6. Time-dependent perturbation theory & applications to radiation

So far, focused on H independent of t.

To solve:

- Diagonalize H $\qquad\qquad H|n\rangle = E_n|n\rangle$
- write $|\psi(t)\rangle = \sum c_n(t)\,|n\rangle$
- $|\psi(t)\rangle = e^{-iHt/\hbar}\,|\psi(0)\rangle = \sum_n e^{-iE_nt/\hbar}\,c_n(0)\,|n\rangle$.

In principle, this formalism [describes <u>any</u> closed QM system.]

[can be very complicated in practice – e.g. multi-spin-1/2, many atoms, ...]

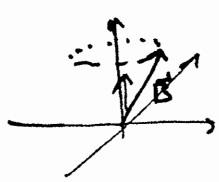
[– does not describe interaction of system with external phenomena]

In many situations, want to isolate a small system described by H_0, describe interactions w/ environment through $V(t)$ (time-dependent)

<u>Examples</u>:

a) spin magnetic resonance

put spin-½ particle ↑ in time-dependent B-field



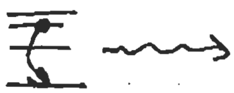
spin precesses around B-field classically...

b) Atom in external EM radiation field: absorbtion / stimulated emission

Phenomena a), b) can be understood by coupling quantum system to a classical EM field (semiclassical approach)

E not conserved since $H(t) = H_0 + V(t)$ is time-dependent.

Also want to consider

c) spontaneous emission 

- For this need to quantize EM field: Quantum field theory.

We will mostly use semiclassical approach, touch on field quantization.

6.1 Time-dependent potentials

Recall the Interaction Picture

$$H = \underbrace{H_0}_{\text{time-independent}} + \underbrace{V(t)}_{\text{time-dependent}}$$

$$|\psi(t)\rangle_I = e^{iH_0t/\hbar}\,|\psi(t)\rangle_S \qquad \left[|\psi(0)\rangle_I = |\psi(0)\rangle_S\right]$$

$$A_I = e^{iH_0t/\hbar} A_S\, e^{-iH_0t/\hbar}$$

[like Heisenberg, but only pull out H_0 dependence]

EOM

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle_I = V_I(t) |\psi(t)\rangle_I$$

[V_I as in Schrödinger picture]

$$\frac{dA_I}{dt} = \frac{1}{i\hbar}[A_I, H_0] + (\dot{A})_I$$

$$(\dot{A})_I \searrow e^{\frac{i}{\hbar}H_0 t}\dot{A}_{(S)}e^{-\frac{i}{\hbar}H_0 t}$$

[H_0 as in Heisenberg picture]

[Compare with Heisenberg picture: $i\hbar \frac{\partial}{\partial t}|\psi\rangle_H = 0$, $\frac{dA_H}{dt} = \frac{1}{i\hbar}[A_H, H] + (\dot{A})_H$]

Expand $|\psi(t)\rangle_I$ using basis of ev's of H_0

$$H_0 |n\rangle = E_n |n\rangle$$

$$|\psi(t)\rangle_I = \sum c_n(t) |n\rangle$$

EOM $\Rightarrow$

$$i\hbar \frac{\partial}{\partial t} \langle n|\psi(t)\rangle_I = \sum_m \langle n| \overbrace{V_I(t)}^{e^{\frac{i}{\hbar}E_n t} V_S(t) e^{-\frac{i}{\hbar}E_m t}} |m\rangle\langle m|\psi(t)\rangle_I$$

$$\boxed{i\hbar \dot{c}_n(t) = \sum_m V_{nm}(t) e^{i\omega_{nm}t} c_m(t)}$$

where

$$V_{nm}(t) = \langle n| V_S(t) |m\rangle$$

$$\omega_{nm} = \frac{E_n - E_m}{\hbar} = -\omega_{mn}$$

Coupled 1st order diff. eq.'s describe time evolution.

[exact description]

6.2 Exactly solvable 2-state problem

Consider a two-state system with

$$H_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

$$V(t) = \begin{pmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{pmatrix} \quad [\, V_{12} = \gamma e^{i\omega t};\; V_{21} = \gamma e^{-i\omega t} \,]$$

In interaction picture

$$i\hbar \dot{c}_1 = \gamma e^{i[\omega + \frac{E_1 - E_2}{\hbar}]t} c_2(t)$$

$$i\hbar \dot{c}_2 = \gamma e^{i[-\omega - \frac{E_1 - E_2}{\hbar}]t} c_1(t)$$

$$\Rightarrow \quad \frac{dc}{dt} = \frac{-i\gamma}{\hbar} \begin{pmatrix} 0 & e^{i(\omega - \omega_{21})t} \\ e^{-i(\omega - \omega_{21})t} & 0 \end{pmatrix} c(t) \qquad (*)$$

where $c(t) = \begin{pmatrix} c_1(t) \\ c_2(t) \end{pmatrix}$, $\quad \omega_{21} = \frac{E_2 - E_1}{\hbar}$

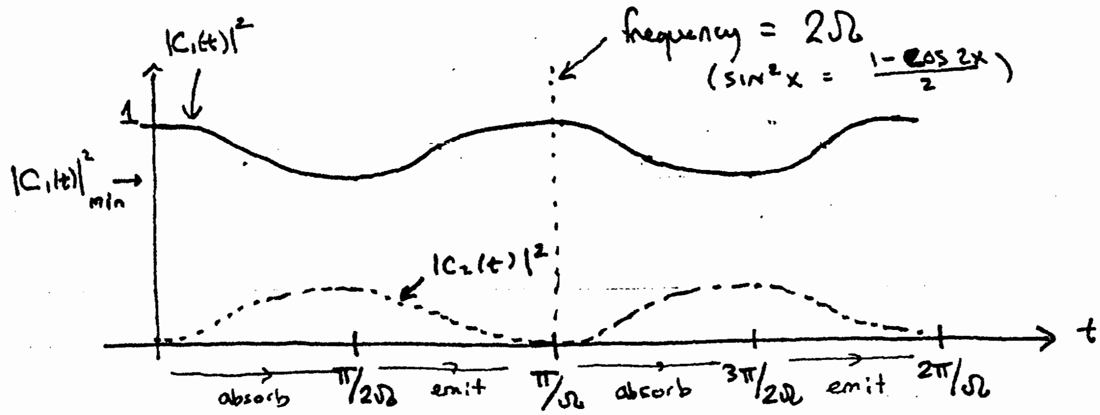
Can find exact solution of $(*)$. [HW]

With initial conditions $c_1(0) = 1$, $c_2(0) = 0$,

$$|c_2(t)|^2 = \frac{\gamma^2}{\gamma^2 + \hbar^2(\omega - \omega_{21})^2/4} \sin^2 \Omega t$$

$$\Omega = \sqrt{\frac{\gamma^2}{\hbar^2} + \frac{(\omega - \omega_{21})^2}{4}}$$

$$|c_1(t)|^2 = 1 - |c_2(t)|^2$$

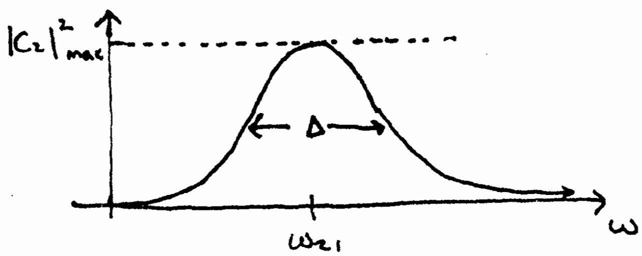


$$|C_1(t)|^2_{min} = \frac{(\omega - \omega_{21})^2}{(\omega-\omega_{21})^2 + 4\delta^2/\hbar^2}$$

At resonance, $\omega = \omega_{21}$

$\omega\Omega = \delta/\hbar$, $\quad |C_1(t)|^2_{min} = 0.$

Amplitude as function of ω:



Δ = full width @ half max
$= 4\delta/\hbar$

- Amplitude peaked @ resonance
- width $\propto \delta$ (strength of perturbation)

- Periodically forced 2-state system is a basic problem
  - demonstrates fundamental features of absorbtion & emission.

Analogous to absorbtion & emission of radiation by particles in EM fields

- simplify atom to 2-level system — E_2 — E_1
- Couple to background rad. field @ frequency ω
  $$\left(V \sim \begin{pmatrix} 0 & e^{i\omega t} \\ e^{-i\omega t} & 0 \end{pmatrix} \right)$$
- when ω near $\omega_{21} = \frac{E_2 - E_1}{\hbar}$, system can absorb a quantum of radiation from BG field
- same with stimulated emission when in E_2.

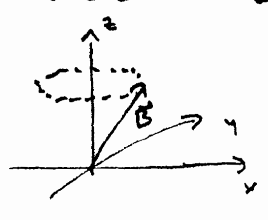
Again, we are doing semiclassical approximation, complete picture of spont. emission requires quantizing b.g. field.

Examples of 2-state systems

a) Spin magnetic resonance

Consider spin $1/2$ particle $(|+\rangle, |-\rangle)$ in magnetic field

$$B = B_0 \hat{z} + B_1 (\hat{x} \cos \omega t + \hat{y} \sin \omega t)$$



[units in $H_0 = \mu_B \frac{\vec{L}}{\hbar} \cdot \vec{B}$]

$$H = -\underset{(2)}{g}\ \underset{\left(\frac{e\hbar}{2mc}\right)}{\mu_B}\ \underset{\left(\frac{\vec{\sigma}}{2}\right)}{\frac{\vec{S}}{\hbar}} \cdot \vec{B}$$

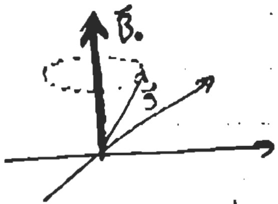
$$= H_0 + V(t)$$

$$H_0 = -\frac{eB_0\hbar}{2mc}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$V(t) = -\frac{eB_1\hbar}{2mc}\begin{pmatrix} 0 & e^{-i\omega t} \\ e^{i\omega t} & 0 \end{pmatrix}$$

Can now apply previous general discussion.

<u>Without</u> B_1,



spin precesses at $\omega = \frac{eB_0}{mc}$ [from last semester]

[phases of C_+, C_- move in opp. direction]

$|C_+|$, $|C_-|$ unchanged – only effect in phases.

$\langle S_z \rangle$ unchanged.

<u>Including</u> B_1, as above, gives oscillations betw. $|C_+|^2, |C_-|^2$.
(spin – flops)

[Classically – precession about a t-dependent axis]

At resonance, $\vec{B}$ rotates @ $\omega = \omega_{21} = \frac{eB_0}{mc}$ [3.98]

– same rate as precession about B_0.

$\Rightarrow$ spin goes all the way down.

Notes:

i) transitions $|+\rangle \to |-\rangle$ occur for any B_1, even very small.

ii) In practice, easier to make

$$\vec{B} = (0,\ B_1 \cos\omega t,\ B_0)$$

$$\Rightarrow e^{i\omega t} \text{ term } + e^{-i\omega t} \text{ term.}$$

Near resonance, $\omega = \omega_0$, relevant, other is irrelevant, so same physical effects.

b) MASERS

Ammonia NH_3 molecule: 2 nearby states $|A\rangle$ — $|S\rangle$ — > small ΔE

Under parity operator P: $x \to -x$,

$$P|A\rangle = -|A\rangle$$

$$P|S\rangle = |S\rangle$$

Electric dipole moment $\vec{\mu}_{el}$ odd under parity: $P\vec{\mu}_{el}P = -\mu_{el}$.

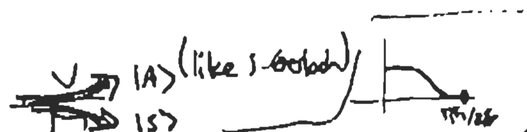
Thus $\langle S|\mu_{el}|S\rangle = \langle A|\mu_{el}|A\rangle = 0$

while $\langle S|\mu_{el}|A\rangle = \langle A|\mu_{el}|S\rangle \neq 0$.

Interaction with E field: $V = -\vec{\mu}_{el}\cdot\vec{E}$

Consider $\vec{E} = |E|_{max}\,\hat{z}\cos\omega t$

Gives example of 2-state problem.



MASER: select beam of $|A\rangle$'s

pass through μwave field $\omega = \frac{E_A - E_S}{\hbar}$ for time $t = \frac{\pi\hbar}{2\delta}$.

All $|A\rangle \to |S\rangle$, amplifies field

MASER = Microwave Amplification by Stimulated Emission of Radiation

Similar story w/ Hydrogen maser using hyperfine 21 cm line (that's why 1420 MHz known)

6.3 Time-dependent perturbation theory

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

Must use perturbative analysis

Expand

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

$C_n^{(0)}$ 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

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

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

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

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

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

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.

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

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

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

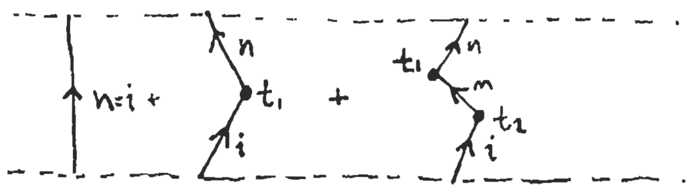
$$C_n^{(2)}(t) = -\frac{1}{\hbar^2}\sum_m \int_{t_0}^{t} dt' \int_{t_0}^{t'} dt''\, e^{i\omega_{nm}t' + i\omega_{mi}t''} V_{nm}(t')\, V_{mi}(t'')$$

[trans prob – next page] $\vdots$

Graphical depiction: "Feynman diagrams"

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

=



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 $V(t) = \hat{V}\sin\omega t$. $\qquad t > 0$

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

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

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

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

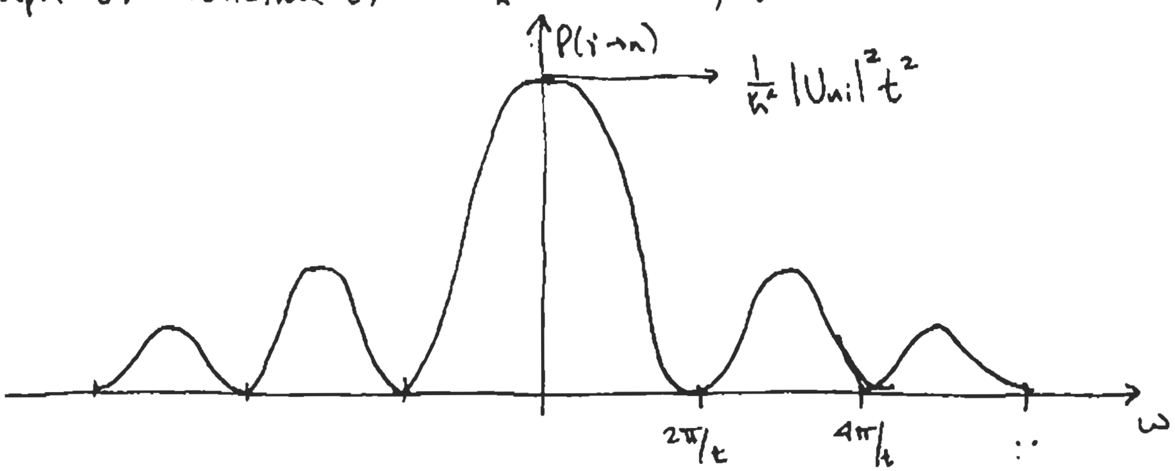
$$C_n^{(1)}(t) = \frac{\hat{V}_{ni}}{\hbar\omega_{ni}}\left[1-e^{i\omega_{ni}t}\right]$$

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, $\Delta E \sim \dfrac{2\pi\hbar}{t}$.

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,

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

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

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

Total transition rate = trans. prob. / unit time

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

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

$[n]$: final states w/ energy $\approx E_i$

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

Back to harmonic perturbation

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

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

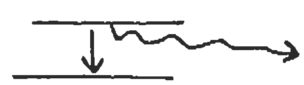
<u>$\omega \cong -\omega_{ni}$: Stimulated emission</u>

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

Transition rate → state w/ energy E_n at large t

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

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

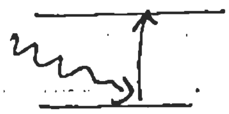
total emission rate 

<u>$\omega \cong \omega_{ni}$: absorbtion</u>

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

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

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

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, $\omega_{i\to n}^{(abs)} = \omega_{n\to i}^{(em.)}$ in semiclassical calc. since $|W_{ni}|^2 = |W_{ni}^{\dagger}|^2$

⇒ <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

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

transversality condition... (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 $A = A_\perp + A_\parallel$]

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

(ignore multi-photon proc
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

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

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

Energy density

$$\mathcal{U} = \frac{1}{2}\left(\frac{E_{max}^2}{8\pi^2} + \frac{B_{max}^2}{8\pi^2}\right)$$

$$= \frac{1}{2\pi}\frac{\omega^2}{c^2}|A_0|^2$$

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

Back to harmonic perturbation

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

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

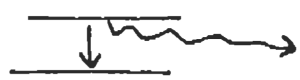
$\omega \cong -\omega_{ni}$: stimulated emission

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

Transition rate → state w/ energy E_n at large t

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

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

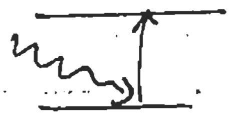
total emission rate 

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

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

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

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

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, $\omega_{i\to n}^{(abs)} = \omega_{n\to i}^{(em.)}$ in semiclassical calc. since $|W_{ni}|^2 = |W_{ni}^{\dagger}|^2$

⇒ <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

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

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

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

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

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

transversality condition... (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 $A = A_\perp + A_\parallel$]

instantaneous Coulomb interaction

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

(ignore multi-photon proc, 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

$$\mathcal{U} = \frac{1}{2}\left(\frac{E_{max}^2}{8\pi^2} + \frac{B_{max}^2}{8\pi^2}\right)$$

$$= \frac{1}{2\pi} \frac{\omega^2}{c^2} |A_0|^2$$

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

For absorbtion:

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

$$V_{ni}^{+} = \langle n| -\frac{e}{mc}\, \vec{p}\cdot\vec{A}_{ws} |i\rangle$$
$$= -\frac{eA_0}{mc} \langle n| e^{i(\frac{\omega}{c})(\hat{n}\cdot\vec{x})}\, \hat{\varepsilon}\cdot\vec{p}|i\rangle$$

Absorbtion cross-section:

$$\sigma_{abs} = \frac{\text{Energy absorbed per unit time}}{\text{Energy flux}}$$

$$= \frac{\hbar\omega\, \omega_{i\to n}}{c\,U}$$

$$= \frac{4\pi^2\hbar}{m^2\omega} \underbrace{\left(\frac{e^2}{\hbar c}\right)}_{\alpha = 1/137} |\langle n| e^{i(\frac{\omega}{c})\hat{n}\cdot\vec{x}}\, \hat{\varepsilon}\cdot\vec{p}|i\rangle|^2 \delta(E_n - E_i - \hbar\omega)$$

(units L^2)

Emission probability: same as absorbtion in semiclassical picture (detailed balance)

Dipole approximation:

if $\lambda = \frac{2\pi c}{\omega} \gg R_{atom}$, or

can neglect subleading terms in $e^{i(\frac{\omega}{c})\hat{n}\cdot\vec{x}} = 1 + i\left(\frac{\omega}{c}\right)\hat{n}\cdot\vec{x} + \ldots$

e.g. for Hydrogen:

$$E_I \cong \frac{me^4}{2\hbar^2} \cong 13.6 \text{ eV}$$

$$a_0 \cong \frac{\hbar^2}{me^2} \cong 0.52 \text{ Å} \qquad \text{(Bohr radius)}$$

$$\Delta E \cong \frac{me^4}{2\hbar^2} = \hbar\omega$$

$$\Rightarrow \quad \omega = \frac{me^4}{2\hbar^3} = \alpha \frac{mce^2}{2\hbar^2} = \frac{\alpha}{2}\frac{c}{a_0} \qquad \left(\alpha = \frac{e^2}{\hbar c} \cong \frac{1}{137}\right)$$

$$\Rightarrow \lambda = \frac{2\pi c}{\omega} \cong \frac{4\pi}{\alpha} a_0 \gg a_0$$

so dipole approx. is valid

- generally good for atoms with small Z.
- doesn't work for processes in which E1 (electric dipole) transitions not possible.

So:

$$\langle n | e^{i\left(\frac{\omega}{c}\right)(\hat{n}\cdot\vec{x})} \hat{\varepsilon}\cdot\vec{p} | i\rangle \longrightarrow \hat{\varepsilon}\langle n|\vec{p}|i\rangle$$

assume wlog $\hat{\varepsilon} = \hat{x}$, $\quad \hat{n} = \hat{z}$

need

$$\langle n|p_x|i\rangle = \frac{m}{i\hbar}\langle n|[x, H_0]|i\rangle$$

$$= i m \omega_{ni} \langle n|x|i\rangle$$

$$\boxed{\sigma_{abs} = 4\pi^2 \alpha\, \omega_{ni} |\langle n|x|i\rangle|^2 \delta(\omega - \omega_{ni})}$$

For electric dipole

6.7 Photoelectric effect

Consider ejection of electron by rad. field (ionization)

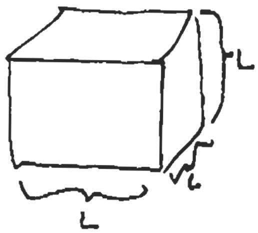
$|i\rangle$ = bound atomic state

$|n\rangle$ = continuum state: plane wave $|p\rangle$

Need to know density of states $\rho(E)$

2 ways to calculate:

a) Box normalization



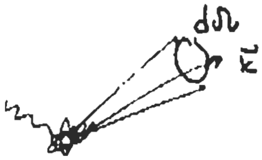
$$\langle \vec{x} | \vec{p} \rangle = \frac{e^{i\vec{k}\cdot\vec{x}}}{L^{3/2}} \qquad \vec{p} = \hbar\vec{k}$$

$$k_i = \frac{2\pi n_i}{L}, \quad n_i \in \mathbb{Z}, \quad i = 1,2,3 \quad (x,y,z)$$

$$E = \frac{\hbar^2 k^2}{2m_e} = \frac{2\pi^2\hbar^2 n^2}{m_e L^2}$$

$$dE = \frac{4\pi^2\hbar^2 n\,dn}{m_e L^2} \qquad n^2 = n_1^2 + n_2^2 + n_3^2$$

Choose solid angle $d\Omega$



$$dN \cong d\Omega\, n^2 dn = \frac{m_e L^2}{4\pi^2\hbar^2}\, n\, d\Omega\, dE$$

$$= \left(\frac{L}{2\pi}\right)^3 \frac{mp}{\hbar^3}\, d\Omega\, dE$$

$$\rho(E) = \frac{dN}{dE} = \left(\frac{L}{2\pi}\right)^3 \frac{mp}{\hbar^3}\, d\Omega$$

$$|\langle p|V|i\rangle|^2 \rho(E) = \left|\int e^{-ip\cdot x/\hbar}\, V\, \psi_i\right|^2 \frac{mp}{(2\pi\hbar)^3}\, d\Omega$$

[note: L dependence cancels]

b) Continuum normalization

$$\langle \vec{x}|\vec{p}\rangle = \frac{1}{(2\pi\hbar)^{3/2}}\, e^{i\vec{p}\cdot\vec{x}/\hbar}$$

$$\sum_n |\langle n|V|i\rangle|^2\, \delta(E_n - E)$$

$$\rightarrow \int d^3\vec{p}\, |\langle\vec{p}|V|i\rangle|^2\, \delta\left(\frac{p^2}{2m} - E\right)$$

$$= \int d\Omega \int p^2 dp\, |\langle\vec{p}|V|i\rangle|^2 \left(\frac{m}{p}\right) \delta(p - \sqrt{2mE})$$

$$\left[\delta(f(p)) = \frac{\delta(p)}{|f'(p)|},\ f(0) = 0\right]$$

$$= d\Omega\, mp\, |\langle p|V|i\rangle|^2$$

$$= \left|\int d^3x\, e^{-i\vec{p}\cdot\vec{x}}\, V\, \psi_i\right|^2 \frac{mp}{(2\pi\hbar)^3}\, d\Omega$$

For photoelectric effect:

$$\frac{d\sigma}{d\Omega} = \frac{4\pi^2 \alpha \hbar}{m^2 \omega} \cdot \frac{mp}{\cancel{(2\pi\hbar)^3}} (\hat{\varepsilon}\cdot\vec{p})^2 |\langle \vec{p}|0\rangle|^2$$

(E1 approximation)

$$= \frac{32 e^2 p \, (\hat{\varepsilon}\cdot p)^2}{m c \omega \hbar^3 a_0^5} \frac{1}{(1/a_0^2 + p^2/\hbar^2)^4}$$

[Fourier xform: homework]

6.8 Quantization of transverse EM field

Computed absorbtion & emission semiclassically
— results proportional to incoming radiation flux

OK for absorbtion, stimulated emission in strong fields

Clearly fails for spontaneous emission.

For better understanding: quantize EM field

Quantization of radiation field (skipping subtleties)

Write

$$A(\bar{x},t) = \frac{1}{\sqrt{V}} \sum_{k,\alpha} c \sqrt{\frac{2\pi\hbar}{\omega}} [a_{k,\alpha} \varepsilon^\alpha e^{i\vec{k}\cdot\vec{x} - i\omega t} + a^*_{k,\alpha} \varepsilon^\alpha e^{-i\vec{k}\cdot\vec{x} + i\omega t}]$$

$$\omega = |k| c$$

Hamiltonian is

$$H = \frac{1}{8\pi^2} \int (B^2 + E^2)\, d^3x$$

$$= \frac{1}{2\cancel{8\pi}} \sum_{k,\alpha} (a^*_{k,\alpha} a_{k,\alpha} + a_{k,\alpha} a^*_{k,\alpha}) \hbar\omega$$

Hamiltonian of a system of uncoupled oscillators

Quantize: $a, a^* \longrightarrow a, a^+$ operators

$$[a_{k,\alpha}, a^+_{k,\alpha}] = \delta_{kk'} \delta_{\alpha\alpha'}$$

Number operator: $N_{k,\alpha} = a^+_{k,\alpha} a_{k,\alpha}$

$$H = \sum_{k,\alpha} N_{k,\alpha} \hbar\omega$$ (dropping infinite contribution $\Sigma\, \hbar\omega/2$ to vac. energy – relevant for Casimir energy...

Hilbert space:

Fock space built by acting with a^+'s on vacuum

$|0\rangle$ = vacuum, $a_{k,\alpha}|0\rangle = 0 \quad \forall\, k,\alpha$

$a^+_{k,\alpha}|0\rangle$ = 1-photon state

$a^+_{k,\alpha} a^+_{k',\alpha'}|0\rangle = a^+_{k',\alpha'} a^+_{k,\alpha}|0\rangle$ = 2 photon state

$\vdots$

Recall SHO matrix elements

$$\langle n' | a^\dagger | n \rangle = \sqrt{n+1}\, \delta_{n', n+1}$$
$$\langle n' | a | n \rangle = \sqrt{n}\, \delta_{n', n-1}$$

Can now compute matrix element for absorbtion/emission

Absorbtion:

$$V_{fi}^{+} = \langle f; n_{k,\alpha}-1 | -\frac{e}{mc}\, \vec{p} \cdot \varepsilon^{(\alpha)} \underbrace{\left[\frac{c}{\sqrt{V}} \sqrt{\frac{2\pi\hbar}{\omega}}\right]}_{A_0} a_{k,\alpha}\, e^{i\frac{\omega}{c}\hat{n}\cdot\vec{x}} | i; n_{k,\alpha} \rangle$$

agrees with semiclassical expression, where

$$A_0 \Rightarrow \frac{c}{\sqrt{V}} \sqrt{\frac{2\pi\hbar}{\omega}} \sqrt{n_{k,\alpha}}$$

Fits in with

$$\mathcal{U} = \frac{1}{2\pi} \frac{\omega^2}{c^2} |A_0|^2 \Rightarrow \int \mathcal{U} = \sum N_{k,\alpha}\, \hbar\omega = H$$

So: same absorbtion result as semiclassical approach.

Emission:

$$V_{fi} = \langle f; n_{k,\alpha}+1 | \frac{-e}{mc}\, \vec{p} \cdot \varepsilon^{*} \left[\frac{c}{\sqrt{V}} \sqrt{\frac{2\pi\hbar}{\omega}}\right] a_{k,\alpha}^{\dagger}\, e^{-i\left(\frac{\omega}{c}\right)\hat{n}\cdot\vec{x}} | i; n_{k,\alpha} \rangle$$

same as before, but

$$A_0 \to \frac{c}{\sqrt{V}}\sqrt{\frac{2\pi\hbar}{\omega}}\sqrt{n_{k,\alpha}+1}$$

for emission formula

[note: $A \sim \sqrt{n}$ still in U]

Corrects emission rate;
agrees at large n, but allows spontaneous emission

6.9 E1 spontaneous emission

Spontaneous emission rate in dipole approximation:

$$n_{k,\alpha} = 0$$

$$\boxed{V_{fi}^{(E1)} = -\frac{e}{mc}\frac{1}{\sqrt{V}}c\sqrt{\frac{2\pi\hbar}{\omega}}\langle f|\hat{\varepsilon}\cdot\vec{p}|i\rangle}$$

generally,

$$\omega_{i,n;f,n+1} = \frac{2\pi}{\hbar}\frac{e^2}{m^2V}\frac{2\pi\hbar}{\omega}_{(n+1)}|\langle f|\hat{\varepsilon}\cdot\vec{p}|i\rangle|^2\rho(E)$$

Can compute $\rho(E)$ for photon of energy $E = \hbar\omega$, fixed polarization [HW]

$$\rho(E) = \left(\frac{L}{2\pi c}\right)^3\frac{\omega^2}{\hbar}\,d\Omega$$

so for spontaneous single photon emission $\left(p = \frac{m}{i\hbar}[x,H]\right)$

$$dw = \frac{e^2\omega^3}{2\pi c^3\hbar}\left|\sum_i \hat{\varepsilon}_i^{(\alpha)}\langle f|x^i|i\rangle\right|^2 d\Omega$$

$$= \boxed{\frac{\alpha}{2\pi}\frac{\omega^3}{c^2}|\langle f|\hat{\varepsilon}\cdot\vec{x}|i\rangle|^2\,d\Omega}$$

spontaneous E1 emission rate

<u>selection rules for E1 transition</u>

Since $\vec{X}$ is a first rank tensor,

$$\langle j_f, m_f \mid X^{(1)}_m \mid j_i, m_i \rangle \sim \langle j_f, m_f \mid 1, m; j_i, m_i \rangle \frac{\langle j_f \| X^{(1)} \| j_i \rangle}{\sqrt{2j_i+1}}$$

(Wigner - Eckart)

$$\Rightarrow \quad j_f = j_i \pm 1 \quad \text{or} \quad j_f = j_i,$$

$$j_i = 0 \not\Rightarrow j_f = 0.$$

Also : $P \vec{x} P = -\vec{x}$, so $|i\rangle, |f\rangle$ have opposite parity

$$P_i P_f = -1.$$

<u>Example:</u> Consider $2p \to 1s$ in Hydrogen

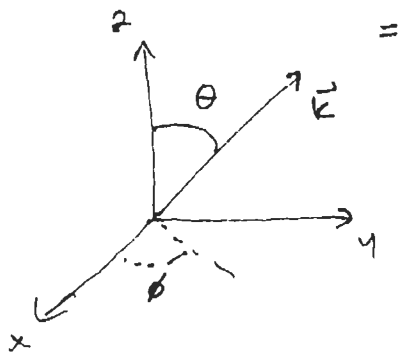
<u>Angular distribution:</u>

in HW did case $m_i = +1 \to m_f = 0.$

$$\vec{X} \sim \left(\frac{1}{\sqrt{2}} (Y_{1,+1} - \underline{Y_{1-1}}), \frac{1}{\sqrt{2}} (Y_{1+1} + \underline{Y_{1-1}}), Y_{10} \right)$$

found $\frac{dW}{d\Omega} \sim \frac{1}{2}\left(1 + \cos^2\theta\right)$

$$= \sum_\alpha \frac{1}{2}\left((\hat{\varepsilon}^{(\alpha)}_x)^2 + (\hat{\varepsilon}^{(\alpha)}_y)^2 \right)$$



Consider case $m_i = 0 \longrightarrow m_f = 0$

$$\frac{dW}{d\Omega} \sim \sum_\alpha \left(\hat{\varepsilon}_z^{(\alpha)}\right)^2 = \sin^2\theta$$

[Note: $\underbrace{\tfrac{1}{2}(1+\cos^2\theta)}_{m_i=1} + \underbrace{\tfrac{1}{2}(1+\cos^2\theta)}_{m_i=-1} + \underbrace{\sin^2\theta}_{m_i=0} = 2$

so isotropic photon distribution if start w/ uniform distributed state]

so

$$dW = \frac{\alpha}{2\pi}\frac{\omega^3}{c^2}\left|\langle f|z|i\rangle\right|^2 \sin^2\theta \cdot 2\pi \sin\theta \, d\theta$$

so spontaneous emission rate is

$$A = \int dW = \frac{4}{3}\frac{\alpha\omega^3}{c^2}\left|\langle f|z|i\rangle\right|^2$$

Note: same for $m = \pm 1$, since $\int_0^\pi \sin^3\theta = \frac{1}{2}\int_0^\pi \sin\theta(1+\cos^2\theta) = \frac{4}{3}$

Performing explicit calculation [HW]

$$A = 6.25 \times 10^8 \ s^{-1}.$$

Prob. state has decayed at time t is

$$|c_i|^2 = e^{-t/\tau}.$$

$$\tau = \frac{1}{A} = \text{mean lifetime} = 1.6 \times 10^{-9} \ s.$$

6.10 Higher multipole transitions

For some transitions $i \to f$

$$\langle f | \hat{\varepsilon} \cdot \vec{p} | i \rangle = 0$$

So E1 transitions not allowed.

Examples:

a) $3d \to 1s$ in hydrogen

[$j_i = 2 \to j_f = 0$ $\Rightarrow \Delta j = 0$, not E1. also, $P_i P_f = +1$]

b) Hyperfine transition in hydrogen

[$P_i = P_f$]

Need to include higher-order terms in $e^{-i\vec{k}\cdot\vec{x}}$

$$e^{-i\vec{k}\cdot\vec{x}} = 1 - \underbrace{\boxed{i\vec{k}\cdot\vec{x}}}_{E2,\ M1} + \ldots$$

For single photon emission

$$V_{fi} = +\frac{e}{m\sqrt{V}}\sqrt{\frac{2\pi\hbar}{\omega}}\langle f | e^{i\vec{k}\cdot\vec{x}}\, \vec{p}\cdot\hat{\varepsilon}^{(\alpha)} | i \rangle$$

$$(\vec{k}\cdot\vec{x})(\vec{p}\cdot\hat{\varepsilon}) = \frac{1}{2} k_i \hat{\varepsilon}_j \left[(x_i p_j - p_i x_j) + (x_i p_j + p_i x_j)\right]$$

$$= \frac{1}{2} k_i \hat{\varepsilon}_j \left[\underbrace{(x_i p_j - x_j p_i)}_{M1} + (x_i p_j + p_i x_j)\right]$$

(since $\vec{k}\cdot\hat{\varepsilon} = 0$)

M1 (magnetic dipole) decay

$$V_{fi}^{(L)} = \frac{ie}{mc\sqrt{V}}\sqrt{\frac{\pi\hbar\omega}{2}} \langle f | (\hat{k}\times\hat{\varepsilon})\cdot \vec{L} | i\rangle$$

Recall spin $\cdot$ B term in H_{int}

$$H^{(SB)} = -\frac{g\mu_B}{\hbar}\vec{S}\cdot\vec{B}$$

$$\vec{B} = \vec{\nabla}\times\vec{A} = \frac{i}{\sqrt{V}}(\vec{k}\times\hat{\varepsilon})\, c\sqrt{\frac{2\pi\hbar}{\omega}}\left[a_{k,\alpha} e^{i\vec{k}\cdot\vec{x} - i\omega t} - a^{+}_{k,\alpha} e^{-i\vec{k}\cdot\vec{x} + i\omega t}\right]$$

$$\Downarrow$$

$$V_{fi}^{(S)} = -\frac{i g\mu_B}{\sqrt{V}\,\hbar}\, c\sqrt{\frac{2\pi\hbar}{\omega}} \langle f | (\vec{k}\times\hat{\varepsilon})\cdot S | i\rangle$$

using $\mu_B = -e\hbar/2mc$

$$\boxed{V_{fi}^{M1} = \frac{ie}{mc\sqrt{V}}\sqrt{\frac{\pi\hbar\omega}{2}} \langle f | (\hat{k}\times\hat{\varepsilon})\cdot(\vec{L} + g\vec{S}) | i\rangle}$$

Matrix element for M1 (magnetic dipole) transitions

M1 selection rules:

$\vec{L} + g\vec{S}$ is a vector operator

$$P(\vec{L} + g\vec{S})P = \vec{L} + g\vec{S},$$

so $j_f = j_i \pm 1$, or $j_f = j_i$, no $j_i = 0 \not\rightarrow j_f = 0$.

$$P_i P_f = +1$$

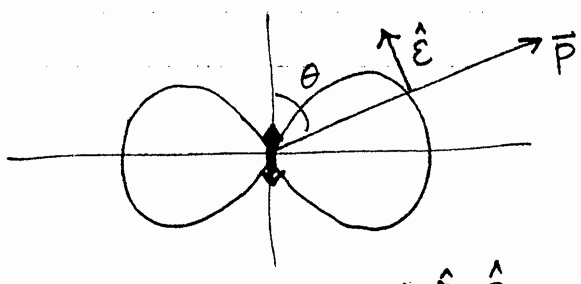
- Can use M1 rule to calculate hyperfine $F=1 \rightarrow F=0$ transition in hydrogen [HW] $(F = I + S)$

- Characteristic strength of M1 interactions

$$\frac{V^{(M1)}}{V^{(E1)}} \sim \frac{\mu_B}{e a_0} \sim \alpha \sim 10^{-2}$$

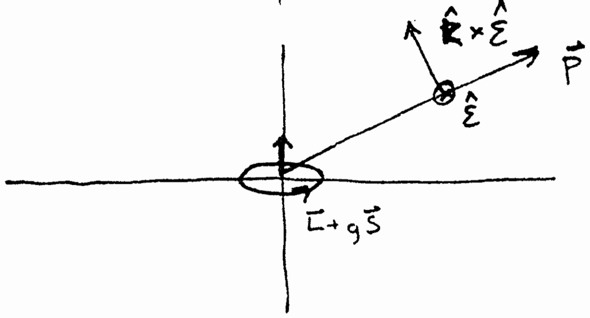
- Compare polarization of E1, M1 radiation

E1 $(\Delta m = 0)$



intensity $\sim \sin^2\theta$
$\sim \varepsilon_z^2 \sim (\varepsilon \cdot \langle \vec{x} \rangle)^2$

M1 $(\Delta m = 0)$



same intensity $\sim \sin^2\theta$

(but down by α)

E2 (electric quadrupole) decay

Return to term $\frac{1}{2} k_i \hat{\varepsilon}_j (x_i p_j + p_i x_j)$

$$= \frac{m}{2i\hbar} k_i \hat{\varepsilon}_j \left(x_i [x_j, H] + [x_i, H] x_j \right)$$

$$= \frac{m}{2i\hbar} k_i \hat{\varepsilon}_j \left\{ x_i x_j H - H x_i x_j \right\}$$

so

$$V_{fi}^{(E2)} = \frac{ie}{m\sqrt{V}} \sqrt{2\pi\hbar\omega} \, \frac{1}{c} \frac{m\hbar\omega}{2i\hbar} \hat{k}_i \hat{\varepsilon}_j \langle f | x_i x_j | i \rangle$$

$$\boxed{V_{fi}^{(E2)} = \frac{e\omega}{c\sqrt{V}} \sqrt{\frac{\pi\hbar\omega}{2}} \langle f | \hat{k}_i \hat{\varepsilon}_j \left(x_i x_j - \tfrac{1}{3}\delta_{ij} x^2\right) | i \rangle}$$

matrix element for E2 (electric quadrupole) transitions

- Can use to calculate $3d \to 1s$ emission [HW]

- Characteristic strength

$$\frac{V^{(E2)}}{V^{(E1)}} \sim \frac{\omega a_0}{c} \sim \alpha \sim 10^{-2}$$

- operator $x_i x_j - \frac{1}{3}\delta_{ij} x^2$ is spin 2 tensor operator

selection rule: $|j_f - j_i| \leq 2 \leq j_i + j_f$

Higher multipoles

Can expand $e^{-i\vec{k}\cdot\vec{x}}$ further ...

Better approach: <u>Vector spherical harmonics</u>

Basic idea:

solve wave equation

$$\nabla^2 \vec{A} - \frac{1}{c^2}\ddot{\vec{A}} = 0$$

in spherical coordinates,

Classify solutions under representations of $SO(3)$ generators

$$\vec{J} = \vec{L} + \vec{S}$$

$$\vec{L} = (\vec{X} \times \vec{p})$$

$$(\vec{S}\cdot\vec{v}) = i\hbar\,\vec{v}\,\times$$

simultaneously rotates vector $\vec{A}$, coordinates.

$S^2\vec{A} = 2\hbar\vec{A}$, since photon has spin 1.

Two types of solutions

$A^{(e)}_{LM}(r,\theta,\phi)$: no radial cpt. to $\vec{B}$

$A^{(m)}_{LM}(r,\theta,\phi)$: no radial cpt. to $\vec{A}$.

Can express in terms of Bessel fns, $Y_{LM}(\theta,\phi)$.

Give wavefunction of photons emitted by multipole transitions. [e.g. $A^{(e)}_{11}$ for $2p \to 1s$ $m=1 \to m=0$]

[For more: see nucl. theory texts]

6.11 Planck's radiation law

Consider an atom in a radiation field which goes between states A & B by emission/absorbtion

$$A \rightleftarrows B + \gamma$$

In thermal equilibrium

$$N(A) \cdot W_{emis} = N(B) \cdot W_{abs}$$

$$\frac{N(B)}{N(A)} = \frac{e^{-E_B/kT}}{e^{-E_A/kT}} = e^{+\hbar\omega/kT} = W_{emis}/W_{abs} = \frac{n_{k,\alpha}+1}{n_{k,\alpha}}$$

so

$$n_{k,\alpha}\left(e^{+\hbar\omega/kT} - 1\right) = 1$$

$$n_{k,\alpha} = \frac{1}{e^{+\hbar\omega/kT} - 1}$$

Energy density per unit volume

$$U(\omega)\,d\omega = \frac{1}{L^3} \cdot \underbrace{2}_{\text{polarization}} \cdot \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \cdot \rho(\omega)$$

$$\rho(\omega) = \hbar\rho(E) = 4\pi\left(\frac{L}{2\pi c}\right)^3 \omega^2$$

$$= \frac{8\pi\hbar}{c^3}\left(\frac{\omega}{2\pi}\right)^3\left(\frac{1}{e^{\hbar\omega/kT} - 1}\right) d\omega$$

in terms of $\nu = \omega/2\pi$

$$U(\nu)\,d\nu = \frac{8\pi h}{c^3}\nu^3 \frac{1}{e^{h\nu/kT} - 1}\,d\nu$$

Planck law (Planck: 1900)

6.12 Damping & natural line width

Back to TDPT

$$H = H_0 + V\cancel{(t)} \qquad \text{(assume } V \text{ t-independent)}$$

$$|\psi(t)\rangle_I = \sum C_n(t)\,|n\rangle$$

$$i\hbar\,\dot{C}_n = \sum_m V_{nm}\,e^{i\omega_{nm}t}\,C_m(t)$$

1st order approx: replace $C_m(t) \to \delta_{m0}$ on RHS

Better approximation (Weisskopf & Wigner) for unstable states:

- Assume $c_i(t) = e^{-\gamma/2\,t}$

$$\gamma = \gamma_1 + i\gamma_2$$

γ_2 = energy shift (pure phase $e^{-i\gamma_2/2\,t}$)

γ_1 : describes decay rate ($|c_i|^2 = e^{-\gamma_1 t}$)

Plug Ansatz for $C_i(t)$ into EoM for $C_n(t)$, $n \neq i$

$$\dot{C}_n(t) = -\frac{i}{\hbar}V_{ni}\,e^{i\omega_{ni}t}\,e^{-\gamma/2\,t}$$

Consistency condition: plug solution for $C_n(t)$ into

$$\dot{C}_i(t) = -\frac{\gamma}{2}e^{-\gamma/2\,t} = -\frac{i}{\hbar}\left(V_{ii}\,e^{-\gamma/2\,t} + \sum_{n\neq i} V_{in}\,C_n(t)\,e^{-i\omega_{ni}t}\right)$$

$\Rightarrow$ fixes γ.

solve for $C_n(t)$

$$C_n(t) = V_{ni} \frac{e^{-i(\omega_{in} - i\gamma/2)t} - 1}{\hbar(\omega_{in} - i\gamma/2)} \qquad (*)$$

$$\Rightarrow \left(-\frac{\gamma}{2} + \frac{i}{\hbar} V_{ii}\right) e^{-\gamma/2\, t} = -\frac{i}{\hbar} \sum_{n \neq i} |V_{ni}|^2 \frac{\left[e^{-\gamma/2\, t} - e^{-i\omega_{ni} t}\right]}{\hbar(\omega_{in} - i\gamma/2)}$$

$$\Rightarrow \quad \gamma = \frac{2i}{\hbar}\left[V_{ii} + \sum_{n \neq i} |V_{ni}|^2 \frac{\left[1 - e^{i(\omega_{in} - i\gamma/2)t}\right]}{\hbar(\omega_{in} - i\gamma/2)} \right]$$

V_{ii} just shifts energy (γ_2)

same as 1st order time-independent pert. theory — drop henceforth

Consider $|i\rangle$ an unstable atomic state

decays $|i\rangle \to |n\rangle = |f\rangle +$ photon w/ energy $\varepsilon = \hbar\omega_{if}$

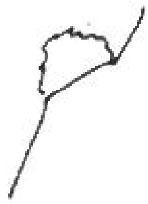
$$\gamma = \frac{2i}{\hbar} \int |V_{ni}|^2 \rho(\varepsilon)\, d\varepsilon \, \frac{\left[1 - e^{i/\hbar[E_{if} - \varepsilon - \cancel{i\hbar\gamma/2}]t}\right]}{E_{if} - \varepsilon - \cancel{i\hbar\gamma/2}}$$

~~impossible to~~ can't solve exactly

Assume γ small, drop on RHS

$$\frac{1 - e^{i/\hbar[E_{if} - \varepsilon]}}{E_{if} - \varepsilon} = \underbrace{\frac{1 - \cos\frac{1}{\hbar}(E_{if} - \varepsilon)t}{E_{if} - \varepsilon}}_{\text{contributes to } \gamma_2} - \underbrace{\frac{i \sin\frac{1}{\hbar}(E_{if} - \varepsilon)t}{E_{if} - \varepsilon}}_{\text{contributes to } \gamma_1}$$

contribution to Γ_2 : energy shift from coupling to radiation field



eg.. Lamb shift – separates $2^2S_{1/2}$, $2^2P_{1/2}$.

Problematic — apparently divergent,
but can be sensibly calculated, get
finite answer (Bethe: nonrel.,
1040 MHz   Weisskopf, Schwinger, Feynman rel.)

contribution to Γ_1 :

as $t \to \infty$ $\qquad \lim_{\alpha\to\infty} \frac{\sin \alpha x}{x} = \pi\,\delta(x)$

$$\Gamma_1 = \frac{2\pi}{\hbar}\int |V_{ni}|^2 \rho(\varepsilon)\, d\varepsilon\, \delta(E_{if} - \varepsilon)$$

$$= \frac{2\pi}{\hbar}|V_{ni}|^2 \rho(E_{if}) = w_{i\to f}$$

So, as expected, Γ_1 is transition prob. per unit time

Natural line width

Back to $(*)$

Transition probability to state $|n\rangle$

$$dp = |V_{ni}|^2 \left| \frac{e^{-i(\omega_{in} - i\Gamma/2)t} - 1}{\hbar(\omega_{in} - i\Gamma/2)} \right|^2 \rho(\omega)\, d\omega$$

$$e^{-i(\omega_{in} - i\gamma/2)t} - 1 = \left(e^{-\gamma/2\, t}\cos\omega_{in} t - 1\right) - i e^{-\gamma/2\, t}\sin\omega_{in} t$$

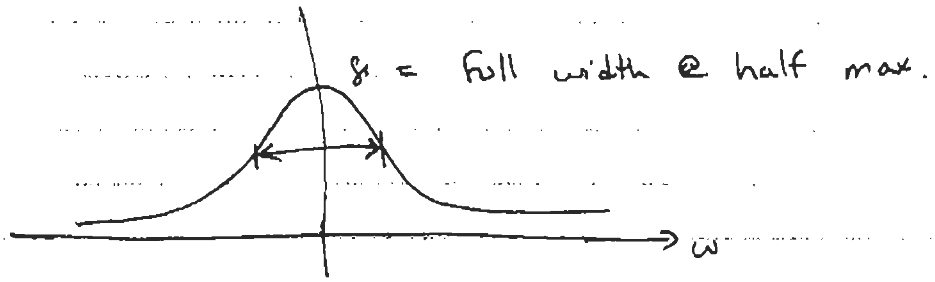
$$\Rightarrow dp = |V_{ni}|^2 \rho(\omega) \frac{1 - 2e^{-\gamma/2\, t}\cos\omega_{in} t + e^{-\gamma t}}{\hbar^2\left[(\omega_{if}-\omega)^2 + \gamma^2/4\right]}\, d\omega$$

γ_1 ; γ_2 just shifts ω_{if}.

as $t \to \infty$,

$$\longrightarrow \frac{1}{\hbar^2}|V_{ni}|^2 \rho(\omega)\, d\omega \, \frac{1}{\left[(\omega_{if}-\omega)^2 + \gamma^2/4\right]}$$

so photon frequency has distribution



state i does not have sharp energy E_i, but natural width

$$\Gamma = \hbar\gamma_1 = \hbar A.$$

A is spontaneous emission decay coefficient.

Ex. $A_{(2p \to 1s)} = 6.25 \times 10^8 \ s^{-1}$

$\Gamma/\hbar = 6.25 \times 10^8$ rad/sec $= 100$ MHz is width of 2p state

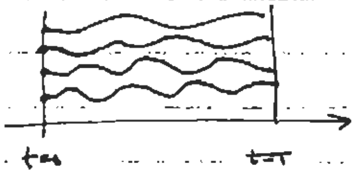
[Fine structure : 10400 MHz
Hyperfine structure : 1420 MHz]

6.13 Adiabatic Theorem & Berry's phase (Sakurai: 464-480)

Time-dependent $H(t)$ with

$$H(t)|n,t\rangle = E_n(t)|n,t\rangle$$

Assume levels never cross



Adiabatic theorem:

Start in state $|i\rangle$, $\quad H(0)|i\rangle = E_i(0)|i\rangle$

If $H(t)$ varies slowly, $|\psi,t\rangle = e^{i\alpha(t)}|i,t\rangle$

(state stays at same level, only phase changes)

Basically, H must change slowly compared to natural oscillation rates in problem
$\dot{H}/H \ll \omega$

Example: spin S particle in changing $\vec{B}$ field

Quantitative understanding:

Expand $\quad |\psi,t\rangle = \sum C_n(t)|n,t\rangle \qquad \langle n,t|m,t\rangle = \delta_{nm}$

$$i\hbar\frac{d}{dt}\left(\sum C_n(t)|n,t\rangle\right) = \sum_n E_n(t)C_n(t)|n,t\rangle$$

$$\Rightarrow \quad i\hbar\dot{C}_m(t) + i\hbar\sum_n C_n(t)\langle m,t|\frac{d}{dt}|n,t\rangle = C_m(t)E_m(t)$$

$$i\hbar \dot{C}_m(t) = C_m(t)E_m(t) - i\hbar C_m(t)\langle m,t|\frac{d}{dt}|m,t\rangle$$

$$\underbrace{-\sum_{n\neq m} i\hbar C_n(t)\langle m,t|\frac{d}{dt}|n,t\rangle}_{\text{assume small} \quad \{\text{justify presently}\}}$$

$$\dot{C}_m(t) = \Big(-\frac{i}{\hbar}E_m(t) - \langle m,t|\frac{d}{dt}|m,t\rangle\Big)C_m(t)$$

$\uparrow$ pure imaginary, since $\frac{d}{dt}\langle m|m\rangle = \langle m|\dot{m}\rangle + \langle \dot{m}|m\rangle = 0$

$$C_m(t) = C_m(0)\, e^{\underbrace{-\frac{i}{\hbar}\int_0^t dt' E_m(t')}_{\text{dynamical phase}} + \underbrace{\int_0^t dt' \langle m,t'|\frac{d}{dt'}|m,t'\rangle}_{\text{Berry's phase (geometrical)}}}$$

Note: phase of basis $|m,t\rangle$ can be chosen arbitrarily,
changes Berry's phase.
Can set $|m,t\rangle = e^{\beta_m(t)}|\widetilde{m,t}\rangle$ so that $\langle\widetilde{m,t}|\frac{d}{dt}|\widetilde{m,t}\rangle = 0$.

Why is $C_n(t)\langle m,t|\frac{d}{dt}|n,t\rangle$ small, $m\neq n$?

Fix $\langle m,t|\frac{d}{dt}|m,t\rangle = 0$

Take $C_m(t) = \tilde{C}_m(t)\, e^{-\frac{i}{\hbar}\int_0^t dt' E_m(t')}$

$$i\hbar \dot{\tilde{C}}_m(t) = -i\hbar \sum_{n\neq m} \tilde{C}_n(t)\langle m,t|\frac{d}{dt}|n,t\rangle\, e^{-\frac{i}{\hbar}\int_0^t (E_n(t') - E_m(t'))dt'}$$

But $\quad \frac{d}{dt}\left(H(t)|n,t\rangle = E_n(t)|n,t\rangle\right)$

$$\Rightarrow \quad \frac{dH(t)}{dt}|n,t\rangle + H(t)\frac{d}{dt}|n,t\rangle = \frac{dE_n(t)}{dt}|n,t\rangle + E_n(t)\frac{d}{dt}|n,t\rangle$$

$$\Rightarrow \quad \langle m,t|\frac{dH}{dt}|n,t\rangle = \left(E_n(t) - E_m(t)\right)\langle m,t|\frac{d}{dt}|n,t\rangle$$

$$\Rightarrow \quad \langle m,t|\frac{d}{dt}|n,t\rangle = \frac{\langle m,t|\frac{dH}{dt}|n,t\rangle}{E_n(t) - E_m(t)}$$

Assume $\tilde{C}_n$, $|n,t\rangle$, $\frac{dH}{dt}$, $E_n(t)$ slowly varying, treat as constant

$$\dot{\tilde{C}}_m(t) = \sum_{n\neq m}\frac{\langle m|\frac{dH}{dt}|n\rangle}{\hbar\omega_{mn}} e^{i\omega_{mn}t}\,\tilde{C}_n$$

$$\tilde{C}_m(t) = \sum_{n\neq m}\frac{\langle m|\frac{dH}{dt}|n\rangle}{i\hbar\omega_{mn}^2}\left(e^{i\omega_{mn}t} - 1\right)\tilde{C}_n$$

Amplitude oscillates.

If $\boxed{\hbar\langle m|\frac{dH}{dt}|n\rangle \ll (E_m - E_n)^2}$, small effect.

this is regime where adiabatic approximation is valid.

Example: Spin ½ particle in rotating B field

$$\vec{B}(t) = B\left(\sin\theta\cos\phi(t),\ \sin\theta\sin\phi(t),\ \cos\theta\right)$$

$$H(t) = 2\vec{B}\cdot\frac{\vec{S}}{\hbar} = \vec{B}\cdot\vec{\sigma} = B\begin{pmatrix}\cos\theta & \sin\theta\, e^{-i\phi} \\ \sin\theta\, e^{i\phi} & -\cos\theta\end{pmatrix}$$

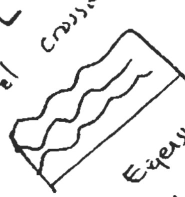
~~Eigenf~~states

$$|+,t\rangle = \begin{pmatrix} \cos\theta/2 \\ \sin\theta/2 \; e^{i\phi(t)} \end{pmatrix} \qquad E_+ = B$$

$$|-,t\rangle = \begin{pmatrix} \sin\theta/2 \\ -\cos\theta/2 \; e^{i\phi(t)} \end{pmatrix} \qquad E_- = -B$$

$$\frac{d}{dt} H(t) = B \begin{pmatrix} 0 & -i\dot{\,} \\ i\dot{\phi}\sin\theta e^{i\phi} & \end{pmatrix}$$

Adiabatic thm: if $\dot{H}/H \ll \omega$ & no level crossing $\left[\hbar \langle m | \frac{dH}{dt} | n\rangle \ll (E_m - E_n)^2 \right]$



Eigenstate of $H(t)$, $[H(t)|n,t\rangle = E_n(t)|n,t\rangle]$

$|\psi,0\rangle = |i\rangle$

$|\psi,t\rangle = e^{i\alpha(t)}|i,t\rangle$

$$\alpha(t) = \underbrace{-\frac{1}{\hbar}\int_0^t dt' E_i(t')}_{\text{dyn. phase}} + \underbrace{\int_0^t dt' \langle i,t'| \frac{d}{dt'} |i,t'\rangle}_{\text{geometrical (Berry's) phase}}$$

$-s\,\theta/2$

$\sin\theta/2 \, e^{i\phi}$

When is adiabatic ap

$\langle +,t| \frac{dH}{dt}$

$E_+ - E_- =$

so adiabatic approx good w

$$\hbar \left| \langle m | \frac{dH}{dt} | n \rangle \right| \ll \min |E_m - E_n|^2$$

$$\Leftrightarrow \quad \hbar B |\dot{\phi} \sin\theta| \ll 4B^2$$

$$\Leftrightarrow \quad \hbar |\dot{\phi}\sin\theta| \ll 4B$$

Take adiabatic approx.. assume initial state $|i,0\rangle = |+,0\rangle$

$$i\hbar \dot{C}_+ = \left(\cancel{\hbar/\hbar} B - i\hbar \underbrace{\langle +,t | \tfrac{d}{dt} | +,t \rangle}_{\sin^2\theta/2 \; i\dot{\phi}} \right) C_+$$

$$\dot{C}_+ = \left(-\tfrac{i}{\hbar} B - i\dot{\phi} \sin^2\theta/2 \right) C_+$$

$$C_+(t) = e^{-\frac{i}{\hbar}Bt \; - \; i\phi \sin^2\theta/2} \; |+,t\rangle$$

dynamical phase

Berry's phase

[note: independent of how ϕ changed over time; depends only on $\phi(t)$.]

For constant rate (exactly solved case)

$$\phi = \frac{2\pi t}{T} = \omega t \qquad \omega = \frac{2\pi}{T}$$

Adiabatic approx good when $\hbar \dot{\phi} \sin\theta \ll 4B$

$$\Leftrightarrow \frac{\hbar}{T} \ll B \;, \qquad T \gg \frac{\hbar}{B}.$$

<u>Berry's phase</u>

Consider H depending on parameter $R(t)$,

R in some space X

Case of particular interest: $\vec{R} \in \mathbb{R}^3$
(e.g. $\vec{R}$ is B-field)

Basis $|n(R)\rangle$:

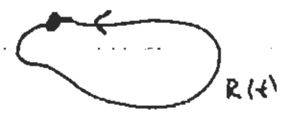
$$H(R)\,|n(R)\rangle = E_n(R)\,|n(R)\rangle .$$

Vary R slowly, so adiabatic approx. is valid.
If $|\psi,0\rangle = |n(R(0))\rangle$,

$$|\psi,t\rangle = e^{-\frac{i}{\hbar}\int_0^t E(t')dt' + i\gamma_n(t)}\,|n(R(t))\rangle .$$

where
$$\dot{\gamma}(t) = i\langle n(R(t))|\frac{d}{dt}|n(R(t))\rangle$$
$$= i\langle n(R(t))|\frac{\partial}{\partial R^j}|n(R(t))\rangle\,\frac{\partial R^j}{\partial t}$$

Consider taking R around a closed loop in X



$$R(T) = R(0)$$

Stokes :
$$\oint_{\partial S}\omega = \int_S d\omega$$

∂S: p-dimensional boundary of a (p+1)-volume S

ω: p-form

S: (p+1)-volume

$d\omega$: (p+1) form

for $p=1$:
$$\oint_{C=\partial S}\omega_i\,dR^i = \iint_S \partial_{[i}\omega_{j]}\,d\sigma^i d\sigma^j$$

antisymmetrize in i,j

If $X = \mathbb{R}^3$, describe with vector calculus

$$\oint_C \vec{\omega}\cdot d\vec{R} = \iint (\vec{\nabla}\times\vec{\omega})\cdot d\vec{S}$$

So

$$\gamma_n = i \iint d\sigma^i d\sigma^j \, \partial_i \langle n(R) | \partial_j | n(R)\rangle$$

~~$= -\iint \vec{V}_n(R)\cdot d\vec{S}$ if $X = \mathbb{R}^3$~~

Note that phase only depends on curve C, not on $R(t)$.

If $X = \mathbb{R}^3$,

$$\gamma_n = -\iint \vec{V}_n(R)\cdot d\vec{S}$$

$$\begin{aligned} V_n^i(R) &= \varepsilon^{ijk}\, \mathrm{Im}\ \partial_j \langle n(R)| \partial_k |n(R)\rangle \\ &= \varepsilon^{ijk}\, \mathrm{Im}\ \big(\partial_j \langle n(R)|\big)\big(\partial_k |n(R)\rangle\big) \\ &= \sum_m \varepsilon^{ijk}\, \mathrm{Im}\ \big(\partial_j \langle n(R)|m\rangle\langle m| \partial_k |n(R)\rangle \end{aligned}$$

But $$\langle m | \frac{\partial}{\partial R^i} | n(R)\rangle = \frac{\langle m | \frac{\partial H}{\partial R^i} | n(R)\rangle}{E_n(R) - E_m(R)}, \quad m \neq n$$

(as with $\frac{d}{dt}$)

So

$$\boxed{V_n(R) = \varepsilon^{ijk} \operatorname{Im} \sum_{m \neq n} \frac{\langle n(R) | \frac{\partial H}{\partial R^i} | m \rangle \langle m | \frac{\partial H}{\partial R^j} | n(R) \rangle}{(E_n - E_m)^2}} \quad (*)$$

Gives Berry's phase through

$$\boxed{\gamma_n(C) = -\iint_S \vec{V}_n(R) \cdot d\vec{S}}$$

For more general X,

$$\gamma_n = -\iint d\sigma^i \, d\sigma^j \, \Omega_{ij}$$

$$\Omega_{ij} = \operatorname{Im} \sum_{m \neq n} \frac{\langle n(R) | \frac{\partial H}{\partial R^i} | m \rangle \langle m | \frac{\partial H}{\partial R^j} | n(R) \rangle}{(\epsilon_n(R) - \epsilon_m(R))^2}$$

Notes:

[note: more restrictive than $\beta_n(t)$!.]

*) Redefining phases $|n(R)\rangle \to e^{i\beta_n(R)} |n(R)\rangle$ doesn't change $V_n(R)$ or $\gamma_n(C)$.

*) $\vec{\nabla} \cdot \vec{V}_n(R) = 0$ [$ddw = 0$, show explicitly for $(*)$ in HW]

*) if path encloses no area $\gamma_n(C) = 0$ 

*) cannot pass through degeneracy pt $\epsilon_n(R) = \epsilon_m(R)$.