6.3 Time-dependent perturbation theory

No analytic solution for generic $H = H_0 + V(t)$.

Must use perturbative analysis

Expand
$$C_n(t) = C_n^{(0)} + \underset{\uparrow \atop \mathcal{O}(V)}{C_n^{(1)}(t)} + \underset{\uparrow \atop \mathcal{O}(V^2)}{C_n^{(2)}(t)} + \ldots$$

$C_n^{(0)}$ is initial state (time-independent)

Use time-evolution operator $U_I(t;t_0)$

$$|\alpha, t_0; t\rangle_I = U_I(t, t_0)\,|\alpha, t_0; t_0\rangle_I$$

U_I satisfies
$$i\hbar \frac{\partial}{\partial t} U_I(t, t_0) = V_I(t)\, U_I(t, t_0)$$

with $U_I(t_0, t_0) = \mathbb{1}$.

$$\Rightarrow \quad U_I(t, t_0) = \mathbb{1} - \frac{i}{\hbar}\int_{t_0}^{t} V_I(t')\, U_I(t', t_0)\, dt'$$

iterating
$$= \mathbb{1} - \frac{i}{\hbar}\int_{t_0}^{t} dt'\; V_I(t')$$
$$- \frac{1}{\hbar^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\; V_I(t')\, V_I(t'') + \ldots$$

$$= \mathbb{1} + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n \; V_I(t_1) V_I(t_2) \cdots V_I(t_n)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i}{\hbar}\right)^n \mathcal{T} \Big[\int_{t_0}^{t} dt_1 \int_{t_0}^{t} dt_2 \cdots \int_{t_0}^{t} dt_n \; V_I(t_1) V_I(t_2) \cdots V_I($$

[Dyson series] ↑ time-ordering operator: higher times t on left

$$U(t, t_0) = \mathcal{T}\left[e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt' \, V_I(t')} \right]$$

in compact form.

Evolution of state:

Starting in state $|i\rangle$ at $t = t_0$,

$$|i, t_0; t\rangle = U_I(t, t_0)|i\rangle$$

$$= \sum_n |n\rangle \underbrace{\langle n | U_I(t, t_0) | i\rangle}_{C_n(t)}$$

since $U_I = e^{iH_0 t/\hbar} \, U_s \, e^{-iH_0 t/\hbar}$,

we have

$$|C_n(t)|^2 = |\langle n | U_I(t, t_0) | i\rangle|^2 = |\langle n | U_s(t, t_0) | i\rangle|^2$$

if $|n\rangle$, $|i\rangle$ are eigenvectors of H_0.

$$\left.\begin{array}{l}\text{Using} \\ V_I(t) = e^{iH_0t/\hbar}\, V(t)\, e^{-iH_0t/\hbar} \\ \omega_{nm} = \dfrac{E_n - E_m}{\hbar}\end{array}\right\} \text{betw } \begin{array}{c} c^{(1)} \\ \& \\ c^{(2)} \end{array}$$

Since $U_I(t,t_0) = e^{iH_0t/\hbar}\, U(t,t_0)\, e^{-iH_0t/\hbar}$

$$|C_n|^2 = |\langle n|U_I(t,t_0)|i\rangle|^2 = |\langle n|U(t,t_0)|i\rangle|^2$$

Last time: $\overset{H = H_0 + V(t)}{|\psi(t)\rangle_I = \sum c_n(t)\,|n\rangle}$

$$C_n(t) = \langle n|\,U_I(t,t_0)\,|i\rangle$$

$|i\rangle$ = initial state

$$U_I(t,t_0) = T\left[e^{-\frac{i}{\hbar}\int_{t_0}^{t} dt'\, V_I(t')}\right]$$

Pert. expansion

$$C_n(t) = C_n^{(0)} + \underset{\substack{\downarrow \\ O(V)}}{C_n^{(1)}(t)} + \underset{\substack{\downarrow \\ O(V^2)}}{C_n^{(2)}(t)} + \dots$$

We can expand, if initial state is $|i\rangle$,

$$C_n(t) = \langle n | U_I(t,t_0) | i\rangle$$
$$= \delta_{ni} - \frac{i}{\hbar}\int_{t_0}^{t} dt' \langle n | V_I(t') | i\rangle$$
$$- \frac{1}{\hbar^2}\int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \sum_m \langle n | V_I(t') | m\rangle\langle m | V_I(t'') | i\rangle$$
$$+ \dots$$

so perturbative expansion is

$$C_n^{(0)} = \delta_{ni}$$

←

$$C_n^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} dt' \langle n | V_I(t') | i\rangle = -\frac{i}{\hbar}\int_{t_0}^{t} dt' \, e^{i\omega_{ni}t'} V_{ni}(t')$$

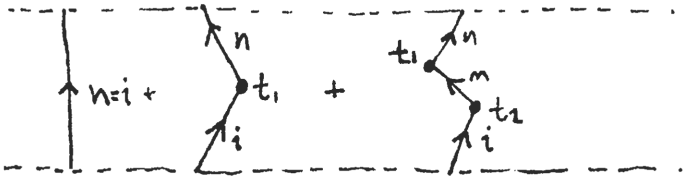
$$C_n^{(2)}(t) = -\frac{1}{\hbar^2}\sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt'' \, e^{i\omega_{nm}t' + i\omega_{mi}t''} V_{nm}(t') V_{mi}(t'')$$

[trans prob — next page] ⋮

Graphical depiction: "Feynman diagrams"

$$\langle n | U(t,t_0) | i\rangle = e^{-iE_nt/\hbar + iE_it_0/\hbar} \langle n | U_I(t,t_0) | i\rangle$$

=



where

$\Rightarrow e^{-iE_n(t''-t')/\hbar}$,

$\Rightarrow \langle m | V(t') | n\rangle$

Transition probability $|i\rangle \to |n\rangle$, $n \neq i$, given by

$$P(i \to n) = |C_n(t)|^2 = |C_n^{(1)}(t) + C_n^{(2)}(t) + \cdots|^2 .$$

6.4 First order perturbation theory

1st order TDPT:

$$C_n^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^{t} dt'\, e^{i\omega_{ni}t'}\, V_{ni}(t') \quad , \qquad n \neq i$$

$$P^{(1)}(i \to n) = |C_n^{(1)}(t)|^2 , \qquad n \neq i$$

1st order TDPT assumes $C_n(t) = \delta_{ni}$ on RHS of EOM for C_n's.

Valid as long as $|C_n(t)|^2 \ll 1$, $n \neq i$

$$1 - |C_i(t)|^2 \ll 1 .$$

Special cases: harmonic / constant perturbation

Assume $V(t) = \hat{V} \sin \omega t$, $t > 0$

$$V_{ni}(t) = \frac{1}{2i} \hat{V}_{ni} \left(e^{i\omega t} - e^{-i\omega t}\right)$$

$$C_n^{(1)}(t) = -\frac{\hat{V}_{ni}}{2\hbar} \int_0^t e^{i\omega_{ni} t} \left[e^{i\omega t} - e^{-i\omega t}\right]$$

$$= \frac{\hat{V}_{ni}}{2\hbar i} \left[\frac{1 - e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega} - \frac{1 - e^{i(\omega_{ni}-\omega)t}}{\omega_{ni}-\omega} \right]$$

If $V(t) = \hat{V}\cos\omega t$

$$C_n^{(1)} = \frac{\hat{V}_{ni}}{2\hbar}\left[\frac{1-e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega} + \frac{1-e^{i(\omega_{ni}-\omega)t}}{\omega_{ni}-\omega}\right]$$

If $\omega = 0$, $V(t) = \hat{V}(t) = \text{const.}$,

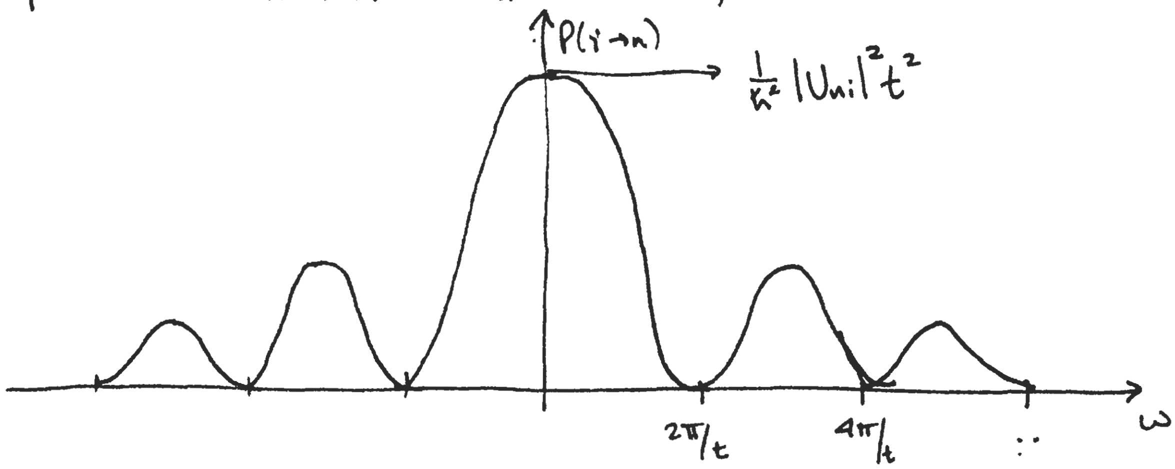
$$C_n^{(1)}(t) = \frac{\hat{V}_{ni}}{\hbar\omega_{ni}}\left[1-e^{i\omega_{ni}t}\right]$$

For constant perturbation,

$$P^{(1)}(i\to n) = |C_n^{(1)}(t)|^2 = \frac{|\hat{V}_{ni}|^2}{(E_n-E_i)^2}\left[2-2\cos\omega_{ni}t\right]$$

$$= \frac{4|\hat{V}_{ni}|^2}{(E_n-E_i)^2}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right]$$

Graph as function of $\omega_{ni} = (E_n-E_i)/\hbar$



[note scaling vs. book]

For $E_n = E_i$, prob. grows as t^2.

But — recall approx only good when $P \ll 1$.

After time t, $\Delta E \sim \frac{2\pi\hbar}{t}$.

Recalls $\Delta E \Delta t \sim \hbar$, time-energy uncertainty relation.

[Note: in completely a treatment H conserved]

Fermi's golden rule

Want total transition probability

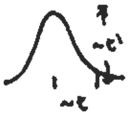
$$P^{(1)}(i \to \text{anything}) = \sum_n |C_n^{(1)}|^2 .$$

When spectrum continuous (or closely spaced)
write density of states $\rho(E)\,dE$

$$\rho(E) = \lim_{\Delta E \to 0} \frac{(\#\text{ of states between } E - \Delta E/2,\ E + \Delta E/2)}{\Delta E}$$

$$P^{(1)}(i \to \text{anything}) = \int dE_n\, \rho(E_n)\, |C_n^{(1)}|^2$$

$$= 4 \int \sin^2\left[\frac{(E_n - E_i)t}{2\hbar}\right] \frac{|V_{ni}|^2}{|E_n - E_i|^2}\, \rho(E_n)\, dE_n$$



For small t, Area $\sim (t^2)(t^{-1}) \sim t$.

so P goes linearly for small t, as it must.

For large t (but still small enough for P.T. to be ok)

$$\lim_{\alpha\to\infty}\frac{\sin^2\alpha x}{\alpha x^2} = \pi\,\delta(x) \qquad \left(\begin{array}{ll}\int = \pi & \forall\,\alpha\\ \lim = 0\,, & x\neq 0.\end{array}\right.$$

Transition rate: $\omega_{i\to n} = \frac{d\,|C_{ni}^{(1)}|^2}{dt}$

$$\boxed{\omega_{i\to n} = \frac{2\pi}{\hbar}\,|\hat{V}_{ni}|^2\,\delta\,(\epsilon_n-\epsilon_i)}$$

Integrating.

$$\lim_{t\to\infty} P^{(1)}[i\to\text{anything}] = \frac{2\pi}{\hbar}\,\overline{|\hat{V}_{ni}|^2}\,\rho(E_n)\,t\,\Big|_{E_n\cong E_i}$$

$$\text{where}\quad \overline{|\hat{V}_{ni}|^2} = \lim_{\Delta E\to 0}\frac{1}{\Delta E}\int_{-\Delta E/2}^{\Delta E/2}|\hat{V}_{ni}|^2\,dE_n$$

[valid when $\hat{V}_{ni}$ depends smoothly on E_n (for relevant states)]

Total transition rate = trans. prob./unit time

$$= \frac{d}{dt}\left(\sum_n |C_n^{(1)}|^2\right)$$

$$\boxed{\omega_{i\to\underset{\substack{\uparrow\\ \text{final states w/ energy}\,\approx\,E_i}}{[n]}} = \frac{2\pi}{\hbar}\,\overline{|\hat{V}_{ni}|^2}\,\rho(E_n)\Big|_{E_n\cong E_i}}$$

<u>Fermi's Golden Rule</u>

[Lecture 4]

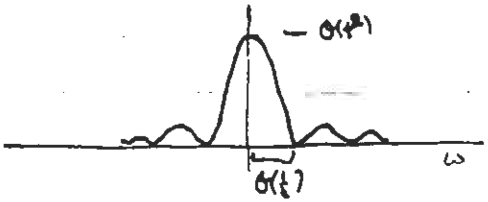
- Problem set 2, due Monday 2/25/02
  Problems 33, 35, 37, 38, 39 From Sakurai Chapter 5

Last time:

1st order TDPT for harmonic/constant $V(t)$.

For constant $V(t) = \hat{V}$, $\quad C_n^{(1)} = \frac{\hat{V}_{ni}}{\hbar\omega_{ni}}\left[1 - e^{i\omega_{ni}t}\right]$

$$P^{(1)}_{(i\to n)} = \frac{4|\hat{V}_{ni}|^2}{(E_n - E_i)^2}\sin^2\left[\frac{(E_n-E_i)t}{2\hbar}\right]$$
$$= |C_n^{(1)}(t)|^2$$



$$\lim_{t\to\infty} \sim t\pi\,\delta(\omega)$$

$$\cancel{\lim_{\alpha\to\infty}\frac{\sin^2 \alpha x}{\alpha x^2} = \pi\,\delta(x)}$$

Transition rate $\omega_{i\to n} = \frac{d}{dt}|C_n^{(1)}|^2 = \frac{2\pi}{\hbar}|\hat{V}_{ni}|^2\delta(E_n - E_i)$

(t big enough for EC, short enough, TDPT ok.)

Introduce density of states $\rho(E)$

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\hat{V}_{ni}|^2}\,\rho(E_n)\Big|_{E_n\simeq E_i}$$

↑ final states w/ $E_n \simeq E_i$

Fermi's Golden Rule

$\left[\;\left[\overline{|\hat{V}|^2} = \lim_{\Delta E\to 0}\frac{1}{\Delta E}\int_{-\Delta E/2}^{\Delta E/2}|\hat{V}_{ni}|^2\,dE_n\right.\right.$ if ρ, $\hat{V}$ smooth on families of final states $\left.\left.\right]\;\right]$

Back to harmonic perturbation

$$V(t) = \mathcal{V} e^{i\omega t} + \mathcal{V}^{+} e^{-i\omega t}$$

$$C_n^{(1)} = \frac{1}{\hbar}\left[\underbrace{\frac{1 - e^{i(\omega_{ni}+\omega)t}}{\omega_{ni}+\omega}}_{\text{peaked near } \omega = -\omega_{ni}} \mathcal{V}_{ni} + \underbrace{\frac{1 - e^{i(\omega_{ni}-\omega)t}}{\omega_{ni}-\omega}}_{\text{peaked near } \omega = \omega_{ni}} \mathcal{V}_{ni}^{+} \right]$$

$\omega \cong -\omega_{ni}$: Stimulated emission

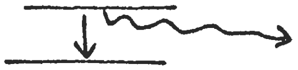
$$|C_n^{(1)}|^2 \approx \frac{4|\mathcal{V}_{ni}|^2}{\hbar^2(\omega+\omega_{ni})^2} \sin^2\left[(\omega+\omega_{ni})^2 t/2\right]$$

Transition rate → state w/ energy E_n at large t

$$\omega_{i\to n} = \frac{2\pi}{\hbar}|\mathcal{V}_{ni}|^2 \delta(E_n - E_i + \hbar\omega)$$

$$\omega_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|\mathcal{V}_{ni}|^2}\rho(E_n)\Big|_{E_n \cong E_i - \hbar\omega}$$

total emission rate



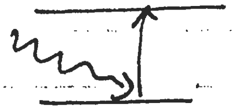
$\omega \cong \omega_{ni}$: absorbtion

$$|C_n^{(1)}|^2 \approx \frac{4|\mathcal{V}_{ni}^{+}|^2}{\hbar^2(\omega-\omega_{ni})^2} \sin^2\left[(\omega-\omega_{ni})^2 t/2\right]$$

$$w_{i\to n} = \frac{2\pi}{\hbar}|V^{+}_{ni}|^2\,\delta(E_n - E_i - \hbar\omega)$$

$$w_{i\to[n]} = \frac{2\pi}{\hbar}\overline{|V^{+}_{ni}|^2}\,\rho(E_n)\Big|_{E_n \cong E_i+\hbar\omega}$$

total absorbtion rate



So - harmonic perturbation causes stimulated emission or absorbtion in units of $\hbar\omega$.

- Just what we expect if background made up of quanta w/ $E=\hbar\omega$!

For transitions to occur & satisfy energy conservation, must have

(a) final states exist over continuous energy range, to match $\Delta E = \hbar\omega$ for fixed perturbation frequency ω

—or-

(b) Perturbation must cover sufficiently wide spectrum of ω so that discrete transition with a fixed $\Delta E = \hbar\omega$ is possible.

- Note that spectral lines are not really sharp, due to decay processes.

Note: For two discrete states, $w^{(abs)}_{i\to n} = w^{(em.)}_{n\to i}$ in semiclassical calc. since $|W_{ni}|^2 = |W^{\dagger}_{ni}|^2$

⇒ <u>Detailed balance</u>

[Really, only true @ $T=\infty$ when rad. field quantized]

Now: Emission & Absorbtion of EM radiation by atoms

6.5 Coupling to radiation field

Recall E & M

$$F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu \qquad \mu = 0,1,2,3$$

$$A_\mu = (-\phi, \vec{A})$$
$$x^\mu = (ct, \vec{x})$$

$$E_i = F_{i0} = -F_{0i} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} - \frac{\partial \phi}{\partial x^i}$$
$$B^i = \tfrac{1}{2}\varepsilon^{ijk} F_{jk} = \varepsilon^{ijk}\partial_j A_k$$

E, B unchanged under gauge xforms

$$A_\mu \to A_\mu + \partial_\mu \Lambda$$

For charged particle, spin $\vec{S}$,

$$H = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 + e\phi - g_s \mu_B \frac{\vec{S}}{\hbar}\cdot(\vec{\nabla}\times\vec{A})$$

In free space (no sources) Maxwell is

$$\partial_\mu F^{\mu\nu} = 0$$

Choose Coulomb (radiation) gauge

$$A_0 = 0, \qquad \underset{\uparrow}{\vec{\nabla}\cdot\vec{A} = 0.}$$

↳ transversality conditi... (Lorentz gauge → get rid of A_0)

Fermi (1930) showed: [see Sakurai: "Advanced QM" for details]

Charged matter + EM fields can be described by [break $A = A_\perp + A_\parallel$]

$$H = \underbrace{\left[\frac{p^2}{2m} + \overset{\substack{\text{instantaneous}\\ \text{Coulomb}\\ \text{interaction}\\ \downarrow}}{V}\right]}_{H_0} \underbrace{- \frac{e}{mc}\vec{p}\cdot\vec{A}_\perp}_{V(t)} + H_{RAD}^{(A_\perp)} + \frac{e^2}{2mc^2}A_\perp^2 - \frac{g\mu}{\hbar}S\cdot B$$

(ignore multi-photon proce
spin effects for now

where $A_\perp$ is purely transverse field. ($\vec{\nabla}\cdot\vec{A}_\perp = 0$
$\vec{\nabla}\times A_\parallel = 0$)

6.6 Absorbtion cross-section

Maxwell eqns for transverse field (drop "$\perp$").

$$\Box A^i = \left(-\frac{1}{c^2}\frac{\partial^2}{\partial t^2} + \nabla^2\right)A^i = 0$$

Plane wave solutions

$$\vec{A} = 2A_0\hat{\varepsilon}\cos\left(\frac{\omega}{c}\hat{n}\cdot\vec{x} - \omega t\right)$$

$$\text{where } \hat{\varepsilon}\cdot\hat{n} = 0$$

Energy density
$$\mathcal{U} = \frac{1}{2}\left(\frac{E_{max}^2}{8\pi^2} + \frac{B_{max}^2}{8\pi^2}\right)$$
$$= \frac{1}{2\pi}\frac{\omega^2}{c^2}|A_0|^2$$

$$\vec{A} = A_0\hat{\varepsilon}\left[\underbrace{e^{i\left(\frac{\omega}{c}\right)\hat{n}\cdot\vec{x} - i\omega t}}_{\text{absorbtion}} + \underbrace{e^{-i\left(\frac{\omega}{c}\right)\hat{n}\cdot\vec{x} + i\omega t}}_{\text{emission}}\right]$$