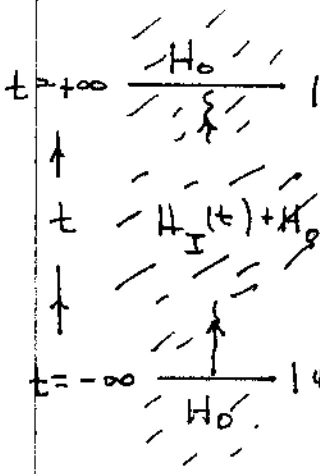
<u>Time dependent perturbation theory</u>

Often we have a system in which there is a clear division of the Hamiltonian into a fixed H_0 and an interaction $H_I(t)$ with <u>explicit</u> time dependence, e.g. switched fields or currents,

$$H = H_0 + H_I(t)$$

The quantum problem is then to find the amplitude for a given $\underbrace{\text{initial state } |i\rangle}_{\text{an eigenstate of } H_0}$ at $t = -\infty$ to evolve into some final H_0 eigenstate $|f\rangle$.



$|\psi(t=+\infty)\rangle$ = a coherent superposition of H_0 eigenstates, <u>not</u> an "H_0 energy" eigenstate.
$= U(\infty,-\infty)|\psi(t=-\infty)\rangle$

$|\psi(t=-\infty)\rangle = |i\rangle$ (an H_0 eigenstate)

n.b. this is the S-matrix problem:

$$\underline{S_{fi}} = \underline{\langle f|\psi(t=+\infty)\rangle} = \underline{\langle f|U(\infty,-\infty)|i\rangle}$$

to find $|\psi(t)\rangle$ with this full H we solve the TDSE

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = [H_0 + H_I(t)] |\psi(t)\rangle$$

or with explicit wfns

$$i\hbar \frac{\partial}{\partial t} \psi(\vec{x},t) = [H_0 + H_I(t)] \psi(\vec{x},t) .$$

To develop pert. thy. it's useful to expand $|\psi(t)\rangle$ in a complete set of H_0 eigenvectors,

$$|\psi(t)\rangle = \sum_n a_n(t) |\psi_n(t)\rangle$$

or

$$\psi(\vec{x},t) = \sum_n a_n(t) \cdot \psi_n(\vec{x}) e^{-i\omega_n t}$$

$\omega_n = E_n/\hbar$

substituting this expansion into the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = [H_0 + H_I(t)] |\psi(t)\rangle$$

& taking the $\langle m| \cdot \{ \quad " \quad = \quad " \quad \}$ overlap gives

$$\underline{i\hbar \dot{a}_m(t) = \sum_n \langle m|H_I(t)|n\rangle e^{i(\omega_m-\omega_n)t} a_n(t)}$$

Thus far this is completely general. Now suppose that at $t = -\infty$ we start in the initial state $|i\rangle$, so $a_m(t=-\infty) = \delta_{mi}$. Also suppose that H_I is weak, so we can carry out an expansion in H_I.

The $\mathcal{O}(H_I)$ term is, setting $a_m(t) = \underbrace{\delta_{mi}}_{a_m^{(0)}(t)} + \underbrace{\mathcal{O}(H_I)}_{a_m^{(1)}(t)}$,

we find

$$i\hbar \dot{a}_m^{(1)}(t) = \langle m|H_I(t)|i\rangle e^{i(\omega_m-\omega_i)t}$$

& integrating,

$$a_m(t) = \underbrace{\delta_{mi}}_{a_m^{(0)}(t)} \underbrace{- \frac{i}{\hbar}\int_{-\infty}^{t} \langle m|H_I(t')|i\rangle e^{i(\omega_m-\omega_i)t'} dt'}_{a_m^{(1)}(t)} \qquad + \mathcal{O}(H_I^2)$$

to calculate the transition probability we now take $t \to +\infty$

$$a_i(\infty) = 1 - \frac{i}{\hbar}\int_{-\infty}^{\infty} \langle i|H_I(t')|i\rangle \, dt' \quad + \mathcal{O}(H_I^2)$$

$\uparrow$
still in i

$$P_i(\infty) = |a_i|^2 = \left(1 - \frac{i}{\hbar}\,\text{''}\right)\left(1 + \frac{i}{\hbar}\cdot\text{''}\right) + \mathcal{O}(H_I^2)$$

$$= 1 \underbrace{+ \mathcal{O}(H_I^2)}$$

would have to do next order pert. thy to get this.

amplitude for transition $i \to m \neq i$ is

$$a_m(+\infty) = -\frac{i}{\hbar}\int_{-\infty}^{\infty} \langle m|H_I(t)|i\rangle e^{i(\omega_m-\omega_i)t'} dt' \quad + \mathcal{O}(H_I^2)$$

$$P_m(+\infty) = |a_m|^2$$

<u>Note</u>: no ΔE transitions without time dependence in H_I ! (In this picture.)
If H_I is ~static,

$$a_m(+\infty) = -\frac{i}{\hbar}\langle m|H_I|i\rangle \underbrace{\int_{-\infty}^{\infty} e^{i(\omega_m-\omega_i)t'} dt'}_{(2\pi)\delta(\omega_m-\omega_i)}$$

Generally there <u>will</u> be time dependence, e.g. external sources or emission/absorption of photons.
In the latter case

$$H_I = - \int d^3x \, \vec{j} \cdot \vec{A}(\vec{x}, t)$$

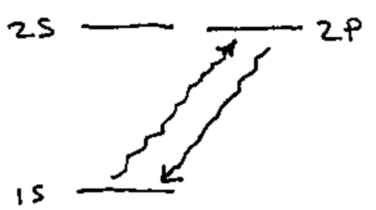
leads to a matrix element of $\vec{\nabla} \Rightarrow \vec{x}$

plane wave for an EM wave,

$$\vec{A} \propto \hat{\epsilon}^{(\kappa)}_{k,\lambda} \underbrace{e^{-i\omega_k t}}_{} e^{+i\vec{k}\cdot\vec{x}}$$

this will drive transitions with a ΔE of $\pm \hbar\omega_k$

e.g.



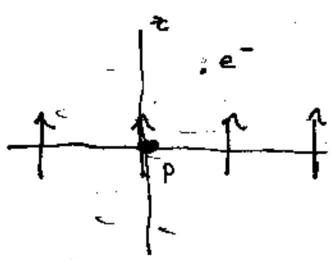
$$\int e^{i\left(\frac{E_f}{\hbar} - \frac{E_i}{\hbar}\right)t} e^{-i\omega_k t} dt$$

$$\propto \delta(E_f - E_i - \hbar\omega_k)$$

photons of freq. ω_k drive $\Delta E = \hbar\omega_k$ transitions.
Thus <u>spectrum</u> (F.T.) of time dependence is crucial for determining transition amplitudes.

A simple example of explicit time dependence in $H_I(t)$.

Suppose we put a bound e^- (e.g. in a H atom) in an external, modulated electric field. What are the transition probabilities to the various atomic excited states?



$$\vec{E} = E\hat{z} \, f(t)$$

$$H_I(t) = -eEz \cdot f(t)$$

Born-order

$$a_f(\infty) = \delta_{fi} - \frac{i}{\hbar}\int_{-\infty}^{\infty} \langle f|H_I(t)|i\rangle\, e^{i(\omega_f-\omega_i)t}\,dt + \mathcal{O}(H_I^2)$$

$$= \delta_{fi} - \frac{i}{\hbar}\,\langle f|\underbrace{-eEz}|i\rangle \underbrace{\int_{-\infty}^{\infty} f(t)\, e^{i(\omega_f-\omega_i)t}\,dt}_{\tilde{F}(\omega)} + \mathcal{O}(H_I^2)$$

$$\hookrightarrow\ -eEr\cos\theta = -eEr\cdot\sqrt{\frac{4\pi}{3}}\,\underbrace{Y_{10}(\Omega)}$$

no special restriction on radial transitions

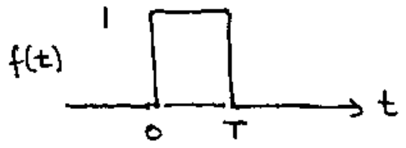
$\therefore$ transitions are only $\Delta l = \pm 1$, $\Delta m = 0$

time-dep

Let's specialize to a real problem.

$$E = 10\,[\mathrm{kV\ cm^{-1}}] \qquad \left(eE = 10^4\,[\mathrm{eV\ cm^{-1}}]\right)$$

$f(t)$ = sq. pulse, switched on for 1 μsec.



$|i\rangle = |1S\rangle$ hydrogenic state

$|f\rangle = |2P\rangle$ hydrogenic state (only $|nP\rangle$ states are reached from $|1S\rangle$ at Born order)

$$\tilde{F}(\omega) = \int_0^T e^{i(\omega_f-\omega_i)t}\,dt = \frac{1}{i(\omega_f-\omega_i)}\left[e^{i\overbrace{(\omega_f-\omega_i)}^{\equiv\,\omega}T} - 1\right]$$

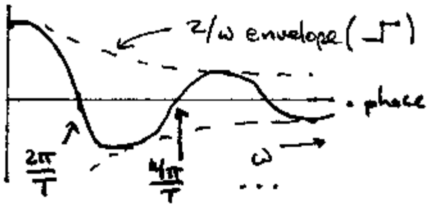
$$= e^{i\omega T/2}\cdot\frac{2}{\omega}\sin(\omega T/2)$$

$$\omega = \frac{1}{\hbar}(\underset{(2P)}{E_f} - \underset{(1S)}{E_i})$$

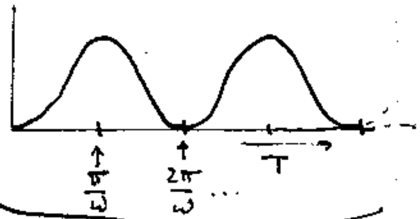
$$a_{1S\to 2P} = -\frac{i}{\hbar}\cdot\langle 2P|-eEz|1S\rangle\cdot\frac{2}{\omega}\sin(\omega T/2)\cdot \underbrace{e^{i\omega T/2}}$$

irrelevant phase, depends on when we started the clock.

$\tilde{F}(\omega) =$



$$\underline{\mathcal{P}_{1S\to 2P} = \left(\frac{eE}{\hbar}\right)^2 |\langle 2P|z|1S\rangle|^2\cdot\frac{4}{\omega^2}\underbrace{\sin^2(\omega T/2)}}$$



to be effective in exciting transitions, the time scale of our pulse should be

$$T \sim \frac{\pi}{\omega} = \frac{\pi\hbar}{\Delta E}$$

our case

$$\Delta E = E_{2p} - E_{1S} = \frac{1}{2}mc^2\alpha^2\left(1-\frac{1}{4}\right) = \frac{3}{8}mc^2\alpha^2 = 10.2\,[eV]$$

(soft X-rays!)

$$\therefore \text{need} \quad T \sim \frac{\pi\hbar}{\Delta E} = \frac{3\pi}{8}\frac{\hbar}{mc^2\alpha^2} = \frac{3\pi}{8}\frac{1.054\cdot 10^{-27}[\text{erg}\cdot\text{sec}]}{511.0\,[\text{keV}]}(137.036)^2$$

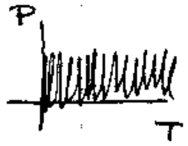
$$\sim 1\cdot\frac{10^{-27}[\text{erg}\cdot\text{sec}]\cdot 2\cdot 10^4}{\frac{1}{2}\cdot 10^6\cdot 1.6\cdot 10^{-12}[\text{erg}]} \sim \frac{2\cdot 10^{-23}}{10^{-6}}[\text{sec}]$$

$$\underline{T \sim 2\cdot 10^{-17}[\text{sec}]}$$

So, our switch is <u>much</u> too slow to drive this transition effectively.

for our case $\langle 2P | z | 1S \rangle = \dfrac{2^{15/2}}{3^5} a_0$,

$$P_{1S\to 2P} = \frac{2^{17}}{3^{10}} \left(\frac{eEa_0}{\hbar}\right)^2 \frac{1}{\omega^2} \underbrace{\sin^2\left(\frac{\omega T}{2}\right)}_{\text{rapidly osc. factor since } T \gg \omega^{-1}\text{, replace by } 1/2 \quad (\omega T \sim 10^{11})}$$



$$\bar{P}_{1S\to 2P} = \frac{2^{16}}{3^{10}} \left(\frac{eEa_0}{\hbar\omega}\right)^2$$

$$\hbar\omega = E_{2P} - E_{1S} = 10.2[eV]$$

$$eEa_0 = 10^4 [eV\,cm^{-1}] \cdot 5.293 \cdot 10^{-9} [cm]$$
$$= 5.29 \cdot 10^{-5} [eV]$$

$$\therefore \left(\frac{eEa_0}{\hbar\omega}\right)^2 = \left(\frac{5.29 \cdot 10^{-5} [eV]}{10.2\,[eV]}\right)^2 = 2.69 \cdot 10^{-11}$$

$$\underline{P_{1S\to 2P} = 2.99 \cdot 10^{-11}}$$

$\therefore$ A few of the H atoms are excited! (3 in a trillion, but even so this is $3 \cdot 10^{-11} \cdot 6 \cdot 10^{23} \sim 2 \cdot 10^{13}$ per mole)

n.b. even so, this is unphysical! $\underline{10^{13}}$ $\underline{\text{X-rays emitted}}$ (10 eV) by the sample when the 2P states deexcite in the next μsec!
This fiction is caused by the hard edge of our assumed pulse which gives $a \sim \frac{1}{\omega}$, $P \sim \frac{1}{\omega^2}$ dependence in the ultraviolet.

The *real* pulse will be much smoother at the $\frac{\hbar}{\Delta E} \sim 10^{-17}$ [sec] time scale, leading to a *much* smaller probability of excitation.

No square pulses in nature!

Fermi's Golden Rule (& radiative transitions)

Thus far we have considered time dependence of transitions between discrete levels, which we can get by just solving the matrix equation

$$i\hbar \frac{\partial}{\partial t}|\psi\rangle = H|\psi\rangle$$

next we consider the transition rate from an initial state $|i\rangle$ into a continuum of states $|f\rangle$.

(e.g. radiative transitions,

$|i\rangle = |2P\rangle$ discrete level

$|f\rangle = |1S\rangle\,|\gamma_{\vec{k},\lambda}\rangle$

↳ there is a continuum of single photon states.

for discrete levels, (Born-order)

$$a_{f\neq i}(\infty) = -\frac{i}{\hbar}\int_{-\infty}^{\infty} \underbrace{\langle f|H_I(t)|i\rangle}\, e^{i(\omega_{1S}-\omega_{2P})t}\,dt$$

has a $\langle f|H_I|i\rangle e^{i\omega_\gamma t}$ part

$$= -\frac{i}{\hbar}\langle f|H_I|i\rangle\, 2\pi\,\delta\big(\underbrace{\omega_{1S}+\omega_\gamma}_{\substack{\uparrow\\ \omega_f,\\ \text{part of a continuum}}} - \underbrace{\omega_{2P}}_{\substack{\uparrow\\ \omega_i,\\ \text{discrete}}}\big)$$

$$P_{f\neq i}(\infty) = \frac{1}{\hbar^2}|\langle f|H_I|i\rangle|^2\, 2\pi\delta(\omega_{1S}+\omega_\gamma-\omega_{2P})\cdot T$$

$\delta(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\,dt$

$\delta(\omega)^2 = \delta(\omega)\,\delta(0)$

$$\Gamma_{i\to f} = \frac{P}{T} = \frac{1}{\hbar^2}|\langle f|H_I|i\rangle|^2\cdot 2\pi\delta(\omega_{1S}+\omega_\gamma-\omega_{2P})$$

$\delta(0) = \frac{T}{2\pi}$

$\therefore [2\pi\delta(\omega)]^2 = 2\pi\delta(\omega)\cdot T$

The transition rate to a set $\{f\}$ of distinguishable final states is

thus no interference

$$\Gamma_i = \sum_f \Gamma_{i\to f}$$

which we can replace by an integral over the final continuum,

$dn \{$ leads $\omega + d\omega$, ω

$$\sum_f = \sum_f \underbrace{\Delta n}_{1} = \sum \frac{\Delta n}{\Delta\omega}\Delta\omega \xrightarrow[\text{continuum limit}]{} \int \underbrace{\frac{dn}{d\omega}}_{\rho(\omega)} d\omega$$

1 (running through a list $n = 1 \dots N$ of final states)

$\rho(\omega)$, density of final states, dn between ω and $\omega + d\omega$,

$$\rho(\omega) = \frac{dn(\omega)}{d\omega}$$

So, for transitions into a continuum,

$$\sum_{\substack{f \\ \text{continuum}}} \Gamma_{i\to f} = \frac{1}{\hbar^2} |\langle f|H_I|i\rangle|^2 \; 2\pi \int \delta(\omega_f - \omega_i)\, \rho(\omega_f) d\omega_f$$

n.b.

$$d\Gamma_f = \frac{2\pi}{\hbar} |\langle f|H_I|i\rangle|^2 \cdot \rho(E_f) \frac{d\Omega_f}{4\pi}$$

into $d\Omega$ if m.e. is not isotropic

$$\boxed{\underset{\text{(in continuum)}}{\Gamma_{i\to f}} = \frac{1}{\hbar^2} |\langle f|H_I|i\rangle|^2 \cdot 2\pi\rho(\omega_f)}$$

Fermi's Golden Rule

$$= \boxed{\frac{2\pi}{\hbar} |\langle f|H_I|i\rangle|^2 \rho(E_f)}$$

units? $[\sec^{-1}] \stackrel{?}{=} \frac{1}{[\text{erg}^2 \sec^2]} \cdot [\text{erg}^2] \cdot \left[\frac{1}{\sec^{-1}}\right]$ ✓

$= \left[\frac{1}{\text{erg}\sec}\right] \cdot [\text{erg}^2] [\text{erg}^{-1}]$ ✓

Actually $d\Gamma_{i\to f} = \frac{2\pi}{\hbar} |\langle f|H_I|i\rangle|^2 \, dn$.