8.06 Quantum Physics III — Course Summary

Zwiebach, *Mastering Quantum Mechanics* Part III (Ch 24–30) + MIT 8.06 notes (2018) · Gaussian units ($\alpha = e^2/\hbar c$)

The course in 8 ideas

1. **Almost nothing is exactly solvable.** Start from a solved $\hat{H}^{(0)}$ and treat the rest as small. First order = average of the perturbation; second order = level repulsion; degenerate levels need the good basis.
2. **Real hydrogen:** relativistic, spin-orbit and Darwin terms are α^2 corrections that depend only on n, j. External fields: Zeeman (B) and Stark (E).
3. **EM fields enter through potentials:** $\hat{\vec{p}} \to \hat{\vec{p}} - \frac{q}{c}\vec{A}$. Gauge invariance, flux quantization, Landau levels; the Pauli equation gives $g = 2$.
4. **Semiclassical (WKB)** when λ varies slowly: amplitude $\propto 1/\sqrt{p}$, phase $\frac{1}{\hbar}\int p\,dx$; quantization $\oint p\,dx = 2\pi\hbar(n+\frac{1}{2})$; tunneling $\sim e^{-2\theta}$.
5. **Time-dependent perturbations cause transitions.** Into a continuum they give a constant rate (golden rule), hence exponential decay and line widths; light–atom physics and selection rules.
6. **Slow change** ⇒ the system follows the instantaneous eigenstate, gaining a dynamical phase plus a geometric Berry phase. Fast crossings jump (Landau–Zener). Molecules: Born–Oppenheimer.
7. **Scattering** is measured as cross sections. Low energy: a few partial waves (phase shifts). Weak V or high energy: Born approximation, the Fourier transform of V.
8. **Identical particles:** (anti)symmetrize. This gives Pauli exclusion, exchange effects and Fermi–Dirac / Bose–Einstein statistics.

1 · Time-independent perturbation theory notes 1 · Ch 25

$\hat{H}(\lambda) = \hat{H}^{(0)} + \lambda\delta\hat{H}$, $\lambda \in [0,1]$. Expand $E_n(\lambda) = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots$, $|n\rangle = |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \ldots$; match powers of λ. Convenient choice $\langle n^{(0)}|n^{(k)}\rangle = 0$ for $k \geq 1$.

Non-degenerate ($\delta H_{kn} \equiv \langle k^{(0)}|\delta\hat{H}|n^{(0)}\rangle$):

$$E_n^{(1)} = \delta H_{nn}, \qquad |n^{(1)}\rangle = \sum_{k\neq n} \frac{\delta H_{kn}}{E_n^{(0)} - E_k^{(0)}}|k^{(0)}\rangle$$

$$E_n^{(2)} = \sum_{k\neq n} \frac{|\delta H_{kn}|^2}{E_n^{(0)} - E_k^{(0)}}$$

- **Why:** first order = average of the perturbation in the unperturbed state; second order = virtual mixing with other levels, weighted by 1/(energy gap).
- $E^{(2)}_{\text{ground}} < 0$ always: levels **repel** at second order.
- **Validity:** $|\delta H_{kn}| \ll |E_n^{(0)} - E_k^{(0)}|$. Series is often only asymptotic (e.g. αx^4 with $\alpha < 0$ has no bound states ⇒ zero radius of convergence).
- Anharmonic $\delta H = \alpha\hat{x}^4$: $E_n^{(1)} = \frac{3\alpha\hbar^2}{4m^2\omega^2}(2n^2+2n+1)$. Use $\hat{x} \propto \hat{a} + \hat{a}^\dagger$.

Degenerate (level $E_n^{(0)}$ with subspace V_N, N-fold):

1. Find the **good basis**: diagonalize $[\delta\hat{H}]_{V_N}$, the $N \times N$ matrix of $\delta\hat{H}$ inside V_N. Eigenvalues = $E^{(1)}$'s.
2. Non-degenerate formulas then work in that basis (sums over states outside V_N).
3. If $E^{(1)}$ doesn't lift degeneracy: diagonalize $M_{ij} = \sum_{p\notin V_N} \frac{\delta H_{ip}\delta H_{pj}}{E_n^{(0)} - E_p^{(0)}}$ inside the still-degenerate space (second-order lifting).

Why: only the good basis states connect smoothly to the exact $\lambda \neq 0$ eigenstates; other bases make $\frac{\delta H_{kn}}{0}$ blow up.

> **Shortcut:** find a Hermitian $\hat{A}$ with $[\hat{A}, \hat{H}^{(0)}] = [\hat{A}, \delta\hat{H}] = 0$ whose eigenvalues are distinct on V_N — its eigenstates are the good basis (e.g. $\hat{L}_z$, $\hat{J}^2$, parity).

Example — linear Stark effect ($n=2$ H, $\delta H = e\mathcal{E}z$): only $\langle 200|z|210\rangle = -3a_0$ is nonzero ⇒ good states $\frac{1}{\sqrt{2}}(|200\rangle \pm |210\rangle)$, $E^{(1)} = \mp 3e\mathcal{E}a_0$; $|21\pm1\rangle$ unshifted. Ground state: no linear Stark effect (parity).

Feynman–Hellmann: $\frac{dE_n}{d\lambda} = \langle n(\lambda)|\frac{d\hat{H}}{d\lambda}|n(\lambda)\rangle$. **Variational:** $E_{\text{gs}} \leq \langle\psi|\hat{H}|\psi\rangle$.

2 · Charged particles in EM fields Ch 24

$$\vec{E} = -\nabla\Phi - \frac{1}{c}\partial_t\vec{A}, \qquad \vec{B} = \nabla\times\vec{A}, \qquad \hat{H} = \frac{1}{2m}\left(\hat{\vec{p}} - \frac{q}{c}\vec{A}\right)^2 + q\Phi$$

Gauge transformation $\vec{A} \to \vec{A} + \nabla\Lambda$, $\Phi \to \Phi - \frac{1}{c}\partial_t\Lambda$ is a symmetry if $\psi \to e^{iq\Lambda/\hbar c}\psi$. $\hat{\vec{p}}$ is canonical and gauge-dependent; the **mechanical momentum** $\hat{\vec{\pi}} = \hat{\vec{p}} - \frac{q}{c}\vec{A} = m\hat{\vec{v}}$ is physical:

$$[\hat{\pi}_x, \hat{\pi}_y] = \frac{i\hbar q}{c}B_z, \qquad m\frac{d^2\hat{\vec{x}}}{dt^2} = q\left[\vec{E} + \frac{1}{2c}\left(\hat{\vec{v}}\times\vec{B} - \vec{B}\times\hat{\vec{v}}\right)\right]$$

- **Flux quantization** (field on a torus): a consistent $\vec{A}$ exists only if $\Phi_B = n\Phi_0$, $\Phi_0 = \frac{2\pi\hbar c}{q}$. Aharonov–Bohm: a loop around flux picks up phase $\frac{q}{\hbar c}\oint\vec{A}\cdot d\vec{l} = \frac{q\Phi_B}{\hbar c}$, even where $\vec{B} = 0$.

Landau levels (uniform $B\hat{z}$, gauge $\vec{A} = Bx\,\hat{y}$): p_y is conserved and x-motion is an oscillator centred at $x_0 = \frac{cp_y}{qB}$:

$$E = \hbar\omega_c\left(n+\tfrac{1}{2}\right) + \frac{p_z^2}{2m}, \qquad \omega_c = \frac{|q|B}{mc}, \qquad \ell_B = \sqrt{\frac{\hbar c}{|q|B}}$$

Each level holds **one state per flux quantum**: $\frac{\#\text{states}}{\text{area}} = \frac{|q|B}{2\pi\hbar c} = \frac{B}{\Phi_0}$. (Basis of the quantum Hall effect.)

3 · Hydrogen fine structure & Zeeman notes 2 · Ch 24.6–7, 25.6–8

$$E_n^{(0)} = -\frac{e^2}{2a_0n^2} = -\frac{\alpha^2mc^2}{2n^2}, \quad a_0 = \frac{\hbar^2}{me^2} \approx 0.53\,\text{Å}, \quad \alpha = \frac{e^2}{\hbar c} \approx \frac{1}{137}$$

Scales: Bohr α^2mc^2 » fine α^4mc^2 » Lamb α^5mc^2 ~ hyperfine $\alpha^4mc^2\frac{m}{m_p}$. $v/c \sim \alpha$.

Pauli equation: $\hat{H} = \frac{(\vec{\sigma}\cdot\hat{\vec{\pi}})^2}{2m} + V$, $\hat{\vec{\pi}} = \hat{\vec{p}} - \frac{q}{c}\vec{A}$, and $(\vec{\sigma}\cdot\vec{\pi})^2 = \vec{\pi}^2 - \frac{q\hbar}{c}\vec{\sigma}\cdot\vec{B}$ ⇒ predicts $g = 2$. **Dirac:** $\hat{H} = c\vec{\alpha}\cdot\hat{\vec{p}} + \beta mc^2 + V$; expanding in v/c gives three corrections:

$$\delta\hat{H}_{\text{rel}} = -\frac{\hat{p}^4}{8m^3c^2}, \qquad \delta\hat{H}_{\text{SO}} = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\hat{\vec{S}}\cdot\hat{\vec{L}}, \qquad \delta\hat{H}_{\text{D}} = \frac{\pi\hbar^2e^2}{2m^2c^2}\delta^3(\vec{r}$$

$$E^{(1)}_{\text{rel}} = -\frac{(E_n^{(0)})^2}{2mc^2}\left[\frac{4n}{\ell+\frac{1}{2}} - 3\right], \qquad E^{(1)}_{\text{D}} = \frac{\alpha^4mc^2}{2n^3} \quad (\ell = 0 \text{ only})$$

$$E^{(1)}_{\text{SO}} = \frac{(E_n^{(0)})^2}{mc^2}\,\frac{n[j(j+1) - \ell(\ell+1) - \frac{3}{4}]}{\ell(\ell+\frac{1}{2})(\ell+1)} \quad (\ell \neq 0)$$

$$\boxed{E^{(1)}_{\text{fs}} = -\frac{\alpha^4mc^2}{2n^4}\left[\frac{n}{j+\frac{1}{2}} - \frac{3}{4}\right]}$$

- **Why each term:** rel = next term of $\sqrt{p^2c^2+m^2c^4}$; SO = electron's magnetic moment in the proton's field seen in its rest frame (with Thomas ½); Darwin = electron position smeared over $\sim\hbar/mc$ (Zitterbewegung), only felt at $r = 0$ ⇒ s-states.
- δH_{rel} commutes with $\hat{\vec{L}}$; δH_{SO} doesn't commute with L_z, S_z ⇒ use the coupled basis $|n\ell jm_j\rangle$ (good basis!).
- Result depends only on n, j: $2s_{1/2}$ & $2p_{1/2}$ stay degenerate (split by Lamb shift, QED). Levels with larger j lie higher.
- $\langle\frac{1}{r}\rangle = \frac{1}{n^2a_0}$, $\langle\frac{1}{r^2}\rangle = \frac{1}{n^3(\ell+\frac{1}{2})a_0^2}$, $\langle\frac{1}{r^3}\rangle = \frac{1}{n^3\ell(\ell+\frac{1}{2})(\ell+1)a_0^3}$, $|\psi_{n00}(0)|^2 = \frac{1}{\pi n^3a_0^3}$.

Zeeman effect: $\delta\hat{H}_Z = \frac{e}{2mc}(\hat{\vec{L}} + 2\hat{\vec{S}})\cdot\vec{B} = \frac{\mu_B}{\hbar}B(\hat{L}_z + 2\hat{S}_z)$, $\mu_B = \frac{e\hbar}{2mc} \approx 5.79\times10^{-9}$ eV/G.
Weak field ($B \ll B_{\text{int}}$, treat after fine structure): basis $|n\ell jm_j\rangle$,

$$E_Z^{(1)} = \mu_B B\,g_J\,m_j, \qquad g_J = 1 + \frac{j(j+1) - \ell(\ell+1) + \frac{3}{4}}{2j(j+1)}$$

removes all degeneracies. **Strong field** (Paschen–Back): basis $|n\ell m_\ell m_s\rangle$, $E = E_n^{(0)} + \mu_B B(m_\ell + 2m_s)$, then fine structure as a perturbation. **Intermediate:** diagonalize $\delta H_{\text{fs}} + \delta H_Z$ in the n shell.

Projection lemma (why g_J): within a j-multiplet, any vector operator acts as $\hat{\vec{V}} = \frac{\langle(\hat{\vec{V}}\cdot\hat{\vec{J}})\rangle}{\hbar^2 j(j+1)}\hat{\vec{J}}$ — only the part of $\vec{S}$ along $\vec{J}$ survives time-averaging.

4 · WKB / semiclassical approximation notes 3 · Ch 26

$$p(x)=\sqrt{2m(E-V(x))},\qquad \lambda(x)=\frac{2\pi\hbar}{p(x)}$$

$$\textbf{allowed: } \psi\simeq\frac{C}{\sqrt{p(x)}}\exp\left(\pm\frac{i}{\hbar}\int^x p(x')dx'\right)$$

$$\textbf{forbidden: } \psi\simeq\frac{C}{\sqrt{|p(x)|}}\exp\left(\pm\frac{1}{\hbar}\int^x |p(x')|dx'\right)$$

Derivation: $\psi=e^{iS(x)/\hbar}$, $S=S_0+\hbar S_1+\dots\Rightarrow S_0'^2=p^2$ (Hamilton–Jacobi, classical), $S_1=\frac{i}{2}\ln p$ (amplitude $\propto p^{-1/2}$: $|\psi|^2\propto$ time spent at x). **Valid when** λ changes slowly: $\left|\frac{d\lambda}{dx}\right|\ll 2\pi$, i.e. $\hbar|p'|\ll p^2$. Fails at turning points ($p=0$).

Connection formulas ($k=p/\hbar$, $\kappa=|p|/\hbar$). Turning point a, allowed on left, forbidden on right:

$$\frac{2}{\sqrt{k}}\cos\left(\int_x^a k\,dx'-\frac{\pi}{4}\right)\Longleftarrow\frac{1}{\sqrt{\kappa}}\exp\left(-\int_a^x\kappa\,dx'\right)$$

$$-\frac{1}{\sqrt{k}}\sin\left(\int_x^a k\,dx'-\frac{\pi}{4}\right)\Longrightarrow\frac{1}{\sqrt{\kappa}}\exp\left(\int_a^x\kappa\,dx'\right)$$

(Mirror image for forbidden-left at b: $\int_b^x$.) Arrows: which direction the matching is reliable. Derived by matching to **Airy functions** of the linearized potential $V\approx V(a)+g(x-a)$.

Bohr–Sommerfeld quantization:

$$\int_a^b k(x)\,dx=\left(n+\tfrac{1}{2}\right)\pi,\quad n=0,1,\dots\quad\textbf{(two soft turning points)}$$

One hard wall: $(n+\frac{3}{4})\pi$; two hard walls: $(n+1)\pi$. Exact for the SHO. Equivalent to $\oint p\,dx=2\pi\hbar(n+\frac{1}{2})$: each state occupies phase-space area $2\pi\hbar$.

Tunneling through a barrier ($a<x<b$ forbidden):

$$T\simeq e^{-2\theta},\qquad\theta=\int_a^b\kappa(x)\,dx=\frac{1}{\hbar}\int_a^b\sqrt{2m(V-E)}\,dx\ \ (\theta\gg1)$$

Square barrier check: $T\simeq\frac{16E}{V_0}\left(1-\frac{E}{V_0}\right)e^{-2\kappa L}$ — WKB gets the exponent, not the prefactor. Uses: α-decay (Gamow), field emission, fusion.

Double well (Ch 26.7): each well alone has a level E_0 with classical frequency ω. Tunneling splits it into an even state (lower) and an odd state (higher):

$$\Delta E=E_{\text{odd}}-E_{\text{even}}\simeq\frac{\hbar\omega}{\pi}e^{-\theta},\qquad\theta=\frac{1}{\hbar}\int_{\text{barrier}}|p|\,dx$$

A particle starting in one well tunnels back and forth with period $2\pi\hbar/\Delta E$ (ammonia inversion).

5 · Time-dependent perturbation theory notes 4 · Ch 27

$\hat H(t)=\hat H^{(0)}+\delta\hat H(t)$ has no energy eigenstates; expand in eigenstates of $\hat H^{(0)}$ and ask for transition probabilities.

Interaction picture: $|\tilde\Psi(t)\rangle=e^{i\hat H^{(0)}t/\hbar}|\Psi(t)\rangle$ removes the trivial $H^{(0)}$ evolution:

$$i\hbar\frac{d}{dt}|\tilde\Psi\rangle=\widetilde{\delta H}(t)|\tilde\Psi\rangle,\qquad\widetilde{\delta H}=e^{i\hat H^{(0)}t/\hbar}\,\delta\hat H\,e^{-i\hat H^{(0)}t/\hbar}$$

$$|\Psi(t)\rangle=\sum_n c_n(t)e^{-iE_nt/\hbar}|n\rangle,\qquad i\hbar\,\dot c_n=\sum_m\delta H_{nm}(t)\,e^{i\omega_{nm}t}c_m$$

with $\omega_{nm}=(E_n-E_m)/\hbar$.

$$c_f^{(1)}(t)=\frac{1}{i\hbar}\int_{t_0}^t\delta H_{fi}(t')\,e^{i\omega_{fi}t'}dt',\qquad P_{f\leftarrow i}=|c_f^{(1)}|^2$$

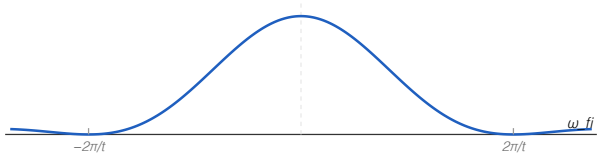
(1st order, starting in $|i\rangle$).

Valid while $P\ll1$. Exact two-level (NMR) solution reduces to this at small t. Note $P_{f\leftarrow i}=P_{i\leftarrow f}$ at first order.

Constant perturbation V turned on at $t=0$:

$$P_{f\leftarrow i}(t)=\frac{4|V_{fi}|^2}{\hbar^2}\frac{\sin^2(\omega_{fi}t/2)}{\omega_{fi}^2}$$

Harmonic $\delta H=2H'\cos\omega t$: same with $\omega_{fi}\to\omega_{fi}\mp\omega\Rightarrow$ **absorption** at $E_f=E_i+\hbar\omega$, **stimulated emission** at $E_f=E_i-\hbar\omega$.



$\sin^2(\omega t/2)/\omega^2$: peak height $\propto t^2$, width $\propto 1/t$, area $\propto t\Rightarrow$ for a continuum of final states the probability grows **linearly** in $t\to$ constant rate.

Fermi's Golden Rule (transitions into a continuum):

$$w=\frac{2\pi}{\hbar}|V_{fi}|^2\rho(E_f),\quad E_f=E_i\qquad\left(\textbf{harmonic: }|H'_{fi}|^2,\ E_f=E_i\pm\hbar\omega\right)$$

Uses $\frac{\sin^2(xt/2)}{x^2}\to\frac{\pi t}{2}\delta(x)$. Free particle in box L^3:
$\rho(E)\,d\Omega=\frac{L^3}{(2\pi)^3}\frac{mk}{\hbar^2}d\Omega$ (L^3 cancels against normalization). Valid for $\frac{2\pi\hbar}{\Delta E}\ll t\ll\frac{1}{w}$.

Ionization of H: golden rule with plane-wave final electron; $dw\propto\cos^2\theta\,d\Omega$.

Decay of a discrete state into a continuum (Ch 27.8): beyond first order the golden-rule rate gives true exponential decay,

$$|c_i(t)|^2=e^{-\Gamma t/\hbar},\qquad\Gamma=2\pi|V|^2\rho,\qquad\tau=\hbar/\Gamma$$

with a Lorentzian line of full width Γ (energy–time: $\Gamma\tau=\hbar$).
Helium autoionization: doubly excited states (e.g. $2s^2$) lie above the $He^+ + e^-$ threshold. Electron–electron repulsion couples them to that continuum, so they decay by ejecting an electron.

Light and atoms

Dipole approximation ($\lambda\gg a_0$): $\delta\hat H=-\hat{\vec d}\cdot\vec{\mathcal{E}}(t)$, $\hat{\vec d}=q\hat{\vec r}$. Isotropic, incoherent light with energy density $U(\omega)$:

$$R_{a\leftarrow b}=\frac{4\pi^2}{3\hbar^2}|\vec d_{ab}|^2U(\omega_{ba})=B_{ab}U(\omega_{ba})$$

Einstein's argument (equilibrium with Planck $U=\frac{\hbar\omega^3}{\pi^2c^3}\frac{1}{e^{\beta\hbar\omega}-1}$) needs spontaneous emission:

$$B_{ab}=B_{ba},\qquad\frac{A}{B}=\frac{\hbar\omega^3}{\pi^2c^3}\ \Rightarrow\ A=\frac{4\omega^3}{3\hbar c^3}|\vec d_{ab}|^2,\qquad\tau=\frac{1}{A}$$

Rates from different channels add: $\tau^{-1}=\sum_i A_i$. Spontaneous = emission stimulated by vacuum fluctuations. H $2p\to1s$: τ ≈ 1.6 ns.

Selection rules (E1): $\langle n'\ell'm'|\hat{\vec r}|n\ell m\rangle\neq0$ only if $\Delta\ell=\pm1$, $\Delta m=0,\pm1$ (z: $\Delta m=0$; $x\pm iy$: $\Delta m=\pm1$). Parity must flip. $\Rightarrow 2s$ is metastable (decays by 2 photons, ~0.1 s).

6 · Adiabatic approximation notes 6 · Ch 28

Classical: slowly varying oscillator conserves the **action** $I=\frac{1}{2\pi}\oint p\,dq=E/\omega$ (adiabatic invariant). Quantum analogue: n in $E=\hbar\omega(n+\frac{1}{2})$ stays fixed. Generally, slow changes preserve $\oint p\,dq=2\pi\hbar(n+\frac{1}{2})$, so quantum numbers are adiabatic invariants.

Adiabatic theorem. Instantaneous eigenstates $\hat H(t)|\psi_n(t)\rangle=E_n(t)|\psi_n(t)\rangle$. If $\hat H$ changes slowly and E_n stays non-degenerate, a system starting in $|\psi_n(0)\rangle$ stays in $|\psi_n(t)\rangle$:

$$|\Psi(t)\rangle\simeq e^{i\theta_n(t)}e^{i\gamma_n(t)}|\psi_n(t)\rangle,$$

$$\theta_n=-\frac{1}{\hbar}\int_0^t E_n(t')dt',\qquad\gamma_n=\int_0^t\nu_n\,dt',\quad\nu_n=i\langle\psi_n|\dot\psi_n\rangle$$

Condition: $\hbar\,|\langle\psi_m|\dot{\hat H}|\psi_n\rangle|\ll(E_n-E_m)^2$ for all $m\neq n$ — rate of change slow compared to the gap.

Berry (geometric) phase for a closed loop C in parameter space $\vec R$:

$$\gamma_n[C]=\oint_C\vec{\mathcal{A}}_n\cdot d\vec R,\qquad\vec{\mathcal{A}}_n(\vec R)=i\langle\psi_n(\vec R)|\nabla_R\psi_n(\vec R)\rangle$$

$$=\int_S\vec{\mathcal{D}}_n\cdot d\vec a,\qquad\vec{\mathcal{D}}_n=\nabla_R\times\vec{\mathcal{A}}_n\ \textbf{(Berry curvature)}$$

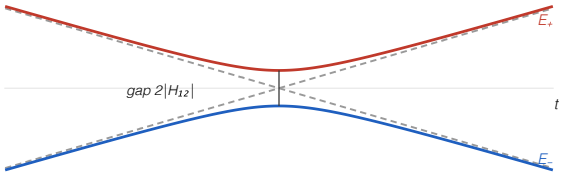
Depends only on the path's geometry, not on how fast it is traversed. Gauge: $|\psi_n\rangle\to e^{i\beta(R)}|\psi_n\rangle$ shifts $\vec{\mathcal{A}}\to\vec{\mathcal{A}}-\nabla\beta$; closed-loop γ invariant (mod 2π) ⇒ physical.

- $\gamma_n=0$ if ψ_n can be chosen real, or if there is only one parameter.
- **Spin in slowly rotating** $\vec B$: $\gamma_\pm=\mp\frac{1}{2}\Omega$, Ω = solid angle traced by $\hat B$. (Spin s: $\gamma=-m_s\Omega$.) Berry curvature = monopole field $\mp\frac{\hat r}{2r^2}$ at the degeneracy $B=0$.

Landau–Zener. Diabatic levels cross linearly, $E_1-E_2=\alpha t$, coupling H_{12} opens a gap $2|H_{12}|$. Probability of a **non-adiabatic** jump (staying on the diabatic line):

$$P_{\text{jump}}=\exp\left(-\frac{2\pi|H_{12}|^2}{\hbar|\alpha|}\right)$$

Slow sweep ($\hbar|\alpha|\ll|H_{12}|^2$) ⇒ adiabatic, follows the curve; fast ⇒ jumps.



Avoided crossing: diabatic levels (dashed) vs adiabatic levels (solid), gap $2|H_{12}|$

Born–Oppenheimer (molecules): electrons fast, nuclei slow ($m/M\ll1$). Solve electrons at fixed nuclear positions $\vec R\to E_{\text{el}}(\vec R)$ is the potential for nuclear motion. Scales
$E_{\text{el}}:E_{\text{vib}}:E_{\text{rot}}\sim1:(m/M)^{1/2}:(m/M)$. Nuclear $\hat P\to\hat P-\vec{\mathcal{A}}$ (Berry connection from the electrons). H_2^+: trial $\psi_\pm\propto\psi_{1s}(r_1)\pm\psi_{1s}(r_2)$; even (bonding) combination gives a bound molecule, odd (antibonding) doesn't.

7 · Scattering (3D, elastic, spinless) notes 7 · Ch 30

$E = \frac{\hbar^2 k^2}{2m}$ (m = reduced mass). Far from the target ($r \gg a$):

$$\psi(\vec{r}) \simeq e^{ikz} + f_k(\theta,\phi)\frac{e^{ikr}}{r}, \qquad \frac{d\sigma}{d\Omega} = |f_k(\theta,\phi)|^2, \qquad \sigma = \int |f_k|^2 d\Omega$$

$d\sigma$ = (scattered particles/time into $d\Omega$)/(incident flux) — an area.

Partial waves (central V): $e^{ikz} = \sum_\ell i^\ell (2\ell+1) j_\ell(kr) P_\ell(\cos\theta)$. Each ℓ outgoing wave acquires $e^{2i\delta_\ell}$:

$$f_k(\theta) = \frac{1}{k}\sum_{\ell=0}^{\infty}(2\ell+1)\, e^{i\delta_\ell}\sin\delta_\ell\, P_\ell(\cos\theta)$$

$$\sigma = \frac{4\pi}{k^2}\sum_\ell (2\ell+1)\sin^2\delta_\ell, \qquad \sigma_\ell \le \frac{4\pi}{k^2}(2\ell+1) \ \ \textbf{(unitarity bound)}$$

$$\textbf{Optical theorem: } \sigma = \frac{4\pi}{k}\,\mathrm{Im}\, f_k(0)$$

Outside the potential: $u_\ell \sim \sin(kr - \frac{\ell\pi}{2} + \delta_\ell)$, $R_\ell \propto \cos\delta_\ell\, j_\ell(kr) - \sin\delta_\ell\, n_\ell(kr)$.

- **Why few partial waves:** classical impact parameter $b \sim \ell/k$; if $b > a$ no scattering ⇒ $\ell_{\max} \sim ka$. Low energy ($ka \ll 1$): $\delta_\ell \sim (ka)^{2\ell+1}$, s-wave dominates, isotropic.
- **Computing δ_ℓ:** match log-derivative $\beta = R'_\ell/R_\ell$ at $r = a$: $\tan\delta_\ell = \frac{kj'_\ell(ka) - \beta j_\ell(ka)}{kn'_\ell(ka) - \beta n_\ell(ka)}$.
- **Hard sphere:** $\tan\delta_\ell = \frac{j_\ell(ka)}{n_\ell(ka)}$, $\delta_0 = -ka$; low energy $\sigma \to 4\pi a^2$ (4× geometric cross-section!). Scattering length: $\delta_0 \simeq -ka_s$, $\sigma \to 4\pi a_s^2$.
- **Resonance:** δ_ℓ passes through $\pi/2$ ⇒ σ_ℓ hits the unitarity bound; Breit–Wigner shape.

Integral equation: $(\nabla^2 + k^2)\psi = U\psi$, $U = \frac{2m}{\hbar^2}V$, Green's function $G(\vec{r}) = -\frac{e^{ikr}}{4\pi r}$:

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} + \int G(\vec{r}-\vec{r}')U(\vec{r}')\psi(\vec{r}')d^3r'$$

$$f = -\frac{1}{4\pi}\int e^{-i\vec{k}'\cdot\vec{r}'}U(\vec{r}')\psi(\vec{r}')d^3r'$$

Born approximation (replace ψ by the incident plane wave), $\vec{K} = \vec{k}' - \vec{k}$, $K = 2k\sin\frac{\theta}{2}$:

$$f_B(\theta) = -\frac{m}{2\pi\hbar^2}\int e^{-i\vec{K}\cdot\vec{r}}V(\vec{r})\,d^3r \xrightarrow{\text{central}} -\frac{2m}{\hbar^2 K}\int_0^\infty rV(r)\sin(Kr)\,d$$

f_B ∝ Fourier transform of V at momentum transfer $\hbar\vec{K}$. Valid for weak V or high energy ($|V|a \ll \hbar v$).

Yukawa $V = \beta\frac{e^{-\mu r}}{r}$: $f_B = -\frac{2m\beta}{\hbar^2(\mu^2+K^2)}$. $\mu \to 0$ gives **Rutherford**: $\frac{d\sigma}{d\Omega} = \frac{(Z_1 Z_2 e^2)^2}{16E^2\sin^4(\theta/2)}$ (exact classically & quantum).

1D half-line scattering (phase shifts, time delay $2\hbar\delta'(E)$, Levinson, Breit–Wigner) is book Ch 29 and on the 8.04 sheet §14–15.

8 · Identical particles notes 8 · Ch 21

Identical = same intrinsic properties ⇒ no experiment distinguishes them. Classically you can still follow trajectories; quantum mechanically you can't once wavefunctions overlap ⇒ **exchange degeneracy**: $|a\rangle_1|b\rangle_2$ and $|b\rangle_1|a\rangle_2$ (and all combos) describe the same physics — ambiguity.

Permutation operators: $\hat{P}_{21}|u\rangle_1|v\rangle_2 = |v\rangle_1|u\rangle_2$; $\hat{P}_{21}^2 = \mathbf{1}$, Hermitian & unitary. N particles: $N!$ permutations $\hat{P}_\alpha$, parity $\epsilon_\alpha = \pm 1$.

$$\hat{S} = \frac{1}{N!}\sum_\alpha \hat{P}_\alpha, \qquad \hat{A} = \frac{1}{N!}\sum_\alpha \epsilon_\alpha \hat{P}_\alpha \qquad \textbf{(projectors)}$$

Symmetrization postulate: states of identical particles are **totally symmetric** (bosons, integer spin) or **totally antisymmetric** (fermions, half-integer spin). Observables commute with all $\hat{P}_\alpha$.

- Two particles: $\psi_\pm = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) \pm \psi_b(1)\psi_a(2)]$. Fermions: N-particle state = **Slater determinant** $\frac{1}{\sqrt{N!}}\det[\psi_{a_i}(j)]$ ⇒ **Pauli exclusion**.
- **Exchange effect:** $\langle(x_1 - x_2)^2\rangle_\pm = \langle x^2\rangle_a + \langle x^2\rangle_b - 2\langle x\rangle_a\langle x\rangle_b \mp 2|\langle x\rangle_{ab}|^2$ — bosons bunch, fermions avoid each other (only if wavefunctions overlap).
- **Space ⊗ spin** ($V \otimes W$): electrons need total antisymmetry ⇒ symmetric space × spin singlet, or antisymmetric space × triplet. Helium: para (singlet) vs ortho (triplet); triplet lower (electrons kept apart ⇒ less repulsion).
- **Occupation numbers** $|n_1, n_2, \ldots\rangle$: fully specify symmetric/antisymmetric states. Fermions $n_i \in \{0,1\}$; bosons $n_i = 0, 1, 2, \ldots$

Counting N particles in g single-particle states:

$$\textbf{distinguishable: } g^N, \qquad \textbf{fermions: } \binom{g}{N}, \qquad \textbf{bosons: } \binom{N+g-1}{N}$$

Maximizing entropy gives mean occupancy

$$\bar{n}(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/kT}+1}\ \text{(FD)}, \quad \frac{1}{e^{(\epsilon-\mu)/kT}-1}\ \text{(BE)}, \quad e^{-(\epsilon-\mu)/kT}\ \text{(MB)}$$

9 · Toolkit, constants & pitfalls

$$\int_{-\infty}^{\infty}\frac{\sin^2 u}{u^2}du = \pi, \qquad \lim_{t\to\infty}\frac{\sin^2(xt/2)}{x^2} = \frac{\pi t}{2}\delta(x)$$

$$\langle n|\hat{x}^2|n\rangle = \tfrac{\hbar}{2m\omega}(2n+1), \quad \langle n|\hat{x}^4|n\rangle = \left(\tfrac{\hbar}{2m\omega}\right)^2(6n^2+6n+3)$$

$$\hat{\vec{L}}\cdot\hat{\vec{S}} = \tfrac{1}{2}(\hat{J}^2 - \hat{L}^2 - \hat{S}^2), \quad e^{ikz} = \sum_\ell i^\ell(2\ell+1)j_\ell(kr)P_\ell(\cos\theta)$$

$$\int P_\ell P_{\ell'} d(\cos\theta) = \tfrac{2}{2\ell+1}\delta_{\ell\ell'}, \quad P_0 = 1,\ P_1 = x,\ P_2 = \tfrac{1}{2}(3x^2-1)$$

$$\textbf{Airy: } y'' = xy;\ \mathrm{Ai}(x) \xrightarrow{x\to+\infty} \tfrac{e^{-\frac{2}{3}x^{3/2}}}{2\sqrt{\pi}x^{1/4}}, \quad \xrightarrow{x\to-\infty} \tfrac{\sin(\frac{2}{3}|x|^{3/2}+\frac{\pi}{4})}{\sqrt{\pi}|x|^{1/4}}$$

e^2	$\alpha\hbar c = 14.4$ eV·Å	μ_B	5.79×10^{-9} eV/G
$\hbar c$	1973 eV·Å	$m_e c^2$	0.511 MeV
$\alpha^2 m_e c^2$	27.2 eV	$\alpha^4 m_e c^2$	1.45×10^{-3} eV
a_0	0.529 Å	$k_B T_{300K}$	0.0259 eV

Which tool? small static change → TIPT (good basis first); large quantum numbers → WKB; time-dependent kick → TDPT / golden rule; slow change → adiabatic + Berry; collision → partial waves (low E) or Born (weak V); identical particles → (anti)symmetrize.

Pitfalls: non-degenerate formulas in a degenerate level; $E^{(2)}$ sum must exclude V_N; SO formula at $\ell = 0$; WKB at turning points; $\pi/4$ phases; golden rule without $\rho(E)$; $K = 2k\sin\frac{\theta}{2}$; forgetting spin when antisymmetrizing.