{n-\ell-1}^{2\ell+1}(\frac{2r}{na_0}) Y_\ell^m(\theta, \phi)$. (see §4.2).
  - Side remark: the degeneracy n^2 is higher than $(2\ell + 1)$, due to a hidden $SO(4)$ symmetry, higher than just 3D rotation symmetry $SO(3)$. There are more conserved observables than the orbital angular momentum $\hat{\boldsymbol{L}}$, including the Laplace-Runge-Lenz vector, $\hat{\boldsymbol{A}} \equiv -(\frac{\mathrm{e}^2}{4\pi\epsilon_0}) \cdot m \cdot \frac{\hat{\boldsymbol{r}}}{r} + \frac{1}{2}(\hat{\boldsymbol{p}} \times \hat{\boldsymbol{L}} - \hat{\boldsymbol{L}} \times \hat{\boldsymbol{p}})$.
- (§4.3) Orbital angular momentum: $\hat{\boldsymbol{L}} = \hat{\boldsymbol{r}} \times \hat{\boldsymbol{p}}$, or $\hat{L}_a = \epsilon_{abc}\hat{r}_b\hat{p}_c$.
  - Levi-Civita symbol: $\epsilon_{abc} = \begin{cases} +1, & abc = xyz, yzx, zxy; \\ -1, & abc = zyx, xzy, yxz; \\ 0, & \text{otherwise.} \end{cases}$. $\epsilon_{abc}\epsilon_{adf} = \delta_{bd}\delta_{cf} - \delta_{bf}\delta_{cd}$.
  - $\hat{L}_a$ are all hermitian (observable). $[\hat{L}_a, \hat{L}_b] = \mathbb{i}\hbar\epsilon_{abc}\hat{L}_c$, or $\hat{\boldsymbol{L}} \times \hat{\boldsymbol{L}} = \mathbb{i}\hbar\hat{\boldsymbol{L}}$.
  - $\hat{\boldsymbol{L}}^2 \equiv \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$ is hermitian and positive semi-definite. $[\hat{\boldsymbol{L}}^2, \hat{L}_a] = 0$.
  - Ladder operators: $\hat{L}_\pm = \hat{L}_x \pm \mathbb{i}\hat{L}_y$. $(\hat{L}_\pm)^\dagger = \hat{L}_\mp$, $[\hat{L}_z, \hat{L}_\pm] = \pm\hbar\hat{L}_\pm$, $[\hat{\boldsymbol{L}}^2, \hat{L}_\pm] = 0$.
  - In polar coordinates, $\hat{L}_a$ does not depend on radius r. $\hat{L}_z = -\mathbb{i}\hbar\frac{\partial}{\partial\phi}$, $\hat{L}_\pm = \pm\hbar e^{\pm\mathbb{i}\phi}(\frac{\partial}{\partial\theta} \pm \mathbb{i}\cot\theta\frac{\partial}{\partial\phi})$
  - Simultaneous eigenstates of $\hat{\boldsymbol{L}}^2$ and $\hat{L}_z$: $|\ell, m\rangle \equiv |\hat{\boldsymbol{L}}^2 = \ell(\ell+1)\hbar^2, \hat{L}_z = m\hbar\rangle$. Here ℓ is non-negative integer, $m = -\ell, -\ell+1, \ldots, \ell$.

  * Proof: suppose we have $|\hat{\boldsymbol{L}}^2 = \alpha\hbar^2, \hat{L}_z = \beta\hbar\rangle$, by the commutation relations, $\hat{L}_\pm|\hat{\boldsymbol{L}}^2 = \alpha\hbar^2, \hat{L}_z = \beta\hbar\rangle \propto |\hat{\boldsymbol{L}}^2 = \alpha\hbar^2, \hat{L}_z = (\beta \pm 1)\hbar\rangle$. By $\hat{\boldsymbol{L}}^2 = \hat{L}_z(\hat{L}_z \pm 1) + \hat{L}_\mp\hat{L}_\pm$, $\hat{L}_\mp\hat{L}_\pm$ is positive semi-definite, we have $\alpha \geq \beta(\beta \pm 1)$. The "ladder" of β generated by $\hat{L}_\pm$ must be truncated on both sides. Namely, there is a $\beta_{\max}$ such that(s.t.) $\hat{L}_+|\hat{\boldsymbol{L}}^2 = \alpha\hbar^2, \hat{L}_z = \beta_{\max}\hbar\rangle = 0$, and a $\beta_{\min}$ s.t. $\hat{L}_-|\hat{\boldsymbol{L}}^2 = \alpha\hbar^2, \hat{L}_z = \beta_{\min}\hbar\rangle = 0$. $\beta_{\max} - \beta_{\min}$ is non-negative integer. Then $\alpha = \beta_{\max}(\beta_{\max}+1) = \beta_{\min}(\beta_{\min}-1)$. The solution is $\beta_{\max} = -\beta_{\min} = \ell$, $\alpha = \ell(\ell+1)$, and $\beta_{\max} - \beta_{\min} = 2\ell$ is non-negative integer.
  * For orbital angular momentum, consider $\hat{L}_z = -\mathrm{i}\hbar\frac{\partial}{\partial\phi}$, and the fact that the wavefunction $\psi(r,\theta,\phi) = \psi(r,\theta,\phi+2\pi)$, the m must be integer, then ℓ must also be integer. [A rigorous argument in Textbook(2nd Ed.) Problem 4.57]
- Wavefunction for $|\ell, m\rangle$: $R(r)Y_\ell^m(\theta,\phi)$.
- $\hat{L}_\pm|\ell,m\rangle = \hbar\sqrt{(\ell \mp m)(\ell \pm m + 1)}|\ell, m \pm 1\rangle$, under Condon-Shortley convention.
  NOTE: this fixes the relative phases between $|\ell, m\rangle$ states with different m.

- (§4.4.1) Spin-1/2: internal 2-dimensional Hilbert space.
  - Spin angular momentum operators: $\hat{\boldsymbol{S}}$. $[\hat{S}_a, \hat{S}_b] = \mathrm{i}\hbar\epsilon_{abc}\hat{S}_c$.
  - Two basis states: $|S = \frac{1}{2}, S_z = +\frac{1}{2}\rangle$, $|S = \frac{1}{2}, S_z = -\frac{1}{2}\rangle$. (Usually $|\uparrow\rangle$, $|\downarrow\rangle$)
  - Under above basis, $\hat{S}_a = \frac{\hbar}{2}\sigma_a$, σ_a are Pauli matrices.
  - $\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$, $\sigma_y = \begin{pmatrix} 0 & -\mathrm{i} \\ \mathrm{i} & 0 \end{pmatrix}$, $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$, $\sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$. $\sigma_a\sigma_b = \delta_{ab}\sigma_0 + \mathrm{i}\epsilon_{abc}\sigma_c$.
    So commutator $[\sigma_a, \sigma_b] = 2\mathrm{i}\epsilon_{abc}\sigma_c$, anti-commutator $\{\sigma_a, \sigma_b\} = 2\delta_{ab}\sigma_0$.
  - Spin-1/2 state: $|\psi\rangle = \psi_\uparrow|\uparrow\rangle + \psi_\downarrow|\downarrow\rangle$, also written as $\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}$.
    The expectation values of spin operators are $\langle\psi|\hat{S}_a|\psi\rangle = \frac{\hbar}{2}\cdot(\psi_\uparrow^*, \psi_\downarrow^*)\cdot\sigma_a\cdot\begin{pmatrix} \psi_\uparrow \\ \psi_\downarrow \end{pmatrix}$.
    Here $\psi_\uparrow$,$\psi_\downarrow$ are complex numbers, with normalization $|\psi_\uparrow|^2 + |\psi_\downarrow|^2 = 1$.
  - Spinor wavefunction: the spin-1/2 wavefunctions may depend on $\boldsymbol{r}$ (or other degrees of freedom), $\begin{pmatrix} \psi_\uparrow(\boldsymbol{r}) \\ \psi_\downarrow(\boldsymbol{r}) \end{pmatrix}$. The normalization is $\int[|\psi_\uparrow(\boldsymbol{r})|^2 + |\psi_\downarrow(\boldsymbol{r})|^2]\,\mathrm{d}\boldsymbol{r} = 1$.
    This is also written as $\psi(\boldsymbol{r}, s)$ with $s = \uparrow, \downarrow$, and $\sum_s\int\mathrm{d}\boldsymbol{r}\,|\psi(\boldsymbol{r},s)|^2 = 1$.
  - Larmor precession (§4.4.2): $\hat{H} = -\gamma\boldsymbol{B}\cdot\hat{\boldsymbol{S}} = -\gamma B_b\hat{S}_b$. By the Heisenberg equation of motion, $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{S}_a\rangle = \frac{\mathrm{i}}{\hbar}\langle[\hat{H}, \hat{S}_a]\rangle = \gamma\epsilon_{bac}B_b\langle\hat{S}_c\rangle$, or $\frac{\mathrm{d}}{\mathrm{d}t}\langle\hat{\boldsymbol{S}}\rangle = -\gamma\boldsymbol{B}\times\langle\hat{\boldsymbol{S}}\rangle$. So $\langle\hat{\boldsymbol{S}}\rangle$ will rotate around $\boldsymbol{B}$ without changing length and angle between $\langle\hat{\boldsymbol{S}}\rangle$ and $\boldsymbol{B}$.

- (§4.4.3) Addition of angular momentum:
  - Consider two independent Hilbert spaces, $\mathcal{H}_{J_1}$ and $\mathcal{H}_{J_2}$, with complete orthonormal basis $|J_1, m_1\rangle$ and $|J_2, m_2\rangle$ respectively. Here $m_i = -J_i, -J_i+1, \ldots, J_i$.
  - In each $\mathcal{H}_{J_i}$, there are angular momentum operators $\hat{J}_{i,a}$, satisfying $[\hat{J}_{i,a}, \hat{J}_{i,b}] = \mathbb{i}\hbar\epsilon_{abc}\hat{J}_{i,c}$, $\hat{J}_{i,z}|J_i, m_i\rangle = \hbar m_i|J_i, m_i\rangle$, $\hat{J}_{i,\pm} \equiv \hat{J}_{i,x} \pm \mathbb{i}\hat{J}_{i,y}$, and $\hat{J}_{i,\pm}|J_i, m_i\rangle = \hbar\sqrt{(J_i \mp m_i)(J_i \pm m_i + 1)}|J_i, m_i \pm 1\rangle$.
  - Make the tensor product Hilbert space $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$, with $(2J_1+1)(2J_2+1)$ complete orthonormal basis $|J_1, m_1\rangle \otimes |J_2, m_2\rangle$ (usuall just $|J_1, m_1\rangle|J_2, m_2\rangle$).
  - In $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$, define total angular momentum operators $\hat{J}_a = \hat{J}_{1,a} + \hat{J}_{2,a}$. Here $\hat{J}_{1,a}$ ($\hat{J}_{2,a}$) acts only on the first (second) factor of $|J_1, m_1\rangle|J_2, m_2\rangle$ basis, so actually $\hat{J}_a = \hat{J}_{1,a} \otimes \mathbb{1}_{J_2} + \mathbb{1}_{J_1} \otimes \hat{J}_{2,a}$, where $\mathbb{1}_{J_i}$ is the identity operator(matrix) in $\mathcal{H}_{J_i}$. $\hat{\boldsymbol{J}}$ still satisfies $[\hat{J}_a, \hat{J}_b] = \mathbb{i}\hbar\epsilon_{abc}\hat{J}_c$. So we can find simultaneous eigenstates of $\hat{\boldsymbol{J}}^2$ and $\hat{J}_z$ in $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2}$, $\hat{\boldsymbol{J}}^2|J, m\rangle = \hbar^2 J(J+1)|J, m\rangle$ and $\hat{J}_z|J, m\rangle = \hbar m|J, m\rangle$.
  - Clebsch-Gordon theorom: the total angular momentum quantum number J can be $|J_1 - J_2|$, or $(|J_1 - J_2| + 1)$, …, up to $(J_1 + J_2)$.
    - This means that by some unitary transformation (basis change), the tensor product Hilbert space $\mathcal{H}_{J_1} \otimes \mathcal{H}_{J_2} \sim \mathcal{H}_{|J_1-J_2|} \oplus \mathcal{H}_{|J_1-J_2|+1} \oplus \cdots \oplus \mathcal{H}_{J_1+J_2}$, the direct sum of subspaces with fixed J quantum number. As consistency check, the dimensions match, $(2J_1+1)(2J_2+1) = \sum_{J=|J_1-J_2|}^{J_1+J_2}(2J+1)$.
  - Clebsch-Gordon coefficient (C-G coefficient): $C^{J_1J_2J}_{m_1m_2m}$, also $\langle J_1, m_1; J_2, m_2|J, m\rangle$.
    - Definition: $|J, m\rangle = \sum_{m_1,m_2} C^{J_1J_2J}_{m_1m_2m}|J_1, m_1\rangle|J_2, m_2\rangle$.
    - $C^{J_1J_2J}_{m_1m_2m}$ is a $(2J_1+1)(2J_2+1)$-dimensional unitary matrix, if we view (J, m) combination as row index, (m_1, m_2) combination as column index.
    - Selection rule: for non-zero $C^{J_1J_2J}_{m_1m_2m}$, $m = m_1 + m_2$, because $\hat{J}_z = \hat{J}_{1,z} + \hat{J}_{2,z}$; and J must be one of $|J_1 - J_2|$, $(|J_1 - J_2| + 1)$, …, $(J_1 + J_2)$.
    - By $0 = \hat{J}_+|J, J\rangle = (\hat{J}_{1,+} + \hat{J}_{2,+})\sum_{m_1,m_2} C^{J_1,J_2,J}_{m_1,m_2,m}|J_1, m_1\rangle|J_2, m_2\rangle$. We have $\sqrt{(J_1 - m_1 + 1)(J_1 + m_1)}C^{J_1,J_2,J}_{m_1-1,m_2,J} = -\sqrt{(J_2 - m_2 + 1)(J_2 + m_2)}C^{J_1,J_2,J}_{m_1,m_2-1,J}$. This solves all $C^{J_1,J_2,J}_{m_1,m_2,J}$ up to overall factor.
  - Example: two spin-1/2, total spin S can be $S = 0 = |\frac{1}{2} - \frac{1}{2}|$ (spin singlet) or $S = 1 = \frac{1}{2} + \frac{1}{2}$ (spin triplet). See §4.4.3.

IV. IDENTICAL PARTICLES (∼ CH.5)

- Generic N-particle wavefunction: $\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N, t)$, $\int |\psi|^2 \prod_i \mathrm{d}\boldsymbol{r}_i = 1$, $\mathrm{i}\hbar\frac{\partial}{\partial t}\psi = \hat{H}_N\psi$, and $\hat{H}_N = H_N(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1, \ldots, \hat{\boldsymbol{r}}_N, \hat{\boldsymbol{p}}_N)$, $\hat{H}_N\psi = H_N(\boldsymbol{r}_1, -\mathrm{i}\hbar\partial_{\boldsymbol{r}_1}, \ldots, \boldsymbol{r}_N, -\mathrm{i}\hbar\partial_{\boldsymbol{r}_N})\psi$.

- *Non-interacting particles*: $\hat{H}_N = \sum_{i=1}^N H_{1,i}(\hat{\boldsymbol{r}}_i, \hat{\boldsymbol{p}}_i)$. If $\hat{H}_{1,i}$ has eigenstates $\psi_{k_i,i}(\boldsymbol{r})$ with eigenvalue $E_{k_i,i}$ (k_i labels eigenstates of $\hat{H}_{1,i}$), then $\psi_{k_1,1}(\boldsymbol{r}_1)\cdots\psi_{k_N,N}(\boldsymbol{r}_N)$ is an eigenstate of $\hat{H}_N$ with eigenvalue $\sum_{i=1}^N E_{n_i,i}$. These direct product wavefunctions form complete orthonormal basis for N-particle Hilbert space of *distinguishable* particles.

  - Generic N-particle states will be superpositions of the direct product basis, and may be *entangled* (cannot be written as a direct product state).

- For *identialcal particles*, legitimate observables $\hat{O}_N(\hat{\boldsymbol{r}}_1, \hat{\boldsymbol{p}}_1, \ldots \hat{\boldsymbol{r}}_N, \hat{\boldsymbol{p}}_N)$ including $\hat{H}_N$ must be invariant under permutations of particle labels $1, 2, \ldots, N$, so that the particles are *indistinguishable*. For example, non-interacting $\hat{H}_N$ must be $\hat{H}_N = \sum_{i=1}^N H_1(\hat{\boldsymbol{r}}_i, \hat{\boldsymbol{p}}_i)$, the sum of identical 1-particle Hamiltonians for each particle.

  - For example, 2-particle potentials must be $\frac{1}{2}\sum_{i,j,i\neq j} V(\boldsymbol{r}_i, \boldsymbol{r}_j)$. Here the $\frac{1}{2}$ factor is to remove double-counting of the same (i, j) pair, and $V(\boldsymbol{r}_i, \boldsymbol{r}_j) = V(\boldsymbol{r}_j, \boldsymbol{r}_i)$.

- Permutation group S_N (not required): *permutation* σ, rearrangement of $\{1, \ldots, N\}$. $\sigma(i)$ for $i = 1, \ldots, N$ is also a number in $1, \ldots, N$, and $\sigma(i) \neq \sigma(j)$ for $i \neq j$. Also represented by $\begin{pmatrix} 1 & 2 & \cdots & n \\ \sigma(1) & \sigma(2) & \cdots & \sigma(n) \end{pmatrix}$. There are $N!$ distinct permutations in S_N.

  - Product $\sigma \cdot \mu$ (usually just $\sigma\mu$) of permutations σ and μ: $(\sigma \cdot \mu)(i) = \sigma(\mu(i))$.
  - Identity permutation $\mathbf{1}$: $\mathbf{1}(i) = i$. So $\sigma \cdot \mathbf{1} = \mathbf{1} \cdot \sigma = \sigma$.
  - Inverse σ^{-1} of a permutation σ: $\sigma^{-1} \cdot \sigma = \sigma \cdot \sigma^{-1} = \mathbf{1}$.
  - *Transposition* $\sigma_{i,j}$ ($i \neq j$): swap of i, j only, $\sigma(i) = j$, $\sigma(j) = i$, and $\sigma(k) = k$ for $k \neq i, j$. Note that $\sigma_{i,j} \cdot \sigma_{i,j} = \mathbf{1}$.
  - Any permutation can be represented as a (non-unique) product of transpositions. For example, $\begin{pmatrix} 1 & 2 & 3 & 4 \\ 4 & 3 & 1 & 2 \end{pmatrix} = \sigma_{2,4}\sigma_{1,3}\sigma_{1,2} = \sigma_{1,3}\sigma_{1,2}\sigma_{1,4} = \sigma_{3,4}\sigma_{2,3}\sigma_{3,4}\sigma_{1,2}\sigma_{2,3} = \ldots$.
  - Even(odd) permutations: product of even(odd) number of transpositions. *Signature (sign)* $\mathrm{sgn}(\sigma) = \pm 1$ for even(odd) permutation σ.

- For *identical particles*, a legitimate wavefunction $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$ should be invariant (up to overall complex phase factor) under permutations of particle labels $1, \ldots, N$.
  - $\psi(\boldsymbol{r}_{\sigma(1)}, \boldsymbol{r}_{\sigma(2)}, \ldots, \boldsymbol{r}_{\sigma(N)}) = R(\sigma) \cdot \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N)$, here $R(\sigma)$ is a complex phase factor ($|R(\sigma)| = 1$) that depends only on the permutation σ.
  - $R(\sigma\mu) = R(\sigma)R(\mu)$. Then $[R(\sigma_{i,j})]^2 = R(\mathbf{1}) = 1$, so $R(\sigma_{i,j}) = \pm 1$, and because $\sigma_{i',j'} = \sigma_{i,i'}\sigma_{j,j'}\sigma_{i,j}\sigma_{i,i'}\sigma_{j,j'}$, $R(\sigma_{i',j'}) = [R(\sigma_{i,i'})]^2[R(\sigma_{j,j'})]^2 R(\sigma_{i,j}) = R(\sigma_{i,j})$.
  - Bosons: $R(\sigma_{i,j}) = +1$, then $R(\sigma) = +1$ for permutation σ. ψ is fully symmetric.
  - Fermions: $R(\sigma_{i,j}) = -1$, then $R(\sigma) = \mathrm{sgn}(\sigma)$. ψ is fully anti-symmetric.
  - Given 1-particle basis $\psi_k(\boldsymbol{r})$ labeled by quantun number k, N-identical-particle state with 1 particle in ψ_{k_1}, 1 particle in ψ_{k_2}, ..., 1 particle in ψ_{k_N}, is:
    bosons: $\propto \sum_\sigma \psi_{k_1}(\boldsymbol{r}_{\sigma(1)}) \cdots \psi_{k_N}(\boldsymbol{r}_{\sigma(N)}) = \mathrm{perm}[\psi_{k_i}(\boldsymbol{r}_j)]$;
    fermions: $\frac{1}{\sqrt{N!}} \sum_\sigma \mathrm{sgn}(\sigma) \cdot \prod_{i=1}^N \psi_{k_i}(\boldsymbol{r}_{\sigma(i)}) = \frac{1}{\sqrt{N!}} \det[\psi_{k_i}(\boldsymbol{r}_j)]$. (Slater determinant)
  - Pauli exclusion principle: if $k_i = k_j$ for $i \neq j$, the above anti-symmetrized N fermion state vanishes. Fermions cannot occupy the same 1-particle state twice.

- Spinful wavefunctions: $\psi(\boldsymbol{r}_1, s_1; \boldsymbol{r}_2, s_2; \ldots; \boldsymbol{r}_N, s_N)$. Here s_i labels discrete internal states (*e.g.* spin) of particle i.
  - $\psi(\boldsymbol{r}_{\sigma(1)}, s_{\sigma(1)}; \ldots; \boldsymbol{r}_{\sigma(N)}, s_{\sigma(N)}) = \psi(\boldsymbol{r}_1, s_1; \ldots; \boldsymbol{r}_N, s_N)$ for bosons;
    $\psi(\boldsymbol{r}_{\sigma(1)}, s_{\sigma(1)}; \ldots; \boldsymbol{r}_{\sigma(N)}, s_{\sigma(N)}) = \mathrm{sgn}(\sigma) \cdot \psi(\boldsymbol{r}_1, s_1; \ldots; \boldsymbol{r}_N, s_N)$ for fermions.
  - Simple case: $\psi = \psi_{\mathrm{orbital}}(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)\chi_{\mathrm{spin}}(s_1, \ldots, s_N)$ factorizes into orbital and spin wavefunctions. Here χ_{spin} is a complex number for given $(s_1, \ldots, s_N)$. The permutation signs will be distributed to the orbital and spin wavefunctions.
  - For two spin-1/2 identical particles, the spin wavefunction can be anti-symmetric (spin singlet), $\chi_{\mathrm{spin}}(\uparrow, \downarrow) = -\chi_{\mathrm{spin}}(\downarrow, \uparrow) = \frac{1}{\sqrt{2}}$, $\chi_{\mathrm{spin}}(\uparrow, \uparrow) = \chi_{\mathrm{spin}}(\downarrow, \downarrow) = 0$, then ψ_{orbital} is anti-symmetric/symmetric for bosons/fermions respectively.
  - The spin triplet states for two spin-1/2 are symmetric. $|S = 1, S_z = 1\rangle = |\uparrow\uparrow\rangle$, $|S = 1, S_z = 0\rangle = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$, $|S = 1, S_z = -1\rangle = |\downarrow\downarrow\rangle$. Then $\psi_{\mathrm{orbital}}(\boldsymbol{r}_1, \boldsymbol{r}_2)$ is symmetric/anti-symmetric for bosons/fermions respectively.
  - For N spin-1/2, the highest total spin (total $S = \frac{N}{2}$) states are fully symmetric, $|S = \frac{N}{2}, S_z\rangle \propto (\hat{S}_-)^{\frac{N}{2} - S_z} |S = \frac{N}{2}, S_z = \frac{N}{2}\rangle = (\sum_i \hat{S}_{i,-})^{\frac{N}{2} - S_z} |\uparrow \ldots \uparrow\rangle$.

V. TIME-INDEPENDENT PERTURBATION THEORY (∼ CH.7)

- The problem: time-independent Hamiltonian $\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}^{(1)}$, λ is a "small" real parameter. $\hat{H}^{(0)}$ has complete orthonormal eigenstates $\psi_n^{(0)}$ with eigenvalues $E_n^{(0)}$. Solve the eigenvalues and eigenstates of $\hat{H}$ as (asymptotic) series of λ.

- Non-degenerate perturbation: energy level $E_n^{(0)}$ is non-degenerate. Assume the n-th eigenvalue for $\hat{H}$ is $E_n = E_n^{(0)} + \sum_{k=1}^{\infty} \lambda^k E_n^{(k)}$, and eigenstate $\psi_n \propto \psi_n^{(0)} + \sum_{k=1}^{\infty} \lambda^k \psi_n^{(k)}$.

  - Here $\psi_n^{(k)}$ is not normalized, and $\langle\psi_n^{(k)}|\psi_n^{(0)}\rangle = 0$ for $k \geq 1$ can be assumed without loss of generality: If $\langle\psi_n^{(k)}|\psi_n^{(0)}\rangle \neq 0$, define $|\tilde{\psi}_n^{(k)}\rangle = |\psi_n^{(k)}\rangle - |\psi_n^{(0)}\rangle\langle\psi_n^{(0)}|\psi_n^{(k)}\rangle$, then $\langle\tilde{\psi}_n^{(k)}|\psi_n^{(0)}\rangle = 0$, and $|\psi_n\rangle \propto (1 + \sum_{k=1}^{\infty} \lambda^k \langle\psi_n^{(0)}|\psi_n^{(k)}\rangle)|\psi_n^{(0)}\rangle + \sum_{k=1}^{\infty} \lambda^k |\tilde{\psi}_n^{(k)}\rangle$
    $\propto |\psi_n^{(0)}\rangle + \frac{1}{1+\sum_{k'=1}^{\infty} \lambda^{k'} \langle\psi_n^{(0)}|\psi_n^{(k')}\rangle} \sum_{k=1}^{\infty} \lambda^k |\tilde{\psi}_n^{(k)}\rangle$, the 2nd term is orthogonal to $\psi_n^{(0)}$ and can be re-expanded into Taylor series of λ.
  - Then $|\psi_n^{(k)}\rangle = \sum_{m,m\neq n} |\psi_m^{(0)}\rangle \cdot c_m^{(k)}$, for $k \geq 1$. And $c_m^{(k=0)} \equiv \delta_{m,n}$.
  - $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$ expanded to λ^k order is ($k \geq 1$),
    $\hat{H}^{(0)}|\psi_n^{(k)}\rangle + \hat{H}^{(1)}|\psi_n^{(k-1)}\rangle = \sum_{j=0}^{k} E_n^{(j)}|\psi_n^{(k-j)}\rangle$. [1]
  - Overlap Eq. [1] with $\langle\psi_n^{(0)}|$, use $\langle\psi_n^{(0)}|\hat{H}^{(0)} = E_n^{(0)}\langle\psi_n^{(0)}|$,
    $\langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(k-1)}\rangle = E_n^{(k)}$. [2]
    For $k > 1$, this is $\sum_{m,m\neq n}\langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_m^{(0)}\rangle c_m^{(k-1)} = E_n^{(k)}$.
  - Overlap Eq. [1] with $\langle\psi_m^{(0)}|$, for $m \neq n$,
    $\sum_{m',m'\neq n}\langle\psi_m^{(0)}|\hat{H}^{(1)}|\psi_{m'}^{(0)}\rangle c_{m'}^{(k-1)} - \sum_{j=1}^{k-1} E_n^{(j)} c_m^{(k-j)} = (E_n^{(0)} - E_m^{(0)})c_m^{(k)}$. [3]
  - $E_n^{(k)}$ and $c_m^{(k)}$ can be solved recursively from Eq. [2,3].
  - 1st order perturbation: $E_n^{(1)} = \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle$, $c_m^{(1)} = \frac{\langle\psi_m^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$.
  - 2nd order perturbation: $E_n^{(2)} = \sum_{m,m\neq n} \frac{\langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_m^{(0)}\rangle\langle\psi_m^{(0)}|\hat{H}^{(1)}|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$.
    2nd order perturbation always lowers the ground state energy, because the denominator is negative, and numerator $|\langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_m^{(0)}\rangle|^2$ is non-negative.
  - Side remark: each term in $E_n^{(k)}$ can be viewed as a "virtual" k-step transition process, starting and ending at $\psi_n^{(0}$. Each step contribute a matrix element of $\hat{H}^{(1)}$, and there are $k-1$ energy difference $E_n^{(0)}-$(intermediate state energy) in the denominator. For notation simplicity, define $T_{n,m} \equiv \langle\psi_n^{(0)}|\hat{H}^{(1)}|\psi_m^{(0)}\rangle$, $\Delta_{n,m} \equiv E_n^{(0)} - E_m^{(0)}$, and $\sum_m'$ as $\sum_{m,m\neq n}$. We have

  - ∗ 3rd order (not required): $E_n^{(3)} = \sum_m' \sum_p' \frac{T_{n,m}T_{m,p}T_{p,n}}{\Delta_{n,m}\Delta_{n,p}} - \sum_m' \frac{T_{n,m}T_{m,n}}{(\Delta_{n,m})^2} T_{n,n}$.
  - ∗ 4th order (not required): $E_n^{(4)} = \sum_m' \sum_p' \sum_q' \frac{T_{n,m}T_{m,p}T_{p,q}T_{q,n}}{\Delta_{n,m}\Delta_{n,p}\Delta_{n,q}}$
    $-(\sum_m' \sum_p' \frac{T_{n,m}T_{m,p}T_{p,n}}{(\Delta_{n,m})^2\Delta_{n,p}} - \sum_m' \frac{T_{n,m}T_{m,n}T_{n,n}}{(\Delta_{n,m})^3})T_{n,n} - \sum_m' \frac{T_{n,m}T_{m,n}}{(\Delta_{n,m})^2} \sum_p' \frac{T_{n,p}T_{p,n}}{\Delta_{n,p}}$.
- Non-degenerate perturbation theory is good for $|\langle\psi_n^{(0)}|\lambda\hat{H}^{(1)}|\psi_m^{(0)}\rangle| \ll |E_n^{(0)} - E_m^{(0)}|$.
- Example: harmonic oscillator under constant force,
  $\hat{H}^{(0)} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2} = \hbar\omega(\hat{a}_+\hat{a}_- + \frac{1}{2})$, $E_n^{(0)} = \hbar\omega(n+\frac{1}{2})$, $|\psi_n^{(0)}\rangle = \frac{(\hat{a}_+)^n}{\sqrt{n!}}|\psi_0^{(0)}\rangle$.
  $\lambda\hat{H}^{(1)} = -f\hat{x} = -f\sqrt{\frac{\hbar}{2m\omega}}(\hat{a}_+ + \hat{a}_-)$. (Let $\lambda = 1$ here, or view f as the parameter)
  - ∗ $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2(\hat{x}-f/m\omega^2)^2}{2} - \frac{f^2}{2m\omega^2}$. Exact eigenvalues are $E_n = \hbar\omega(n+\frac{1}{2}) - \frac{f^2}{2m\omega^2}$.
  - ∗ $T_{n,m} = -f\sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n}\delta_{n,m+1} + \sqrt{m}\delta_{n+1,m})$, $\Delta_{n,m} = \hbar\omega(n-m)$.
  - ∗ $E_n^{(1)} = T_{n,n} = 0$.
  - ∗ $E_n^{(2)} = \sum_p' \frac{T_{n,p}T_{p,n}}{\Delta_{n,p}} = (-f\sqrt{\frac{\hbar}{2m\omega}})^2(\frac{n}{\hbar\omega} + \frac{n+1}{-\hbar\omega}) = -\frac{f^2}{2m\omega^2}$, from $p = n \mp 1$.
  - ∗ Exercise (not required): check $E_n^{(3)} = 0$ and $E_n^{(4)} = 0$.
  - ∗ Note: $\hat{H}(-f) = \hat{I}\cdot\hat{H}(f)\cdot\hat{I}^{-1}$, where $\hat{I}$ is the unitary spatial-inversion operator $(x \to -x)$, then $E_n(-f) = E_n(f)$, odd-order perturbations must vanish.

- Degenerate perturbation: energy level $E_n^{(0)}$ is g-fold degenerate ($g > 1$), with orthonormal eigenstates $\psi_{n,i}^{(0)}$ ($i = 1, \ldots, g$). Assume an eigenvalue for $\hat{H}$ is $E_{n,i} = E_n^{(0)} + \sum_{k=1}^{\infty} \lambda^k E_{n,i}^{(k)}$, and eigenstate $\psi_{n,i} \propto \sum_{j=1}^{g} \psi_{n,j}^{(0)} c_{j,i} + \sum_{k=1}^{\infty} \lambda^k \psi_{n,i}^{(k)}$, for $i = 1, \ldots, g$.
  - Here $\psi_{n,i}^{(k)}$ is not normalized, and $\langle\psi_{n,j}^{(0)}|\psi_{n,i}^{(k)}\rangle = 0$ for $k \geq 1$ for any $i, j = 1, \ldots, g$.
  - $c_{j,i}$ is a $g \times g$ unitary matrix to be solved. Define new basis for the degenerate subspace, $|\tilde{\psi}_{n,i}^{(0)}\rangle = \sum_{j=1}^{g} |\psi_{n,j}^{(0)}\rangle c_{j,i}$. Then $\lim_{\lambda\to 0} \psi_{n,i} = \tilde{\psi}_{n,i}^{(0)}$.
  - Assume $|\psi_{n,i}^{(k)}\rangle = \sum_{m,m\neq n} |\psi_m^{(0)}\rangle c_{m,i}^{(k)}$, for $k \geq 1$.
  - Consider $\hat{H}|\psi_{n_i}\rangle = E_{n,i}|\psi_{n,i}\rangle$, for λ^1 order, overlap with $\langle\psi_{n,j'}^{(0)}|$, we have
  - 1st order *secular equation*: $\sum_{j=1}^{g} \langle\psi_{n,j'}^{(0)}|\hat{H}^{(1)}|\psi_{n,j}^{(0)}\rangle c_{j,i} = E_{n,i}^{(1)} c_{j',i}$.
    Each column of $c_{j,i}$ matrix is an eigenvector of $\hat{H}^{(1)}$ restricted on the degenerate subspace with $g \times g$ matrix element $\langle\psi_{n,j'}^{(0)}|\hat{H}^{(1)}|\psi_{n,j}^{(0)}\rangle$.
  - If the g eigenvalues $E_{n,i}^{(1)}$ of 1st order secular equation are non-degenerate, each column of $c_{j,i}$ (namely $|\tilde{\psi}_{n,i}^{(0)}\rangle$) is determined up to phase factors. Then higher order perturbations are given by non-degenerate perturbation theory under $\tilde{\psi}_{n,i}^{(0)}$ basis. For example, $|\psi_{n,i}^{(1)}\rangle = \sum_{m,m\neq n} |\psi_m^{(0)}\rangle \frac{\langle\psi_m^{(0)}|\hat{H}^{(1)}|\tilde{\psi}_{n,i}^{(0)}\rangle}{E_n^{(0)} - E_m^{(0)}}$, $E_{n,i}^{(2)} = \sum_{m,m\neq n} \frac{|\langle\psi_m^{(0)}|\hat{H}^{(1)}|\tilde{\psi}_{n,i}^{(0)}\rangle|^2}{E_n^{(0)} - E_m^{(0)}}$.

  - If some (or all) of $E^{(1)}_{n,i}$ are degenerate, we need to find proper basis in that degenerate subspace, $\tilde{\tilde{\psi}}^{(0)}_{n,i} = \sum_j \tilde{\psi}^{(0)}_{n,j}\tilde{c}_{j,i}$, from the 2nd order secular equation, $\sum_j \left(\sum_{m,m\neq n} \frac{\langle\tilde{\psi}^{(0)}_{n,j'}|\hat{H}^{(1)}|\psi^{(0)}_m\rangle\langle\psi^{(0)}_m|\hat{H}^{(1)}|\tilde{\psi}^{(0)}_{n,j}\rangle}{E^{(0)}_n - E^{(0)}_m} \right) \tilde{c}_{j,i} = E^{(2)}_{n,i}\tilde{c}_{j',i}$.
  - If there is an observable $\hat{A}$ that commutes with $\hat{H}^{(0)}$ and $\hat{H}^{(1)}$, then you can divide the Hilbert space by the different eigenvalues of $\hat{A}$, and degenerate perturbation theory may be avoided in each subspace. See §7.2.2.
  - Almost-degenerate case: if the off-diagonal matrix element of perturbation is larger than energy difference between the two original levels connected by this matrix element, $|\langle\psi^{(0)}_n|\lambda\hat{H}^{(1)}|\psi^{(0)}_m\rangle| \gg |E^{(0)}_n - E^{(0)}_m|$, then these two levels should be treated by degenerate perturbation theory. See for example §7.4.2.

- Hellmann-Feynman theorem: if $\hat{H}_\lambda$ depends on parameter λ, and ψ_λ is the *non-degenerate normalized* n-th eigenstate with eigenvalue $E_n(\lambda)$, $\hat{H}_\lambda\psi_\lambda = E_n(\lambda)\psi_\lambda$, then $\frac{\partial}{\partial\lambda}E_n(\lambda) = \langle\psi_\lambda|\frac{\partial\hat{H}_\lambda}{\partial\lambda}|\psi_\lambda\rangle$.
  - Proof: take derivative w.r.t. λ on, $E_n(\lambda)\cdot\langle\psi_\lambda|\psi_\lambda\rangle = \langle\psi_\lambda|\hat{H}_\lambda|\psi_\lambda\rangle$. And then use $\hat{H}_\lambda|\psi_\lambda\rangle = E_n(\lambda)|\psi_\lambda\rangle$ and $\langle\psi_\lambda|\hat{H}_\lambda = \langle\psi_\lambda|E_n(\lambda)$.
  - This can be used to evaluate certain expectation values under energy eigenstates. For example, harmonic oscillator $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2}$ has eigenvalue $E_n = \hbar\omega\cdot(n+\frac{1}{2})$, then $\langle\psi_n|\hat{x}^2|\psi_n\rangle = \langle\psi_n|\frac{1}{m\omega}\frac{\partial\hat{H}}{\partial\omega}|\psi_n\rangle = \frac{1}{m\omega}\frac{\partial E_n}{\partial\omega} = \frac{\hbar}{m\omega}(n+\frac{1}{2})$.
  - The "$\frac{\partial}{\partial\lambda}$" needs careful treatment, on what other parameters to be held fixed. For example, to evaluate $\langle\frac{1}{r^2}\rangle$ in a eigenstate of a 3D central potential problem, you can formally take derivative w.r.t. the orbital angular momentum quantum number ℓ (although ℓ should be integers), because the radial equation is (see III), $-\frac{\hbar^2}{2m}[\frac{1}{r^2}\partial_r(r^2\partial_r) - \frac{\ell(\ell+1)}{r^2}]R(r) = E\cdot R(r)$, then $\langle\frac{1}{r^2}\rangle = \frac{2m}{\hbar^2(2\ell+1)}\frac{\partial E}{\partial\ell}$. However, when computing $\frac{\partial E}{\partial\ell}$, it is usually not the "principal quantum number" that should be held fixed. For the 3D harmonic oscillator and hydrogen atom problems, $(n-\ell)$ should be held fixed instead, because it labels the energy levels for a given ℓ. See Textbook Problem 7.42.

VI. VARIATIONAL PRINCIPLE (∼ CH.8)

- For a Hamiltonian (hermitian operator) $\hat{H}$, its ground state energy (lowest eigenvalue) $E_0 = \min_\psi \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$. Here $\min_\psi$ is the minimum with respect to all wavefunction ψ.
  - Conversely, for any ψ, $\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$. The equal sign happens if and only if ψ is (one of) the ground state(s).
  - In practice, we cannot go over all states ψ in the Hilbert space. Usually we compute the expectation value $E(\vec{\lambda}) \equiv \frac{\langle\psi(\vec{\lambda})|\hat{H}|\psi(\vec{\lambda})\rangle}{\langle\psi(\vec{\lambda})|\psi(\vec{\lambda})\rangle}$ under states $\psi(\vec{\lambda})$ parametrized by parameter $\vec{\lambda}$ (which can contain more than one parameters λ_i). Then $\min_{\vec{\lambda}} E(\vec{\lambda})$, the minimum of $E(\vec{\lambda})$ with respect to $\vec{\lambda}$, can be a good approximation (upper bound) for the ground state energy.
  - In practice, we may not obtain the analytic formula for $E(\vec{\lambda})$. And some times $E(\vec{\lambda})$ has to be evaluated by Monte Carlo with statistical error.
  - To minimize $E(\vec{\lambda})$, it may be helpful to know its gradient $\frac{\partial}{\partial\lambda_i}E(\vec{\lambda})$, and then use methods like "steepest descent". Similar to the Hellmann-Feynman theorem, $\frac{\partial}{\partial\lambda_i}E(\vec{\lambda}) = \frac{2}{\langle\psi(\vec{\lambda})|\psi(\vec{\lambda})\rangle}\{\mathrm{Re}[\langle\psi(\vec{\lambda})|\hat{H}|\frac{\partial}{\partial\lambda_i}\psi(\vec{\lambda})\rangle] - E(\vec{\lambda})\cdot\mathrm{Re}[\langle\psi(\vec{\lambda})|\frac{\partial}{\partial\lambda_i}\psi(\vec{\lambda})\rangle]\}$.
    If $\psi(\vec{\lambda})$ is always normalized, the second term vanishes.
  - Although you may get very accurate ground state energy by this variational method, the wavefunction you get may not be very accurate approximation to the true ground state wavefunction. Example: $\hat{H}$ has two levels $E_0 < E_1$ with orthonormal eigenstates $\psi_{0,1}$, take a not-very-accurate $\psi = \psi_0 + 0.1\psi_1$, then the expectation value $\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = E_0 + \frac{0.01}{1.01}(E_1 - E_0)$ is very close to E_0.
- Extension (see Textbook Problem 8.4): once we find a good approximation $\tilde{\psi}_0$ to the ground state, then the first excited state energy can be *approximated* by $\min_{\psi,\langle\psi|\tilde{\psi}_0\rangle=0} \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$. Here the minimum is taken in the subspace orthogonal to $\tilde{\psi}_0$.
  - Related theorem (not required) (see *e.g.* Section I.4 of "Methods of Mathematical Physics" volume I by Courant & Hilbert): Hermitian $\hat{H}$ in n-dimensional Hilbert space has eigenvalues $E_1 \leq E_2 \leq \cdots \leq E_n$. Restrict $\hat{H}$ onto a $(n-1)$ dimensional subspace (orthogonal to one state in original Hilbert space), with new eigenvalues $E'_1 \leq E'_2 \leq \cdots \leq E'_{n-1}$. Then $E_1 \leq E'_1 \leq E_2 \leq E'_2 \leq \cdots \leq E'_{n-1} \leq E_n$.

VII. THE WKB APPROXIMATION (∼ CH.9)

- Consider eigenvalue problem of $\hat{H} = -\frac{\hbar^2}{2m}\partial_x^2 + V(x)$, $\hat{H}\psi(x) = E \cdot \psi(x)$.

- The eigenstate "wave" function is $\psi(x) = A(x) \cdot e^{\mathbb{i}\phi(x)}$, where A,ϕ are real functions (amplitude and phase). Rewrite it as $\psi(x) = A_0 e^{\mathbb{i}u(x)}$, where $u(x) = \phi(x) - \mathbb{i}\log\frac{A(x)}{A_0}$ is a complex function. The Schrödinger equation becomes $(\frac{\mathrm{d}u}{\mathrm{d}x})^2 - \mathbb{i}\frac{\mathrm{d}^2u}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}[E - V(x)]$. Define $K(x) \equiv \sqrt{\frac{2m}{\hbar^2}[E - V(x)]}$ and $\kappa(x) \equiv \sqrt{\frac{2m}{\hbar^2}[V(x) - E]}$.

- *Assume* $|\frac{\mathrm{d}^2u}{\mathrm{d}x^2}| \ll |(\frac{\mathrm{d}u}{\mathrm{d}x})^2|$, this equation can be solved recursively, $\frac{\mathrm{d}}{\mathrm{d}x}u_0 = \pm K(x)$; and $\frac{\mathrm{d}}{\mathrm{d}x}u_{n+1} = \pm\sqrt{[K(x)]^2 + \mathbb{i}\frac{\mathrm{d}^2}{\mathrm{d}x^2}u_n}$, for $n = 0, 1, \ldots$. In particular, $\frac{\mathrm{d}}{\mathrm{d}x}u_1 = \pm\sqrt{[K(x)]^2 + \mathbb{i}\frac{\mathrm{d}^2}{\mathrm{d}x^2}u_0} = \pm\sqrt{[K(x)]^2 \pm \mathbb{i}\frac{\mathrm{d}}{\mathrm{d}x}K(x)}$.

- *Assume* $|\frac{\mathrm{d}}{\mathrm{d}x}K(x)| \ll |[K(x)]^2|$, the 1st order result is $\frac{\mathrm{d}}{\mathrm{d}x}u_1 \approx \pm K(x) + \mathbb{i}\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}x}\log[K(x)]$. We get the WKB approximation, $\psi(x) \propto \frac{1}{\sqrt{K(x)}}\exp[\pm\mathbb{i}\int^x K(x')\mathrm{d}x']$.

  - Classically-allowed region: $E > V(x)$. $K(x)$ is real (local wavevector), ψ is traveling waves (to the right/left for $\pm$ sign). The probability amplitude $|\psi(x)|^2$ is inversely proportional to the classical velocity $\sqrt{\frac{2[E-V(x)]}{m}}$ at x. The probability current for $\frac{A}{\sqrt{K(x)}}e^{\pm\mathbb{i}\int^x K(x')\mathrm{d}x'}$ is a constant $\pm|A|^2$.
  - Classically-forbidden region: $E < V(x)$. $K(x) = \mathbb{i}\kappa(x)$ is pure imaginary, ψ is exponentially decaying/growing functions $\frac{1}{\sqrt{\mathbb{i}\kappa(x)}}\exp[\mp\int^x \kappa(x)\mathrm{d}x]$.
  - Close to the *turning point* [where $V(x) = E$], the above assumptions and the WKB approximation does not work.

- Connection formula: consider a turning point x_0, with $V(x) \sim E + V'(x_0)(x - x_0)$ around it. First consider the case $V'(x_0) > 0$, define $z = (\frac{2mV'(x_0)}{\hbar^2})^{1/3}(x - x_0)$.

  - ψ approximately satisfy the *Airy's equation*, $\frac{\mathrm{d}^2}{\mathrm{d}z^2}\psi = z \cdot \psi$. The solution is $\psi = a \cdot \mathrm{Ai}(z) + b \cdot \mathrm{Bi}(z)$. Here Ai, Bi are *Airy functions*, with asymptotic behavior:
    for $z \gg 0$, $\mathrm{Ai}(z) \sim \frac{1}{2\sqrt{\pi}z^{1/4}}e^{-\frac{2}{3}z^{3/2}}$, $\mathrm{Bi}(z) \sim \frac{1}{\sqrt{\pi}z^{1/4}}e^{\frac{2}{3}z^{3/2}}$;
    for $z \ll 0$, $\mathrm{Ai}(z) \sim \frac{1}{\sqrt{\pi}(-z)^{1/4}}\sin[\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}]$, $\mathrm{Bi}(z) \sim \frac{1}{\sqrt{\pi}(-z)^{1/4}}\cos[\frac{2}{3}(-z)^{3/2} + \frac{\pi}{4}]$.
  - For $x \gg x_0$, $\psi(x)$ is linear superposition of $\frac{1}{\sqrt{\kappa(x)}}\exp(\mp\int_{x_0}^x \kappa(x')\mathrm{d}x')$, decays/grows exponentially, and $\int_{x_0}^x \kappa(x')\mathrm{d}x' \approx \frac{2}{3}z^{3/2}$.

  - For $x \ll x_0$, $\psi(x)$ is linear superposition of $\frac{1}{\sqrt{K(x)}}\exp(\mp\mathbb{i}\int_x^{x_0} K(x')\mathrm{d}x')$, traveling to the right/left, and $\int_x^{x_0} K(x')\mathrm{d}x' \approx \frac{2}{3}(-z)^{3/2}$.
  - Match the Airy functions asymptotic form with the WKB results, where $|z| \gg 1$ but the linear approximation to $V(x)$ is still good (possible when $\hbar \to 0$).

    For $V'(x_0) > 0$ case, $\psi(x) \sim \begin{cases} \frac{1}{\sqrt{K(x)}}\left\{2A\sin[\phi(x)+\frac{\pi}{4}]+B\cos[\phi(x)+\frac{\pi}{4}]\right\}, & x \ll x_0; \\ \frac{1}{\sqrt{\kappa(x)}}\left\{A\exp[-\gamma(x)]+B\exp[\gamma(x)]\right\}, & x \gg x_0. \end{cases}$

    where $\phi(x) \equiv \int_x^{x_0} K(x')\mathrm{d}x'$, and $\gamma(x) \equiv \int_{x_0}^{x} \kappa(x')\mathrm{d}x'$, are both positive.
  - For $V'(x_0) < 0$ case, $\psi(x) \sim \begin{cases} \frac{1}{\sqrt{K(x)}}\left\{2A\sin[\phi(x)+\frac{\pi}{4}]+B\cos[\phi(x)+\frac{\pi}{4}]\right\}, & x \gg x_0; \\ \frac{1}{\sqrt{\kappa(x)}}\left\{A\exp[-\gamma(x)]+B\exp[\gamma(x)]\right\}, & x \ll x_0. \end{cases}$

    but here $\phi(x) \equiv \int_{x_0}^{x} K(x')\mathrm{d}x'$, and $\gamma(x) \equiv \int_x^{x_0} \kappa(x')\mathrm{d}x'$, are both positive.

- Applications: tunneling through a smooth potential barrier.

  $V(x) > E$ for $a < x < b$; $V(x) < E$ otherwise. Assume incoming(A) and reflected(B) waves in $x < a$, and transmitted waves(F) in $x > b$. Define $\phi(x) \equiv \int_x^a K(x')\mathrm{d}x'$, and $\gamma(x) \equiv \int_a^x \kappa(x')\mathrm{d}x'$. And $\gamma \equiv \gamma(b) = \int_a^b \frac{1}{\hbar}\sqrt{2m[V(x)-E]}\mathrm{d}x$ is assumed to be large.

  $$\psi(x) \sim \begin{cases} \frac{1}{\sqrt{K(x)}}\left\{B\exp[\mathbb{i}(\phi(x)+\frac{\pi}{4})]+A\exp[-\mathbb{i}(\phi(x)+\frac{\pi}{4})]\right\}, & x \ll a; \\ \frac{1}{\sqrt{\kappa(x)}}\left\{\frac{\mathbb{i}(B-A)}{2}\exp[-\gamma(x)]+(B+A)\exp[\gamma(x)]\right\}, & a \ll x \ll b; \\ \frac{2}{\sqrt{K(x)}}F\exp[\mathbb{i}(\int_b^x K(x')\mathrm{d}x'+\frac{\pi}{4})], & x \gg b. \end{cases}$$

  Note that $\gamma(x) = \gamma - \int_x^b \kappa(x')\mathrm{d}x'$. The connection formula at b is: $\frac{\mathbb{i}(B-A)}{2}e^{-\gamma} = F$, and $(B+A)e^{\gamma} = \frac{\mathbb{i}F}{2}$. So $F = -\mathbb{i}\frac{4}{4e^{\gamma}+e^{-\gamma}}A \approx -\mathbb{i}Ae^{-\gamma}$, the transmission coefficient $T \equiv \frac{|F|^2}{|A|^2} \approx e^{-2\gamma}$.

- Applications: bound state in a smooth potential well.

  $V(x) < E$ for $a < x < b$; $V(x) > E$ otherwise. Define $\phi(x) \equiv \int_a^x K(x')\mathrm{d}x'$.

  $$\psi(x) \sim \begin{cases} \frac{1}{\sqrt{\kappa(x)}}A\exp[-\int_x^a \kappa(x')\mathrm{d}x'], & x \ll a; \\ \frac{2}{\sqrt{K(x)}}A\sin[\phi(x)+\frac{\pi}{4}] = \frac{2}{\sqrt{K(x)}}(-A)\sin[\int_x^b K(x')\mathrm{d}x' - \phi(b) - \frac{\pi}{4}], & a \ll x \ll b; \\ \frac{1}{\sqrt{\kappa(x)}}A'\exp[-\int_b^x \kappa(x')\mathrm{d}x'], & x \gg b. \end{cases}$$

  The connection formula at b is: $\phi(b) - \frac{\pi}{2} = n\pi$ and $A' = (-1)^n A$, with integer n. This is the *Bohr-Sommerfeld quantization condition* $\int_a^b \frac{1}{\hbar}\sqrt{2m[E-V(x)]}\mathrm{d}x = (n+\frac{1}{2})\pi$, or $\oint p\cdot\mathrm{d}x = (n+\frac{1}{2})h$, where $\oint$ is integrating over a closed classical trajectory in the phase space (x-p space).

VIII. QUANTUM DYNAMICS (∼ CH.11)

A. Time-dependent Perturbation Theory

- The problem: Hamiltonian $\hat{H}(t) = \hat{H}_0 + \lambda\hat{V}(t)$, λ is a "small" parameter. $\hat{H}^{(0)}$ has complete orthonormal eigenstates $\psi_n^{(0)}(\boldsymbol{r})$ with eigenvalues $E_n^{(0)}$. Assume the solution to $\mathrm{i}\hbar\frac{\partial}{\partial t}\psi = \hat{H}(t)\psi$ is $\psi(\boldsymbol{r},t) = \sum_n c_n(t)e^{-\mathrm{i}E_n^{(0)}t/\hbar}\psi_n^{(0)}(\boldsymbol{r})$. Solve the coefficients $c_n(t)$ as (asymptotic) series of λ.

- The differential equations for $c_n(t)$ is, $\frac{\mathrm{d}}{\mathrm{d}t}c_n(t) = -\frac{\mathrm{i}}{\hbar}\sum_m \lambda V_{n,m}(t)e^{\mathrm{i}\omega_{n,m}t}\cdot c_m(t)$.
  Here $V_{n,m}(t) \equiv \langle\psi_n^{(0)}|\hat{V}(t)|\psi_m^{(0)}\rangle$, $\omega_{m,n} \equiv \frac{1}{\hbar}(E_m^{(0)} - E_n^{(0)})$.
  Assume $c_n(t) = \sum_{k=0}^{\infty}\lambda^k c_n^{(k)}(t)$, and $c_n^{(0)}(t) = c_n(0)$, $c_n^{(k)}(t=0) = 0$ for $k \geq 1$.
  Then $c_n^{(k)}(t) = \int_0^t -\frac{\mathrm{i}}{\hbar}\sum_m V_{n,m}(t')e^{\mathrm{i}(E_n^{(0)}-E_m^{(0)})t'}\cdot c_m^{(k-1)}(t')\,\mathrm{d}t'$,
  this can in principle solve $c_n(t)$ to all orders of λ (Dyson series).

- "Sudden approximation": if $\hat{V}(t)$ is nonzero for a "short" period $0 < t < \epsilon$, and $\hat{V}(t)$ is "bounded" (for example, $\sqrt{\sum_m |V_{n,m}(t)|^2} \leq V_0 < +\infty$, for any n), then $|c_n(\epsilon) - c_n(0)| \leq \frac{1}{\hbar}\lambda V_0\epsilon$, the final state equals to the initial state when $\epsilon \to 0$.

- "Pulse" perturbation (see Textbook Problem 11.4): $\hat{V}(t) = \hat{V}_0\cdot f(t)$, here $\hat{V}_0$ is independent of t, and $f(t) \sim \delta(t)$ has a "sharp" peak at $t = 0$ with $\int f(t)\mathrm{d}t = 1$. Then the above series expansion solution does not work. If the peak width $\epsilon \ll \frac{1}{\omega_{m,n}}$, then for $-\epsilon < t < \epsilon$, the equation is approximately $\frac{\mathrm{d}}{\mathrm{d}t}c_n(t) = f(t)\cdot\sum_m \frac{-\mathrm{i}}{\hbar}(\hat{V}_0)_{n,m}\cdot c_m(t)$. The solution is $c_n(\epsilon) = \exp[\int_{-\epsilon}^{\epsilon} f(t)\mathrm{d}t\cdot\sum_m \frac{-\mathrm{i}}{\hbar}(\hat{V}_0)]_{n,m}\cdot c_m(-\epsilon) = \exp[\frac{-\mathrm{i}}{\hbar}(\hat{V}_0)]_{n,m}\cdot c_m(-\epsilon)$. Here $\exp[\frac{-\mathrm{i}}{\hbar}(\hat{V}_0)]$ is the exponential of the constant matrix $\frac{-\mathrm{i}}{\hbar}(\hat{V}_0)$.

- Transition probability, $P_{n\to m}(t)$: initial ($t = 0$) state is one of original eigenstates, $c_m(0) = \delta_{m,n}$, turn on the perturbation for time up to t, the final probability $|c_m(t)|^2$ is the "transition probability from initial state n to final state m over time t" ($m \neq n$).

- Transition rate, $\Gamma_{n\to m} \equiv \lim_{t\to+\infty}\frac{P_{n\to m}(t)}{t}$.

- Usually just use the 1st order result: $c_n(t) \approx c_n(0) + \sum_m \frac{-\mathrm{i}}{\hbar}\int_0^t \lambda V_{n,m}(t')e^{\mathrm{i}\omega_{n,m}t'}\mathrm{d}t'\cdot c_m(0)$.
  Then the transition probability $P_{n\to m}(t) \approx |\frac{-\mathrm{i}}{\hbar}\int_0^t \lambda V_{m,n}(t')e^{\mathrm{i}\omega_{m,n}t'}\mathrm{d}t'|^2$.

- Harmonic perturbation: $\hat{V}(t) = \hat{V}_+e^{-\mathrm{i}\omega t} + \hat{V}_-e^{\mathrm{i}\omega t}$. $\hat{V}_- = (\hat{V}_+)^\dagger$ are time-independent.
  Then $\frac{-\mathrm{i}}{\hbar}\int_0^t \lambda V_{m,n}(t')e^{\mathrm{i}\omega_{m,n}t'}\mathrm{d}t' = \frac{-\mathrm{i}}{\hbar}[(\lambda V_+)_{m,n}\frac{e^{\mathrm{i}(\omega_{m,n}-\omega)t}-1}{\omega_{m,n}-\omega} + (\lambda V_-)_{m,n}\frac{e^{\mathrm{i}(\omega_{m,n}+\omega)t}-1}{\omega_{m,n}+\omega}]$.

$P_{n\to m}(t) = \frac{1}{\hbar^2}\left[|(\lambda V_+)_{m,n}|^2 \cdot \frac{4\sin^2(\frac{(\omega_{m,n}-\omega)t}{2})}{(\omega_{m,n}-\omega)^2} + |(\lambda V_-)_{m,n}|^2 \cdot \frac{4\sin^2(\frac{(\omega_{m,n}+\omega)t}{2})}{(\omega_{m,n}+\omega)^2} + (\text{cross terms})\right]$.
Use $\lim_{t\to+\infty}\frac{\sin^2(xt)}{x^2 t} = \pi\delta(x)$, we have the "Fermi's golden rule":
$\Gamma_{n\to m} = \frac{2\pi}{\hbar}\left[|(\lambda V_+)_{m,n}|^2\delta(E_m^{(0)} - E_n^{(0)} - \hbar\omega) + |(\lambda V_-)_{m,n}|^2\delta(E_m^{(0)} - E_n^{(0)} + \hbar\omega)\right]$.

- Under 1st order approximation, the system can absorb or emit one energy quantum $\hbar\omega$ (*e.g.* one photon) in the transition.
- *Lifetime* of a state: the total "decay rate" of state n is $\Gamma_n \equiv \sum_{m,m\neq n}\Gamma_{n\to m}$. Then $P_{n\to n}(t) \sim (1-\Gamma_n t) \sim e^{-\Gamma_n t}$, the *lifetime* of state n is $\tau_n = \frac{1}{\Gamma_n}$. This can be formally represented by an imaginary part of energy, $-\mathbb{i}\frac{\Gamma_n\hbar}{2}$.
- About the δ functions: define *density of states* $\rho(E) = \sum_m \delta(E - E_m^{(0)})$, here $\sum_m$ may be an integral, define average square matrix element from state n to energy level E, $\overline{|(\lambda V_\pm)_{n\to E}|^2} \equiv \frac{1}{\rho(E)}\sum_m \delta(E-E_m^{(0)})|(\lambda V_\pm)_{m,n}|^2$, then the 1st order result is, $\Gamma_n = \frac{2\pi}{\hbar}\rho(E_n^{(0)}+\hbar\omega)\overline{|(\lambda V_+)_{n\to(E_n^{(0)}+\hbar\omega)}|^2} + \frac{2\pi}{\hbar}\rho(E_n^{(0)}-\hbar\omega)\overline{|(\lambda V_-)_{n\to(E_n^{(0)}-\hbar\omega)}|^2}$.
- Detailed balance (§11.3): $\Gamma_{n\to m} = \Gamma_{m\to n}$. Absorption rate = emission rate.

- (§11.2) Application: coupling to classical electromagnetic wave (see also Sakurai's "Modern Quantum Mechanics", Section 5.7).
  - Time-dependent electrostatic potential $\phi(\boldsymbol{r},t)$ and vector potential $\boldsymbol{A}(\boldsymbol{r},t)$. Electric field $\boldsymbol{E} = -\nabla\phi - \frac{\partial\boldsymbol{A}}{\partial t}$, magnetic field $\boldsymbol{B} = \nabla\times\boldsymbol{A}$.
  - Hamiltonian for a non-relativistic particle with mass m and electric charge q, $\hat{H} = \frac{\hat{\boldsymbol{P}}^2}{2m} + q\phi(\boldsymbol{r},t) + V(\boldsymbol{r})$. $\hat{\boldsymbol{P}} \equiv -\mathbb{i}\hbar\nabla - q\boldsymbol{A}$. $[\hat{P}_a, \hat{P}_b] = \mathbb{i}\hbar q\epsilon_{abc}B_c$. Under Coulomb gauge($\nabla\cdot\boldsymbol{A} = 0$), $\hat{H} = [\frac{1}{2m}\hat{\boldsymbol{p}}^2 + V(\boldsymbol{r})] + [q\phi(\boldsymbol{r},t) - \frac{q}{m}\boldsymbol{A}(\boldsymbol{r},t)\cdot\hat{\boldsymbol{p}} + \frac{q^2}{2m}\boldsymbol{A}^2]$.
    - The Schrödinger equation is preserved under "gauge transformation", $\boldsymbol{A}\to\boldsymbol{A} + \frac{\hbar}{q}\nabla\theta$, $\phi\to\phi - \frac{\hbar}{q}\frac{\partial}{\partial t}\theta$, $\psi\to e^{\mathbb{i}\theta}\psi$, where $\theta = \theta(\boldsymbol{r},t)$. Exercise: check $\hat{\boldsymbol{P}}\psi\to e^{\mathbb{i}\theta}\hat{\boldsymbol{P}}\psi$, $(\mathbb{i}\hbar\frac{\partial}{\partial t} - q\phi)\psi \to e^{\mathbb{i}\theta}(\mathbb{i}\hbar\frac{\partial}{\partial t} - q\phi)\psi$.
    - Classical equations of motion: Exercise: check that $\hat{H}$ produces, $m\frac{\mathrm{d}^2}{\mathrm{d}t^2}\langle\boldsymbol{r}\rangle = -\langle\nabla V\rangle + q\langle\boldsymbol{E}\rangle + q\langle\frac{\hat{\boldsymbol{P}}}{m}\times\boldsymbol{B}\rangle$, for time-independent fields.
  - Monochromatic linear-polarized electromagnetic wave: choose $\phi(\boldsymbol{r},t) = 0$, $\boldsymbol{A}(\boldsymbol{r},t) = 2A_0\boldsymbol{\mathcal{E}}\cos(\frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r} - \omega t)$, here $\boldsymbol{\mathcal{E}}$ is a unit vector (polarization vector), $\boldsymbol{n}$ is another unit vector (propagation direction), and $\boldsymbol{n}\cdot\boldsymbol{\mathcal{E}} = 0$ (transverse wave). Then $\boldsymbol{E}(\boldsymbol{r},t) = 2A_0\omega\boldsymbol{\mathcal{E}}\sin(\frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r} - \omega t)$.

- Ignore $\boldsymbol{A}^2$ term, treat $[-\frac{q}{m}\boldsymbol{A}(\boldsymbol{r},t)\cdot\hat{\boldsymbol{p}}]$ as time-dependent perturbation, for monochromatic wave, it is a harmonic perturbation, $\hat{V}_+ = -\frac{q}{m}A_0 e^{\mathbb{i}\frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r}}\boldsymbol{\mathcal{E}}\cdot\hat{\boldsymbol{p}}$.
- Electric dipole approximation: when the relevant wavelength $\lambda = \frac{c}{\omega}$ is much larger than relevant wavefunctions' length scale, we can approximate $e^{\mathbb{i}\frac{\omega}{c}\boldsymbol{n}\cdot\boldsymbol{r}} \sim 1$. Then $(\hat{V}_+)_{m,n} = -qA_0\boldsymbol{\mathcal{E}}\cdot\langle\psi_m^{(0)}|\frac{\hat{\boldsymbol{p}}}{m}|\psi_n^{(0)}\rangle = -qA_0\boldsymbol{\mathcal{E}}\cdot\langle\psi_m^{(0)}|\frac{\mathbb{i}}{\hbar}[\hat{H}_0,\hat{\boldsymbol{r}}]|\psi_n^{(0)}\rangle$
  $= -\mathbb{i}\omega_{m,n}A_0\boldsymbol{\mathcal{E}}\cdot\langle\psi_m^{(0)}|q\boldsymbol{r}|\psi_n^{(0)}\rangle$. Here $\omega_{m,n}\equiv\frac{E_m^{(0)}-E_n^{(0)}}{\hbar}$. At resonance, $\omega_{m,n}=\pm\omega$, then $(\hat{V}_+)_{m,n} = \mp\frac{\mathbb{i}}{2}\boldsymbol{E}_0\cdot\mathbf{p}_{m,n}$, where $\boldsymbol{E}_0 = 2A_0\omega\boldsymbol{\mathcal{E}}$ is the amplitude of electric field, $\mathbf{p}_{m,n}\equiv\langle\psi_m^{(0)}|q\boldsymbol{r}|\psi_n^{(0)}\rangle$ is the electric dipole matrix element. This justifies formulas (11.39-11.40) in §11.2.1.
  - For hydrogen atom problem, $V(\boldsymbol{r}) = -\frac{Zq^2}{4\pi\epsilon_0 r}$, wavefunctions length scale is $R_{\text{atom}}\sim\frac{a_0}{Z}$, where a_0 is Bohr radius, relevant energy scale $\hbar\omega\sim\frac{Zq^2}{4\pi\epsilon_0(a_0/Z)}$, so $\frac{R_{\text{atom}}}{\lambda}\sim Z\cdot\alpha$, where $\alpha\equiv\frac{q^2}{4\pi\epsilon_0\hbar c}\sim\frac{1}{137}$ is fine-structure constant. For light atoms (small Z), we can use the electric dipole approximation.
- The energy density for this electromagnetic wave is $u = \frac{\epsilon_0}{2}E_0^2$. So
  $\Gamma_{n\to m} = u\cdot\frac{\pi}{\epsilon_0\hbar}|\mathbf{p}_{m,n}|^2[\delta(E_m^{(0)}-E_n^{(0)}-\hbar\omega)+\delta(E_m^{(0)}-E_n^{(0)}+\hbar\omega)]$.
  For incoherent electromagnetic radiation (§11.2.3), with frequency distribution $\rho(\omega)$ for energy density, (energy density for frequency in $[\omega,\omega+\mathrm{d}\omega]$ is $\rho(\omega)\mathrm{d}\omega$), the "stimulated" transition rate is $\Gamma_{n\to m} = \frac{\pi}{3\epsilon_0\hbar^2}|\mathbf{p}_{m,n}|^2\rho(|\omega_{m,n}|)$.
- Spontaneous emission (§11.3): rate "A"$= \frac{\pi}{3\epsilon_0\hbar^2}|\mathbf{p}_{m,n}|^2\cdot\hbar\omega\cdot\rho_0(\omega)$, where ρ_0 is the "density of states" for photons, $\frac{\omega^2}{\pi^2c^3}$. This can be viewed as coupling to zero-point fluctuation of electromagnetic fields.

- (§11.3.3) Dipole selection rule: for central potential problem, states $\psi_{n\ell m}$ are labeled by "principal quantum number" n, orbital angular momentum quantum number ℓ, and magnetic quantum number m. Conservation of angular momentum restricts possible nonzero dipole matrix elements $\langle\psi_{n'\ell'm'}|\boldsymbol{r}|\psi_{n\ell m}\rangle$.
  - Nonzero $\langle\psi_{n'\ell'm'}|\hat{z}|\psi_{n\ell m}\rangle$ must have $m'=m$, because $[\hat{L}_z,\hat{z}]=0$, then $0=\langle\psi_{n'\ell'm'}|[\hat{L}_z,\hat{z}]|\psi_{n\ell m}\rangle = (m'-m)\hbar\langle\psi_{n'\ell'm'}|\hat{z}|\psi_{n\ell m}\rangle$.
  - Nonzero $\langle\psi_{n'\ell'm'}|\hat{x}|\psi_{n\ell m}\rangle = (m'-m)\mathbb{i}\langle\psi_{n'\ell'm'}|\hat{y}|\psi_{n\ell m}\rangle = (m'-m)^2\langle\psi_{n'\ell'm'}|\hat{x}|\psi_{n\ell m}\rangle$, must have $m'=m\pm1$, because $[\hat{L}_z,\hat{y}] = -\mathbb{i}\hbar\hat{x}$, $[\hat{L}_z,\hat{x}] = \mathbb{i}\hbar\hat{y}$.
  - Nonzero $\langle\psi_{n'\ell'm'}|\boldsymbol{r}|\psi_{n\ell m}\rangle$ must have $\ell'=\ell\pm1$. (see §11.3.3)

B. Adiabatic Approximation (∼ §11.5)

- Adiabatic theorem: For $\mathrm{i}\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}(t)|\psi(t)\rangle$, if $\hat{H}(t)$ changes "slowly", and $\psi(t=0)$ is the n-th instantaneous eigenstate of $\hat{H}(t=0)$, then $\psi(t)$ will remain to be the n-th instantaneous eigenstate of $\hat{H}(t)$.
  - Suppose $|\psi_{n,t}\rangle$ is the n-th instantaneous eigenstate of $\hat{H}(t)$,
    $\hat{H}(t)|\psi_{n,t}\rangle = E_n(t)|\psi_{n,t}\rangle$. [4]
    Define $\theta_n(t) = \frac{1}{\hbar}\int_0^t E_n(t')\mathrm{d}t'$. Assume $|\psi(t)\rangle = \sum_n c_n(t)e^{-\mathrm{i}\theta_n(t)}|\psi_{n,t}\rangle$. Then
    $\frac{\mathrm{d}}{\mathrm{d}t}c_m(t) = -\sum_n c_n(t)e^{\mathrm{i}[\theta_m(t)-\theta_n(t)]}\langle\psi_{m,t}|\frac{\partial}{\partial t}\psi_{n,t}\rangle$. [5]
    Take $\frac{\partial}{\partial t}$ on Eq. [4], overlap with $\langle\psi_{m,t}|$, for $m\neq n$, $\langle\psi_{m,t}|\frac{\partial}{\partial t}\psi_{n,t}\rangle = \frac{\langle\psi_{m,t}|\frac{\partial\hat{H}}{\partial t}|\psi_{n,t}\rangle}{E_n(t)-E_m(t)}$.
    $\frac{\mathrm{d}}{\mathrm{d}t}c_m(t) = -c_m(t)\langle\psi_{m,t}|\frac{\partial}{\partial t}\psi_{m,t}\rangle - \sum_{n,n\neq m} c_n(t)e^{\mathrm{i}[\theta_m(t)-\theta_n(t)]}\frac{\langle\psi_{m,t}|\frac{\partial\hat{H}}{\partial t}|\psi_{n,t}\rangle}{E_n(t)-E_m(t)}$. [6]
  - If $|\frac{\langle\psi_{m,t}|\frac{\partial\hat{H}}{\partial t}|\psi_{n,t}\rangle}{E_n(t)-E_m(t)}|\cdot(\text{time scale}) \ll 1$, the 2nd term in Eq. [6] can be ignored. Define $A_m(t) = -\mathrm{i}\langle\psi_{m,t}|\frac{\partial}{\partial t}\psi_{m,t}\rangle$, $\gamma_m(t) = \int_0^t A_m(t')\mathrm{d}t'$, then $c_m(t)\sim e^{-\mathrm{i}\gamma_m(t)}c_m(t=0)$. A_m and γ_m are real, $A_m-(A_m)^* = -\mathrm{i}\frac{\partial}{\partial t}(\langle\psi_{m,t}|\psi_{m,t}\rangle) = 0$.
- Berry's phase (γ_m above): If $\hat{H}$ depends on a vector parameter $\vec{R}(t)$, so instantaneous eigenvalues $E_n(\vec{R})$ and eigenstates $\psi_{n,\vec{R}}$ are also functions of $\vec{R}$.
  - $\gamma_n(T) = -\mathrm{i}\int_0^T\langle\psi_n|\nabla_{\vec{R}}\psi_n\rangle\cdot\frac{\mathrm{d}\vec{R}}{\mathrm{d}t}\,\mathrm{d}t = -\mathrm{i}\int_{\vec{R}(0)}^{\vec{R}(T)}\langle\psi_n|\nabla_{\vec{R}}\psi_n\rangle\cdot\mathrm{d}\vec{R} = \int_{\vec{R}(0)}^{\vec{R}(T)}\vec{A}_n(\vec{R})\cdot\mathrm{d}\vec{R}$. $\vec{A}_n \equiv -\mathrm{i}\langle\psi_n|\nabla_{\vec{R}}\psi_n\rangle$ is the "Berry connection" (analogue of vector potential). Here $\vec{A}_n$ is a vector in parameter space, $(\vec{A}_n)_i \equiv -\mathrm{i}\langle\psi_n|\frac{\partial}{\partial R_i}\psi_n\rangle$.
  - Gauge transformation: redefine $\tilde{\psi}_{n,\vec{R}} = e^{\mathrm{i}\theta(\vec{R})}\psi_{n,\vec{R}}$, then $\tilde{\vec{A}}_n = \vec{A}_n + \nabla_{\vec{R}}\theta$, $\tilde{\gamma_n} = \gamma_n + [\theta(\vec{R}(T)) - \theta(\vec{R}(0))]$.
  - For periodic evolution, $\vec{R}(T) = \vec{R}(0)$, the Berry's phase, $\gamma_n = \oint\vec{A}_n\cdot\mathrm{d}\vec{R}$, is well-defined modulo integer multiple of 2π. It only depends on the path in parameter space, independent of speed of evolution (is a "geometric phase").
  - By Stokes theorem, $\oint_{\text{closed path}}\vec{A}_n\cdot\mathrm{d}\vec{R} = \iint_{\text{area enclosed}}\vec{B}_n\cdot\mathrm{d}\vec{a}$, here $\vec{B}_n \equiv \nabla_{\vec{R}}\times\vec{A}_n$ is the "Berry curvature" (analogue of magnetic field, gauge invariant), $\mathrm{d}\vec{a}$ is area element for the surface enclosed by $\vec{R}(t)$.
  - The "cross product" of two vectors is a rank-2 antisymmetric tensor, $(\vec{A}\times\vec{A}')_{i,j} \equiv A_iA'_j - A_jA'_i = -(\vec{A}\times\vec{A}')_{j,i}$. So $(\vec{B}_n)_{i,j} \equiv \frac{\partial}{\partial R_i}(\vec{A}_n)_j - \frac{\partial}{\partial R_j}(\vec{A}_n)_i$. In 3D space, $\vec{B}_n$ is dual to a vector, $\frac{1}{2}\epsilon_{ijk}(\vec{B}_n)_{i,j}$.

- Area element $\mathrm{d}\vec{a}$ is also a rank-2 antisymmetric tensor, if the surface is defined by real parameters u, v as $\vec{R}(u,v)$, then $(\mathrm{d}\vec{a})_{i,j} = (\frac{\partial R_i}{\partial u}\frac{\partial R_j}{\partial v} - \frac{\partial R_j}{\partial u}\frac{\partial R_i}{\partial v})\mathrm{d}u\mathrm{d}v$. The surface integral's integrand is $\vec{B}_n \cdot \mathrm{d}\vec{a} \equiv \frac{1}{2}\sum_{i,j}(\vec{B}_n)_{i,j}(\mathrm{d}\vec{a})_{i,j}$.
- $\vec{B}_n = -\mathbb{i}[\langle\nabla_{\vec{R}}\psi_n|] \times [|\nabla_{\vec{R}}\psi_n\rangle] = -\mathbb{i}\sum_m \langle\nabla_{\vec{R}}\psi_n|\psi_m\rangle \times \langle\psi_m|\nabla_{\vec{R}}\psi_n\rangle$,
  namely, $(\vec{B}_n)_{i,j} = -\mathbb{i}(\langle\frac{\partial}{\partial R_i}\psi_n|\frac{\partial}{\partial R_j}\psi_n\rangle - \langle\frac{\partial}{\partial R_j}\psi_n|\frac{\partial}{\partial R_i}\psi_n\rangle)$
  $= -\mathbb{i}\sum_m(\langle\frac{\partial}{\partial R_i}\psi_n|\psi_m\rangle\langle\psi_m|\frac{\partial}{\partial R_j}\psi_n\rangle - \langle\frac{\partial}{\partial R_j}\psi_n|\psi_m\rangle\langle\psi_m|\frac{\partial}{\partial R_i}\psi_n\rangle)$,
  note the $m = n$ term does not contribute, because $\langle\psi_n|\nabla_{\vec{R}}\psi_n\rangle = -\langle\nabla_{\vec{R}}\psi_n|\psi_n\rangle$, so the "cross product" vanishes; for $m \neq n$, $\langle\psi_m|\nabla_{\vec{R}}\psi_n\rangle = \frac{\langle\psi_m|\nabla_{\vec{R}}\hat{H}|\psi_n\rangle}{E_n - E_m}$, similar to $\langle\psi_{m,t}|\frac{\partial}{\partial t}\psi_{n,t}\rangle$. Then $\vec{B}_n = -\mathbb{i}\sum_{m,m\neq n}\frac{\langle\psi_n|\nabla_{\vec{R}}\hat{H}|\psi_m\rangle\times\langle\psi_m|\nabla_{\vec{R}}\hat{H}|\psi_n\rangle}{(E_m-E_n)^2}$
- Sum of Berry curvatures for all eigenstates vanishes, $\sum_n \vec{B}_n = 0$.

- Example: spin-1/2, parameter $\vec{R}$ is unit 3D vector ($|\vec{R}| = 1$), $\hat{H}(\vec{R}) = \vec{R}\cdot\frac{2}{\hbar}\hat{\boldsymbol{S}}$.
  - Under $|\hat{S}_z = \pm\frac{\hbar}{2}\rangle$ eigenbasis ($|\uparrow\rangle, |\downarrow\rangle$), $\hat{H} = \vec{R}\cdot\boldsymbol{\sigma} = R_x\sigma_x + R_y\sigma_y + R_z\sigma_z$, here $\sigma_{x,y,z}$ are Pauli matrices. Then $\hat{H}^2 = \vec{R}^2\cdot\mathbb{1}_{2\times2} = \mathbb{1}_{2\times2}$, eigenvalues are $E_\pm = \pm1$.
  - If $\vec{R} = (\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta)$, then (up to complex phase factors),
    $|\psi_+(\vec{R})\rangle = \cos\frac{\theta}{2}|\uparrow\rangle + \sin\frac{\theta}{2}e^{\mathbb{i}\varphi}|\downarrow\rangle$, $|\psi_-(\vec{R})\rangle = -\sin\frac{\theta}{2}|\uparrow\rangle + \cos\frac{\theta}{2}e^{\mathbb{i}\varphi}|\downarrow\rangle$.
    $\langle\psi_+|\boldsymbol{\sigma}|\psi_+\rangle = \vec{R}$, $\langle\psi_-|\boldsymbol{\sigma}|\psi_-\rangle = -\vec{R}$. Also note that $\nabla_{\vec{R}}\hat{H} = \boldsymbol{\sigma}$.
  - Any spin-1/2 state $\psi_\uparrow|\uparrow\rangle + \psi_\downarrow|\downarrow\rangle$ is a $|\psi_+(\vec{R})\rangle$ state upto a complex phase factor. All inequivalent spin-1/2 states are faithfully parametrized by $\vec{R}$.
  - For the E_+ level, the Berry curvature $\vec{B}_+ = -\mathbb{i}\frac{\langle\psi_+|\boldsymbol{\sigma}|\psi_-\rangle\times\langle\psi_-|\boldsymbol{\sigma}|\psi_+\rangle}{(E_+-E_-)^2}$
    $= -\frac{\mathbb{i}}{4}[\langle\psi_+|\boldsymbol{\sigma}\times\boldsymbol{\sigma}|\psi_+\rangle - \langle\psi_+|\boldsymbol{\sigma}|\psi_+\rangle\times\langle\psi_+|\boldsymbol{\sigma}|\psi_+\rangle] = \frac{1}{4}\langle\psi_+|2\boldsymbol{\sigma}|\psi_+\rangle = \frac{1}{2}\vec{R}$.
  - For a closed path in the parameter space of $\vec{R}$ (unit sphere S^2, also called "Bloch sphere"), the Berry's phase $= (\frac{1}{2}$ of the surface area enclosed on the sphere).
  - $\iint_{\text{Bloch sphere}}\vec{B}_+\cdot\mathrm{d}\vec{a} = 2\pi \neq 0$. There is a "magnetic monopole" in the center ! So you CANNOT define a smooth single-valued $\vec{A}_+$ over entire sphere.
  - You can define $\vec{A}_+$ on the sphere excluding one point, *e.g.* the above $|\psi_+(\vec{R})\rangle$ produces $\vec{A}_+ = -\frac{1-\cos\theta}{2\sin\theta}\vec{e}_\varphi$, where $\vec{e}_\varphi$ is the unit vector along φ-direction, which is well-defined except at the "south pole" $\theta = \pi$.

- (§4.5.2) Aharonov-Bohm effect: for a closed path in real space, enclosing magnetic flux $\Phi = \oint \boldsymbol{A}(\boldsymbol{R})\cdot\mathrm{d}\boldsymbol{R}$, from a static magnetic field, adiabatically transporting a "local"

electron wavefunction (*e.g.* a bound state in a small potential well moving with $\boldsymbol{R}$) will generate Berry's phase $\frac{q\Phi}{\hbar}$, here q is the electric charge.

- Consider $\hat{H} = \frac{[\hat{\boldsymbol{p}} - q\boldsymbol{A}(\boldsymbol{r})]^2}{2m} + V(\boldsymbol{r})$, $\mathrm{i}\frac{\partial}{\partial t}\psi = \hat{H}\psi$, in a region with $\boldsymbol{B} = \nabla \times \boldsymbol{A} = 0$. Define $\psi'(\boldsymbol{r}) = e^{-\mathrm{i}\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \frac{q}{\hbar}\boldsymbol{A}(\boldsymbol{r}')\cdot \mathrm{d}\boldsymbol{r}'} \cdot \psi(\boldsymbol{r})$. Here the integral is from a fixed point $\boldsymbol{r}_0$ to $\boldsymbol{r}$ through a smooth path in the region. Then $\mathrm{i}\frac{\partial}{\partial t}\psi' = [\frac{\hat{\boldsymbol{p}}^2}{2m} + V(\boldsymbol{r})]\psi'$. By semi-classical (WKB-like) approximation, ψ for particle traveling along this path acquires total phase, $\int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \frac{1}{\hbar}\boldsymbol{p}\cdot \mathrm{d}\boldsymbol{r} + \int_{\boldsymbol{r}_0}^{\boldsymbol{r}} \frac{q}{\hbar}\boldsymbol{A}\cdot \mathrm{d}\boldsymbol{r}$, (kinetic phase) + ("A-B phase").
- If the region is "not simply connected" (has a hole, and magnetic fulx Φ through the hole, $\oint_{\text{hole}} \boldsymbol{A}\cdot \mathrm{d}\boldsymbol{r} = \Phi$). The "A-B phase" depends on path from $\boldsymbol{r}_0$ to $\boldsymbol{r}$, different paths around the hole produce interference pattern depending on Φ.
- Bohr-Sommerfeld quantization condition is, $\oint \boldsymbol{p}\cdot \mathrm{d}\boldsymbol{r} + \oint q\boldsymbol{A}\cdot \mathrm{d}\boldsymbol{r} = (n + \frac{1}{2})h$.
  For cyclotron motion, suppose the cyclotron orbit radius is r, angular frequency $\omega = qB/m$ (solved by $q\cdot r\omega \cdot B = m\cdot r\omega^2$), then $(mr\omega\cdot 2\pi r - q\pi r^2 B) = (n+\frac{1}{2})h$. This produces the exact Landau level energy, $E_n = \frac{m(r\omega)^2}{2} = \hbar\omega(n+\frac{1}{2})$.
- Magnetic flux changes "momentum" quantization [Textbook Eq. (10.74)]: use cylindrical coordinates (r,θ,z); magnetic flux Φ along $r=0$ line, $\boldsymbol{A} = \frac{\Phi}{2\pi r}\boldsymbol{e}_\theta$; particle is on a ring $(r=R, z=0)$, $\hat{H} = \frac{\hat{P}_\theta^2}{2m}$, $\hat{P}_\theta = -\mathrm{i}\hbar\frac{1}{r}\partial_\theta - \frac{q\Phi}{2\pi r}$. Wavefunction ψ must be periodic w.r.t. $\theta \mod 2\pi$. "Momentum" eigenvalues are $\hat{P}_\theta = \frac{2\pi\hbar n - q\Phi}{2\pi R}$, for integer n. Quantized energy levels depend on Φ. Adiabatically change Φ by $\Phi_0 \equiv \frac{2\pi\hbar}{q}$ (*magnetic flux quantum*) will shift the energy levels by one step in n.
- Dirac quantization condition for magnetic monopole: a real magnetic monopole with magnetic charge q_m at $\vec{r}=0$ will produce magnetic field $\vec{B} = \frac{\mu_0}{4\pi}\frac{q_m}{r^2}\frac{\vec{r}}{r}$ at $\vec{r}$. The magnetic flux through a sphere enclosing the monopole is $\Phi = \iint \vec{B}\cdot \mathrm{d}\vec{a} = \mu_0 q_m$. Consider a electric charge q_e moving around the monopole, *e.g.* along the equator, the A-B phase obtained can be computed by the magnetic flux either through the upper hemisphere or the lower hemisphere, $\frac{q_e\Phi_{\text{upper hemisphere}}}{\hbar} = \frac{\mu_0 q_m q_e}{2\hbar}$ or $-\frac{q_e\Phi_{\text{lower hemisphere}}}{\hbar} = -\frac{\mu_0 q_m q_e}{2\hbar}$. Therefore $q_m q_e = \frac{2\pi n\hbar}{\mu_0}$, for some integer n.
  - ∗ If there is one magnetic monopole q_m somewhere in the universe, then all electric charges must be quantized !

IX. SCATTERING (∼ CH.10)

- Hamiltonian is free particle kinetic energy plus a (short-ranged) scattering potential $V(\boldsymbol{r})$, we will consider only 3D non-relativistic particle here. $\hat{H} = \frac{\hat{\boldsymbol{p}}^2}{2m} + V(\boldsymbol{r})$.
  - We will only consider *elastic scattering* here. Scattering potential is time-independent. Particle's energy is conserved.
- Scattering can be viewed as (degenerate) time-independent perturbation problem: The eigenstate for energy $E = \frac{\hbar^2 k^2}{2m}$ is incoming plane wave $e^{\mathrm{i}kz}$ (assumed to be along $+z$ direction), plus outgoing scattered waves, $\psi(r,\theta,\phi) = e^{\mathrm{i}kz} + f(\theta,\phi)\frac{e^{\mathrm{i}kr}}{r}$.
  - Current density of incoming plane wave is $\frac{\hbar k}{m}$. Scattered particle current through a solid angle element $\mathrm{d}\Omega$ is $\frac{\hbar k}{m}|f(\theta,\phi)|^2\mathrm{d}\Omega$. The ratio is the ...
  - Differential cross section: $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = |f(\theta,\phi)|^2$. (See Textbook Figure 11.3)
  - Scattering cross section: $\sigma \equiv \int \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\mathrm{d}\Omega$. Total scattered particle current divided by incoming current density. Note: both $\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}$ and σ have units of "area".
- Scattering can also be viewed as time-dependent perturbation problem: Initial($t \to -\infty$) state is plane wave (broad wave packet) $e^{\mathrm{i}kz}$; slowly turn on/off the scattering potential, $e^{-\epsilon|t|}V(\boldsymbol{r})$, ($\epsilon \to 0+$); final($t \to +\infty$) state contains outgoing scattered waves and "forward scattering" (remnant of incoming wave).
- General solution: stationary Schrödinger equation becomes, $(\nabla^2 + k^2)\psi = \frac{2mV(\boldsymbol{r})}{\hbar^2}\psi$.
  - Define the Green's function: $G(\boldsymbol{r},\boldsymbol{r}')$ satisfies, $(\nabla^2_{\boldsymbol{r}} + k^2)G(\boldsymbol{r},\boldsymbol{r}') = -4\pi\delta(\boldsymbol{r}-\boldsymbol{r}')$. Note: $G(\boldsymbol{r},\boldsymbol{r}')$ as a function of $\boldsymbol{r}$ is a spherical wave emitted from $\boldsymbol{r}'$.
  - $G(\boldsymbol{r},\boldsymbol{r}') = G(\boldsymbol{r}-\boldsymbol{r}')$. Fourier transform $G(\boldsymbol{r})$, $g(\boldsymbol{k}') \equiv \frac{1}{(2\pi)^3}\int G(\boldsymbol{r})e^{-\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}}\mathrm{d}\boldsymbol{r}$, then $g(\boldsymbol{k}') = \frac{4\pi}{(2\pi)^3}\frac{1}{k'^2-k^2}$. But we need to avoid the poles at $k' = k$.
  - Green's function: $G_+(\boldsymbol{r}) = \frac{4\pi}{(2\pi)^3}\int \frac{1}{k'^2-(k^2+\mathrm{i}\epsilon)}e^{\mathrm{i}\boldsymbol{k}'\cdot\boldsymbol{r}}\mathrm{d}\boldsymbol{k}'$ ($\epsilon \to 0+$)
    $= \frac{1}{2\pi^2}\int_0^\infty (k')^2\mathrm{d}k' \int_{-1}^1 \mathrm{d}(\cos\theta)\int_0^{2\pi}\mathrm{d}\phi\, \frac{e^{\mathrm{i}k'r\cos\theta}}{k'^2-(k^2+\mathrm{i}\epsilon)} = \frac{1}{\mathrm{i}\pi r}\int_{-\infty}^{\infty}\frac{k'}{k'^2-(k^2+\mathrm{i}\epsilon)}e^{\mathrm{i}k'r}\mathrm{d}k' = \frac{e^{\mathrm{i}kr}}{r}$.
    This is an *outgoing* spherical wave.
  - Lippman-Schwinger equation: $\psi(\boldsymbol{r}) = \frac{e^{\mathrm{i}kz}}{(2\pi)^{3/2}} - \frac{1}{4\pi}\int G_+(\boldsymbol{r},\boldsymbol{r}')\frac{2mV(\boldsymbol{r}')}{\hbar^2}\psi(\boldsymbol{r}')\mathrm{d}\boldsymbol{r}'$. When $|\boldsymbol{r}| \gg |\boldsymbol{r}'|$, $|\boldsymbol{r}-\boldsymbol{r}'| \approx r - \frac{\boldsymbol{r}}{r}\cdot\boldsymbol{r}'$. Define outgoing wavevector $\boldsymbol{k}' = k\cdot\frac{\boldsymbol{r}}{r}$.

- $\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{(2\pi)^{3/2}}(e^{\mathbb{i}\boldsymbol{k}\cdot\boldsymbol{r}} + \frac{e^{\mathbb{i}kr}}{r} f(\boldsymbol{k}', \boldsymbol{k}))$. Here $\boldsymbol{k}$ ($\boldsymbol{k}'$) is incoming(outgoing) wavevector. The scattering amplitude $f(\boldsymbol{k}', \boldsymbol{k}) = -\frac{(2\pi)^{3/2}}{4\pi} \int e^{-\mathbb{i}\boldsymbol{k}'\cdot\boldsymbol{r}'} \frac{2mV(\boldsymbol{r}')}{\hbar^2} \psi_{\boldsymbol{k}}(\boldsymbol{r}') \mathrm{d}\boldsymbol{r}'$.

- (First-order) Born approximation:
  $f(\boldsymbol{k}', \boldsymbol{k}) \approx -\frac{(2\pi)^{3/2}}{4\pi} \int e^{-\mathbb{i}\boldsymbol{k}'\cdot\boldsymbol{r}'} \frac{2mV(\boldsymbol{r}')}{\hbar^2} \frac{e^{\mathbb{i}\boldsymbol{k}\cdot\boldsymbol{r}}}{(2\pi)^{3/2}} \mathrm{d}\boldsymbol{r}' = -\frac{m}{2\pi\hbar^2} \int e^{-\mathbb{i}\boldsymbol{q}\cdot\boldsymbol{r}'} V(\boldsymbol{r}') \mathrm{d}\boldsymbol{r}'$.
  Here $\boldsymbol{q} = \boldsymbol{k}' - \boldsymbol{k}$ is the "momentum transfer". For central potential $V(r)$,
  $f(\boldsymbol{k}', \boldsymbol{k}) \approx f(q) = -\frac{2m}{\hbar^2} \int_0^\infty \frac{r\sin(qr)}{q} V(r) \mathrm{d}r$, depends only on $q = |\boldsymbol{q}| = 2k\sin(\frac{\theta}{2})$.
  - Range of validity of Born approximation: need "$\frac{1}{r} f(\boldsymbol{k}', \boldsymbol{k})$" to be small in the range of V. Consider a finite-range $V(r)$, $|V(r)| \le V_0$, and $V(r > a) = 0$.
    For small q, we need $\frac{2mV_0 a^2}{\hbar^2} \ll 1$; for large q, we need $\frac{2mV_0}{\hbar^2 q^2} \ll 1$.
  - Example: Coulomb potential (Rutherford scattering, Textbook Example 11.6).
    $V(r) = -\frac{A}{r}$, then $f(q) = \frac{2mA}{\hbar^2 q^2} = \frac{A}{4E\sin^2(\frac{\theta}{2})}$. The total cross section diverges.

- Partial wave analysis: for central scattering potential $V(r)$,
  $\psi(r, \theta, \phi) = e^{\mathbb{i}kr\cos\theta} + f(\theta)\frac{e^{\mathbb{i}kr}}{r}$. Expand into Legendre polynomials $P_\ell(\cos\theta)$.
  - $e^{\mathbb{i}kr\cos\theta} = \sum_{\ell=0}^\infty (2\ell+1)\mathbb{i}^\ell j_\ell(kr) P_\ell(\cos\theta) \sim \sum_{\ell=0}^\infty (2\ell+1)\frac{e^{\mathbb{i}kr} - (-1)^\ell e^{-\mathbb{i}kr}}{2\mathbb{i}kr} P_\ell(\cos\theta)$, for large r, contains both outgoing and incoming spherical waves.
  - Expand $f(\theta)$, $f(\theta) = \sum_{\ell=0}^\infty (2\ell+1) f_\ell P_\ell(\cos\theta)$, f_ℓ are complex numbers.
    Total cross section $\sigma = 2\pi \int_0^\pi |f(\theta)|^2 \sin\theta \mathrm{d}\theta = \sum_{\ell=0}^\infty 4\pi(2\ell+1)|f_\ell|^2$.
    For large r, $\psi \sim \sum_{\ell=0}^\infty (2\ell+1)\frac{(1+2\mathbb{i}kf_\ell)e^{\mathbb{i}kr} - (-1)^\ell e^{-\mathbb{i}kr}}{2\mathbb{i}kr} P_\ell(\cos\theta)$.
  - $1 + 2\mathbb{i}kf_\ell = e^{2\mathbb{i}\delta_\ell}$, for conservation of probability current in each channel. Here δ_ℓ is the "phase shift" in angular momentum ℓ channel. Then $f_\ell = \frac{1}{k} e^{\mathbb{i}\delta_\ell} \sin\delta_\ell$.
  - Total cross section $\sigma = \sum_{\ell=0}^\infty \sigma_\ell$. σ_ℓ is cross section in angular momentum ℓ channel, $\sigma_\ell = 4\pi(2\ell+1)|f_\ell|^2 = \frac{4\pi}{k^2}(2\ell+1)\sin^2\delta_\ell \le \frac{4\pi}{k^2}(2\ell+1)$.
  - To compute δ_ℓ, solve radial equation $[-\frac{1}{r}\frac{\mathrm{d}^2}{\mathrm{d}r^2} r + \frac{\ell(\ell+1)}{r^2} + \frac{2mV(r)}{\hbar^2}]R(r) = k^2 R(r)$, then $R(r) \sim j_\ell(kr)\cos\delta_\ell - n_\ell(kr)\sin\delta_\ell \sim \frac{\sin(kr + \delta_\ell - \frac{\ell\pi}{2})}{kr}$, for large r.

- Optical theorem: $\frac{4\pi}{k}\mathrm{Im}[f(\theta \to 0)] = \sigma$. (See *e.g.* Sakurai's "Modern Quantum Mechanics" Section 7.3). Forward scattering amplitude is related to total cross section.
  - In partial wave expansion, $\sigma_\ell = \frac{4\pi}{k}(2\ell+1)\mathrm{Im}(f_\ell)$, using $P_\ell(1) = 1$.