- For electric dipole transitions, the spin-dependent part is

$$H_{int} = -\frac{e}{2mc} g_s \hbar\, \underset{\sim}{s} \cdot \underset{\sim}{\mathcal{H}}^{e}_{LM}$$

$$\underset{\sim}{\mathcal{H}}^{e}_{LM} = \nabla \times \underset{\sim}{A}^{e}_{LM} = \frac{1}{k} \nabla \times (\nabla \times A^{m}_{LM})$$

$$\text{But } \nabla \times (\nabla \times \underset{\sim}{A}) = -\nabla^2 \underset{\sim}{A} + \nabla(\nabla \cdot \underset{\sim}{A})^{\,\,\shortparallel\,0}$$

$$= +k^2 \underset{\sim}{A}$$

$$\therefore \underset{\sim}{\mathcal{H}}^{e}_{LM} = k A^{m}_{LM}$$

$$= +k \frac{i^L (2L+1)}{\sqrt{L(L+1)}} j_L(kr) \underset{\sim}{L}\, C_{LM}.$$

$$\simeq +\frac{k\, i^L (2L+1)}{\sqrt{L(L+1)}} \frac{(kr)^L}{(2L+1)!!} \underset{\sim}{L}\, C_{LM}.$$

For magnetic multipole transitions, the orbital part is

$$H^{m}_{int} = \frac{-e}{mc} \underset{\sim}{A}^{m}_{LM} \cdot \underset{\sim}{P}$$

$$\underset{\sim}{A}^{m}_{LM} \cdot \underset{\sim}{P} = \frac{i^L (2L+1)}{\sqrt{L(L+1)}} j_L(kr)\, \underset{\sim}{L}\, C_{LM} \cdot \frac{\hbar}{i} \nabla$$

$$\underset{\sim}{L}\, C_{LM} \cdot \nabla = \frac{\hbar}{i} \underset{\sim}{r} \times \nabla C_{LM} \cdot \nabla$$

$$= -\frac{\hbar}{i} \nabla C_{LM} \cdot \underset{\sim}{r} \times \nabla$$

$$= -\nabla [j_L(kr) C_{LM}] \cdot \underset{\sim}{L}$$

The spin part is

$$H_{int} = \frac{-e}{2mc} \hbar g_s \bar{S} \cdot \underset{\sim}{H}_{LM}^{m}$$

$$\underset{\sim}{H}_{LM}^{m} = \nabla \times \underset{\sim}{A}_{LM}^{m} = k A_{LM}^{e}$$

$$\propto \nabla (r^L C_{LM}) \quad kr \ll 1.$$

Collecting the results, the total interaction operator is

$$H_q^{int}(\underset{\sim}{k}, \underset{\sim}{r}) = -\sum_{LM} \frac{(ik)^L}{(2L-1)!!} \sqrt{\frac{L+1}{2L}} \mathcal{D}_{Mq}^{L}(R)$$

$$\times \left\{ Q_{LM} + \underset{\sim}{Q}_{LM}' \cdot \frac{\underset{\sim}{S}}{L+1} - iq M_{LM} \right\}$$

$$Q_{LM} = e g_L (r^L C_{LM})$$

$$\underset{\sim}{Q}_{LM}' = -k \mu_B g_S \underset{\sim}{r} (r^L C_{LM})$$

$$M_{LM} = \mu_B \nabla (r^L C_{LM}) \cdot \left\{ 2 g_L \frac{\underset{\sim}{L}}{L+1} + g_s \underset{\sim}{S} \right\}$$

One must be very careful to include all the terms. For example, consider spin-forbidden electric dipole transitions - eg. $2^3P - 1^1S$.

$$H_{int} = -\frac{e}{2mc}\left[2\underset{\sim}{A}\cdot\underset{\sim}{P} + \hbar\,\underset{\sim}{\sigma}\cdot\underset{\sim}{H} \right]$$

$$\underset{\sim}{A}^{e}_{LM} = \frac{i}{k}\sqrt{\frac{L+1}{L}}\,\frac{(2L+1)}{(2L+1)!!}\,\nabla\left[(ikr)^L C_{LM}\right]$$

$$\underset{\sim}{A}^{e}_{10} = -\frac{\sqrt{2}}{3}\nabla(z) = -\frac{\sqrt{2}}{3}\,\hat{k}.$$

$$\underset{\sim}{H}^{e}_{LM} = \frac{+k\, i^L(2L+1)}{\sqrt{L(L+1)}}\,\frac{(kr)^L}{(2L+1)!!}\,\underset{\sim}{L}\,(\cos\Theta)$$

$$= \frac{+k^2}{\sqrt{2}}\,(y\hat{i} - x\hat{j}) = \frac{+\omega^2}{\sqrt{2}c^2}\,(y\hat{i} - x\hat{j})$$

The A.p term cannot connect directly the 2^3P and 1^1S states due to spin orthogonality, but it can connect the states indirectly through spin-orbit mixing.

$$|2^3P_1\rangle = |2^3P_1\rangle_0 + \sum_{n} \frac{|n^1P_1\rangle\langle n^1P_1|H_{so}|2^3P_1\rangle}{E(2^3P_1) - E(n^1P_1)}$$

$$= |2^3P_1\rangle_0 + \sum_{n} c_n\,|n^1P_1\rangle$$

Then $\langle 1^1S_0|H_{int}|2^3P_1\rangle$ $\qquad c_n = \Theta(c^{-2})$

$$= -\frac{e}{2mc}\Big[\sum_n c_n \langle 1^1S_0|2\underset{\sim}{A}\cdot\underset{\sim}{p}|n^1P_1\rangle + \hbar\,\langle 1^1S_0|\underset{\sim}{\sigma}\cdot\underset{\sim}{H}|2^3P_1\rangle \Big]$$

$$= -\frac{e}{2mc}\Big[-\sqrt{2}\sum_n c_n \langle 1'S|p_z|n'P\rangle + \frac{\omega^2}{\sqrt{2}c^2}\langle 1'S|(y\hat{i}-x\hat{j})\cdot\underset{\sim}{\sigma}|2\,^3P_1\rangle\Big]$$

In converting from the ~~length~~ velocity form to the ~~velocity~~ length form, we did not include the spin-orbit interaction in the Hamiltonian.

$$H_{so} = \frac{e\hbar}{4m^2c^2}\cdot\frac{Ze}{r^3}\underset{\sim}{L}\cdot\underset{\sim}{\sigma} = \frac{\mu_B}{mc}\frac{Ze}{r^3}\underset{\sim}{L}\cdot\underset{\sim}{S}$$

For ordinary spin-allowed transitions, we wrote

$$-\frac{e}{mc}\langle\alpha|p_z|\beta\rangle = \frac{e}{mc}\frac{m}{\hbar i}\langle\alpha|Hz-zH|\beta\rangle$$

$$= \frac{e}{ic}\,\omega_{\alpha\beta}\langle\alpha|z|\beta\rangle$$

Since we are now retaining terms of $O(c^{-2})$, we must add to the above the spin-orbit commutator

$$\frac{e}{mc}\frac{m}{\hbar i}\langle\alpha|H_{so}z - zH_{so}|\beta\rangle$$

$$= \frac{e}{mc}\cdot\frac{e^2Z^2}{4mc^2}\langle\alpha|\frac{1}{r^3}\underset{\sim}{\sigma}\cdot\big[\underset{\sim}{L}\,z\big]|\beta\rangle$$

$$\big[\underset{\sim}{L}\,z\big] \rightarrow \frac{\hbar}{i}(y\hat{i}-x\hat{j})$$

It can be shown that this contribution exactly cancels the $\underset{\sim}{\sigma}\cdot\underset{\sim}{H}$ contribution.

Therefore in the length form,

$$\langle 1\,{}^1S_0 | H_{int} | 2\,{}^3P_1 \rangle = -\frac{e}{2mc} \sum_n c_n \langle 1\,{}^1S_0 | z | n\,{}^1P_1 \rangle$$

.. all of this is much simpler in the Dirac theory. The Hamiltonian is simply

$$H = -e\phi + \beta mc^2 + \underset{\sim}{\alpha}\cdot(c\underset{\sim}{p} - e\underset{\sim}{A})$$

In lowest order, the interaction operator is just

$$-e\,\underset{\sim}{\alpha}\cdot\underset{\sim}{A}. \qquad \alpha = \begin{pmatrix} 0 & \sigma \\ \sigma & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The above is not very useful because for many-electron atoms, it is usually the non-rel. wave function that is known best and so one must find the equivalent non-relativistic interaction operator.

<u>Summary of Multipole Transition Probabilities.</u>

1. Electric Multipole.
   .. For spontaneous emission of a single photon from initial state Ψ_i to final state Ψ_f.

$$\vec{Q}_{LM}^{(e)} = \cancel{\sqrt{\frac{4\pi}{2L+1}}\,r^L Y_L^M} \quad e r^L C_{LM}^{*} \qquad \text{parity} = (-1)^L$$

$$A_{LM}^{(e)} = \frac{2(L+1)}{L(2L+1)[(2L-1)!!]^2} \,|\langle f | Q_{LM}^{e} | i \rangle|^2 \left(\frac{\omega}{c}\right)^{2L+1}$$

$$\omega = E_i - E_f. \qquad \tau = 2.4189\times10^{-17}\text{ sec.}$$

2. Magnetic multipole.

$$\vec{Q}^{(m)}_{LM} = \nabla(r^L C^*_{LM})\left[\frac{e}{mc(L+1)}\,\underset{\sim}{L} + \underset{\sim}{\mu}\right] \qquad \text{parity} = (-1,$$

$$\underset{\sim}{\mu} = \frac{e\hbar}{2mc}\,\underset{\sim}{\sigma}.$$

$$A^{(m)}_{LM} = \frac{2(L+1)}{L(2L+1)[(2L-1)!!]^2}\left(\frac{\omega}{c}\right)^{2L+1}|\langle f|Q_{LM}|i\rangle|^2$$

Relative magnitudes.

$$\omega \sim Z^2$$
$$r \sim 1/Z$$

$$Q^{(e)}_{LM} \sim Z^{-L}$$

$$A^{(e)}_{LM} \sim \left(\frac{Z^2}{c}\right)^{2L+1} Z^{-2L} = \frac{Z^{2(L+1)}}{c^{2L+1}}\ (n \neq n') = \frac{Z}{c^{2L+}}$$

For E1, $A^{(e)}_{1M} \approx \frac{Z^4}{c^3}\ (n \neq n')$, $(n = n$

- For spin-forbidden EL,

$$\frac{H_{SO}}{\Delta E} \sim \frac{Z^4}{c^2 Z} = \frac{Z^3}{c^2}$$

$$A^{e'}_{LM} \sim \frac{Z^{2(L+1)}}{c^{2L+1}}\cdot\left(\frac{Z^3}{c^2}\right)^2 = \frac{Z^{2(L+4)}}{c^{2L+5}} \qquad (n \neq n')$$

$$A^{(e)'}_{1M} \sim \frac{Z^{10}}{c^7}$$

$$\text{ratio} = \cancel{\frac{Z^7}{c^5}}\ \ \frac{Z^8}{c^4} = (\alpha Z)^4 Z^5$$

$$\simeq 1 \text{ at } Z = 9$$

$$Q_{LM}^{(m)} \sim \frac{Z^{-L+1}}{c} = \frac{Z^3}{c^{2L+3}} \quad (n = n')$$

$$A_{LM}^{(m)} \sim \left(\frac{Z^2}{c}\right)^{2L+1} \left(\frac{Z^{-2L+2}}{c^2}\right) = \frac{Z^{2(L+2)}}{c^{2L+3}} \quad (n \neq n')$$

If the leading term of the transition integral vanishes, as in $1s2s\ {}^3S_1 - 1s^2\ {}^1S_0$, the next correction term is $O(\omega^2 r^2/c^2)$.

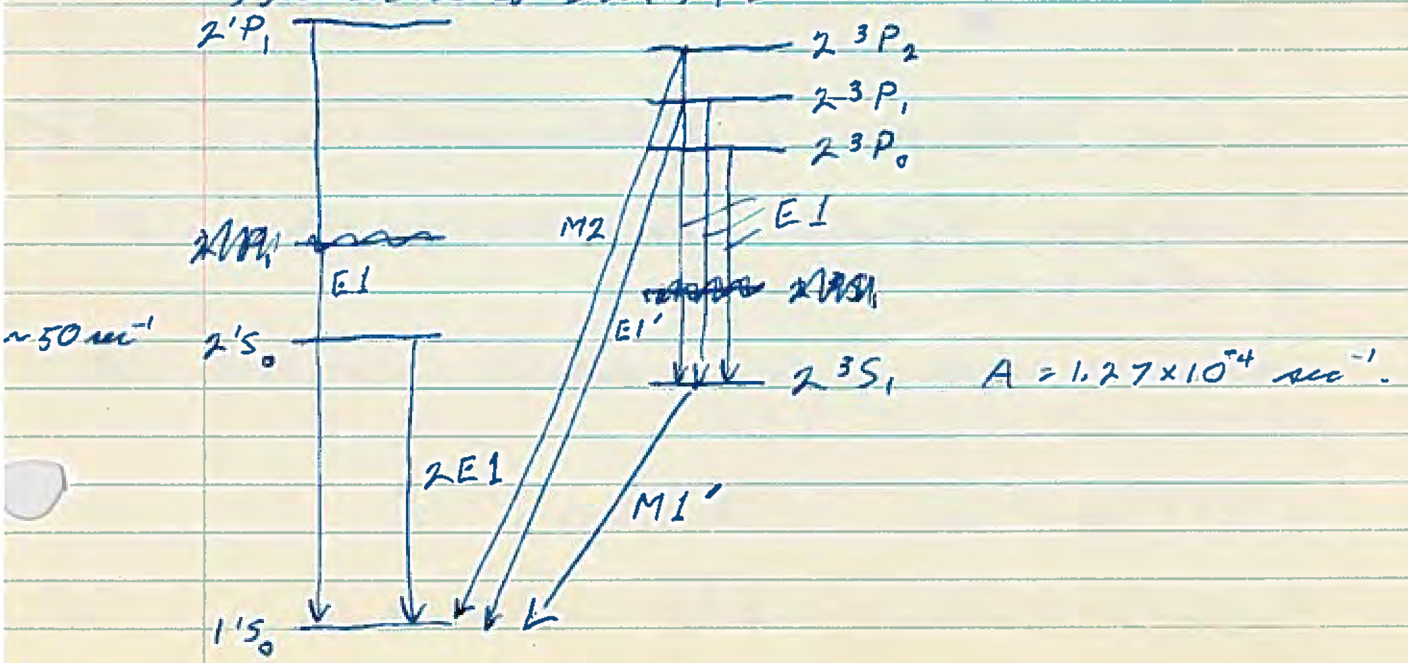
$$A_{LM}^{(m)\prime} \sim \frac{Z^{2(L+2)}}{c^{2L+3}} \left(\frac{Z^2}{c^2}\right)^2 = \frac{Z^{2(L+4)}}{c^{2L+7}} \sim \frac{A_{LM}^{(e)\prime}}{c^2}$$

The $O(c^{-2})$ correction terms to $\vec{Q}_{1M}^{(m)}$ have recently been calculated. The $1^1S - 2^3S$ transition integral is

$$\langle 1s^2\,{}^1S_0 | Q_{10} | 1s2s\,{}^3S_1 \rangle$$

$$= \mu_B \langle 1^1S | \sum_{j=1}^{2} \Big\{ \underbrace{L_{zj} + \sigma_{zj}}_{=0} - \frac{2}{3m^2c^2} p_j^2 \sigma_{zj} - \frac{1}{6}\left(\frac{\omega}{c}\right)^2 r_j^2 \sigma_j + \frac{Ze^2}{3mc^2} \frac{\sigma_{zj}}{r_j} | 2\,{}^3S_1 \rangle$$

Transitions in Helium



For 2^3P_1

$$\frac{A(E1')}{A(E1)} \approx \frac{Z^{9}}{c^4}$$

$A(E1')$ becomes dominant for the ions beyond C V.

For 2^3P_2

$$\frac{A(M2)}{A(E1)} \sim \frac{Z^8/c^7}{Z^{4}/c^3} = \frac{Z^7}{c^4}$$

$A(M2)$ becomes dominant for the ions beyond Cl XVI

- The two-electron ions exist over a wider range of temp. and pressure conditions than any other ionization stage and thus are commonly observed.

Application to Planetary Nebulae
- In the H II region, $T_e \sim 10^4\,°K$, $N_e \sim 10^4$ cm
Most atomic species are singly ionized.

$$\frac{N(He^+)}{N(He)} \sim 10.$$

Time between inelastic collisions $\sim 10^3 - 10^4$ s

Problem - explain observed He triplet spectrum.

- Balance rates of formation and destruction of He 2^3S, 2^3P, 3^3D.

$$\beta(2^3S) N_e N(He^+) = N(2^3S)[A(2^3S - 1^1S)$$

$$+ q(2^3S - 2^1S) N_e + q(2^3S - 2^1P) N_e + R] \qquad (1)$$

$$q(2^3S - 2^3P)\,N(2^3S)\,N_e + \beta(2^3P)\,N_e\,N(He^+)$$
$$= N(2^3P)\,A(2^3P - 2^3S) \qquad (2)$$

$$q(2^3S - 3^3D)\,N(2^3S)\,N_e + \beta(3^3D)\,N_e\,N(He^+)$$
$$= N(3^3D)\,A(3^3D - 2^3P) \qquad (3)$$

β = effective radiative recombination rate
$He^+ + e^- \rightarrow He(2^3S)$

N_e = no. of electrons

q = ~~neutron~~ thermally averaged
e^- collision induced transition rate.
R = photoionization rate.

The ratio $N = N(2^3S)/N(He^+)$ can be calculated directly from (1). Alternatively, we can solve (2) and (3) for N in terms of the observed intensity ratio
$I = I(2^3P - 2^3S)/I(3^3D - 2^3P) = I(10{,}830)/I(5876)$

$$\frac{I(~~\lambda\lambda~~10830)}{I(5876)} = \frac{N(2^3P)\,A(2^3P-2^3S)}{N(3^3D)\,A(3^3D-2^3P)} \cdot \frac{5876}{10830} = \frac{1}{1.85}$$

$$N = \frac{1.85\,\beta(3^3D)\,I - \beta(2^3P)}{q(2^3S-2^3P) - 1.85\,q(2^3S-3^3D)\,I}$$

Oscillator Strength.

The oscillator strength for a transition between states n and n' is defined by

$$f_{nn'} = \frac{2m}{\hbar e^2}\omega_{nn'} |\langle n|\hat{e}\cdot\vec{Q}_1^{(e)}|n'\rangle|^2$$

Then, in a.u.,

$$A_{nn'} = 2\omega_{nn'}^2 f_{nn'} \quad \tau^{-1}.$$

The $f_{nn'}$ are dimensionless quantities satisfying the sum rule

$$\sum_{n'} f_{nn'} = N \qquad N = \text{no. of electrons.}$$

For a transition between states labelled by γLM, $\gamma' L' M'$,

$$f(\gamma LM \to \gamma' L' M') = 2\omega |\langle\gamma' L' M'|\hat{e}\cdot\vec{Q}_1^{(e)}|\gamma LM\rangle|^2$$

$$= \frac{2}{3}\omega |\langle\gamma' L' M'|\vec{Q}_1^{(e)}|\gamma LM\rangle|^2$$

$$= \frac{2}{3}\omega |\langle\gamma' L' M'|\sum_i \vec{r}_i|\gamma LM\rangle|^2$$

In terms of reduced matrix elements,

$$\langle\gamma' L' M'|\sum_i r_i^q|\gamma LM\rangle = (-1)^{L'-M'}\begin{pmatrix} L' & 1 & L \\ -M' & q & M\end{pmatrix}\langle\gamma' L'\|\sum_i \vec{r}_i\|\gamma L\rangle$$

The averaged oscillator strength for the transition is

$$\bar{f}(\gamma L \to \gamma' L') = \frac{1}{2L+1}\sum_{MM'} f(\gamma LM \to \gamma' L' M')$$

$$= \frac{1}{2L+1}\,\frac{2}{3}\omega \sum_{MM'q}\left|\begin{pmatrix} L' & 1 & L \\ -M' & q & M\end{pmatrix}\right|^2 \langle\gamma' L'\|\sum_i \vec{r}_i\|\gamma L\rangle$$

In general

$$\sum_{MM'} \left| \begin{pmatrix} L' & k & L \\ -M' & q & M \end{pmatrix} \right|^2 = \frac{1}{2k+1}$$

$$\sum_{q} \frac{1}{2k+1} = 1$$

$$\therefore \bar{F}(\gamma L \to \gamma' L') = \frac{2}{3} \frac{\omega}{(2L+1)} \left| \langle \gamma' L' \| \sum_i \vec{r}_i \| \gamma L \rangle \right|^2 .$$

For the inverse process,

$$\bar{F}(\gamma' L' \to \gamma L) = -\frac{(2L+1)}{(2L'+1)} \bar{F}(\gamma L \to \gamma' L')$$

go to 121 -

Quantum Mechanical Transition Probabilities

The Schrodinger equation is

$$H \Psi = i\hbar \frac{\partial}{\partial t} \Psi . \qquad (1)$$

If H does not depend explicitly on time, then

$$\Psi_m(\vec{r}, t) = \psi_m(\vec{r}) e^{-E_m t/\hbar}$$

$$H \psi_m(\vec{r}) = E_m \psi_m(\vec{r}).$$

H = total Hamilt. including both atom + radiation field.

Consider two states of the system ϕ_a and ϕ_b. These may not be eigenfcns of H, but can be expanded in terms of them. The general sol'n. of (1) is

$$\Psi(\vec{r}, t) = \sum_m a_m \psi_m(\vec{r}) e^{-iE_m t/\hbar}$$

Suppose the state is initially in state ϕ_a

$\phi_a = \Psi(\vec{r},0) = \sum_n a_n \psi_n$. $\quad a_n = \int \psi_n^* \phi_a \, d\tau$.

after time t, the state is

$\Psi(\vec{r},t) = \sum_n a_n \psi_n e^{-iE_n t/\hbar}$

$= \sum_n a_n e^{-iHt/\hbar} \psi_n$

$= e^{-iHt/\hbar} \phi_a = e^{-iHt/\hbar} \Psi(\vec{r},0)$

The operator $e^{-iHt/\hbar} = 1 + \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-iHt}{\hbar} \right)^n$

is the time-development operator.

The quantity $\left| \int \phi_b^* \Psi(\vec{r},t) \, d\tau \right|^2$

= prob. of finding state ϕ_b in time-developed state.

$\therefore \; S_{a \to b}(t) = \left| \int \phi_b^* e^{-iHt/\hbar} \phi_a \, d\tau \right|^2$.

Expansion of $S_{a\to b}$ in Eigenfunctions of H.

$H|\alpha\rangle = E_\alpha |\alpha\rangle$
$H|\beta\rangle = E_\beta |\beta\rangle$

Expand $|a\rangle = \sum_\alpha \langle \alpha | a \rangle |\alpha\rangle$

$|b\rangle = \sum_\beta \langle \beta | b \rangle |\beta\rangle$

$S_{a\to b}(t) = \langle b | e^{-iHt/\hbar} | a \rangle \langle a | e^{+iHt/\hbar} | b \rangle$

$= \sum_{\alpha\beta} \langle b|\beta\rangle \langle \beta | e^{-iE_\alpha t/\hbar} | \alpha \rangle \langle \alpha | a \rangle$

$\times \langle a | \alpha \rangle \langle \alpha | e^{iE_\beta t/\hbar} | \beta \rangle \langle \beta | b \rangle$

$$= \sum_{\alpha\beta} \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle e^{-i(E_\alpha - E_\beta)t/\hbar}$$

Terms with $\alpha = \beta$ just give

$$\sum_\alpha \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\alpha\rangle\langle\alpha|b\rangle = \sum_\alpha |\langle b|\alpha\rangle\langle\alpha|a\rangle|^2$$

For each term $\alpha, \neq \beta$, there is a corresponding term β, α.

$$S_{a\to b} = \sum_\alpha |\langle b|\alpha\rangle\langle\alpha|a\rangle|^2$$

$$+ \sum_{\alpha>\beta} \Big\{ \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle e^{-i\omega_{\alpha\beta}t} + \langle b|\beta\rangle\langle\beta|a\rangle\langle a|\alpha\rangle\langle\alpha|b\rangle e^{i\omega_{\alpha\beta}t} \Big\}$$

Since $S_{a\to b}$ is real, the imaginary parts must cancel out, as they do. Also

$$\langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle \text{ is real.}$$

Since

$$|\langle b|a\rangle|^2 = \langle b|a\rangle\langle a|b\rangle$$

$$= \sum_{\alpha\beta} \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle$$

$$= \sum_\alpha |\langle b|\alpha\rangle\langle\alpha|a\rangle|^2 + 2\sum_{\alpha>\beta} \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle$$

the above becomes

$$S_{a\to b}(t) = -2\sum_{\alpha>\beta} \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle[1 - \cos(\omega_{\alpha\beta}t)]$$

The transition probability is obtained by taking the limit

$$P_{a\to b} = \lim_{t\to\infty} \frac{S_{a\to b}(t)}{t}$$

Using $\delta(x) = \frac{1}{\pi} \lim_{t \to \infty} \frac{1-\cos(xt)}{x^2 t}$,

$$P_{a\to b}(t) = -2\pi \sum_{\alpha>\beta} \omega_{\alpha\beta}^2 \langle b|\alpha\rangle\langle\alpha|a\rangle\langle a|\beta\rangle\langle\beta|b\rangle\delta(\omega_{\alpha\beta}$$

The above is exact, but not very useful because the expansion coefs. are not known.

The states $|a\rangle$ and $|b\rangle$ represent atomic wave functions in the absence of radiation field. They are expanded as l.c.'s of the exact $|\alpha\rangle$ and $|\beta\rangle$ which include the radiation field in H and therefore require a complete solution to Q.E.D.!

<u>Perturbation Expansion</u>:

- If a complete set of atomic eigenfns $|a\rangle, |b\rangle, |c\rangle, \cdots$ are known, then the exact eigenfunctions ~~are found~~ $|\alpha\rangle, |\beta\rangle, \cdots$ are found by diagonalyzing $\langle H\rangle$

Perturbation theory is useful if the off-diagonal matrix elements are not too large $O(1/c^2)$

$$|\alpha\rangle \simeq |a\rangle - \sum_c \frac{\langle c|H|a\rangle}{\langle c|H|c\rangle - \langle a|H|a\rangle} |c\rangle$$

$$|\beta\rangle \simeq |b\rangle - \sum_c \frac{\langle c|H|b\rangle}{\langle c|H|c\rangle - \langle b|H|b\rangle} |b\rangle$$

$$E_a \simeq \langle a|H|a\rangle, \quad E_b \simeq \langle b|H|b\rangle$$

If $\langle a|H|b\rangle \neq 0$, then

$$\langle a|\alpha\rangle \simeq \langle b|\beta\rangle \simeq 1$$

$$-\langle b|\alpha\rangle = \langle\beta|a\rangle = \frac{\langle b|H|a\rangle}{E_b - E_a}$$

Thus, in lowest order,

$$P_{a\to b} = \frac{2\pi}{\hbar^2} |\langle b|H|a\rangle|^2 \delta(\omega_{ab}).$$

If $\langle b|H|a\rangle = 0$, it is necessary to go to second order.

$$|\alpha\rangle = |a\rangle - \sum_{c \neq a} \frac{\langle c|H|a\rangle}{E_c - E_a}|c\rangle + \sum_{\substack{c,d\\ \neq a}} \frac{\langle d|H|c\rangle\langle c|H|a\rangle}{(E_c - E_a)(E_d - E_a)}|d\rangle$$

$$\langle \alpha|a\rangle = \langle b|\beta\rangle = 1$$

$$\langle \beta|a\rangle = \sum_c \frac{\langle b|H|c\rangle\langle c|H|a\rangle}{(E_a - E_b)(E_c - E_b)}$$

$$\langle b|\alpha\rangle = \sum_c \frac{\langle b|H|c\rangle\langle c|H|a\rangle}{(E_b - E_a)(E_c - E_a)}$$

and $P_{a\to b} = \dfrac{2\pi}{\hbar^2}\left|\sum_c \dfrac{\langle b|H|c\rangle\langle c|H|a\rangle}{E_c - E_a}\right|^2 \delta(\omega_{ab})$

$$E_c = \langle c|H|c\rangle \qquad E_a = \langle a|H|a\rangle$$

The above $\delta(\omega_{ab})$ is not completely correct because the initial and final states need not have exactly the same energy in second order - i.e. the transition is not completely sharp, but can have a finite width.

- Suppose $E_a \neq E_b$ ie $\langle a|H|a\rangle \neq \langle b|H|b\rangle$.

~~Assume $|\langle a|H|a\rangle - \langle b|H|b\rangle| > |\langle a|H|a\rangle - \langle x|H|x\rangle|$~~

Assume a state $|x\rangle$ exists such that $|\langle a|H|a\rangle - \langle b|H|b\rangle| > |\langle a|H|a\rangle - \langle x|H|x\rangle|$

$\langle a|H|x\rangle \neq 0$, but $\langle b|H|x\rangle = 0$.

The exact eigenfunction $|\beta\rangle$ is expanded

$$|\beta\rangle = |x\rangle - \sum_c \frac{\langle c|H|x\rangle}{E_c - E_x}|c\rangle$$

$$+ \sum_{c,d} \frac{\langle d|H|c\rangle\langle c|H|x\rangle\,|d\rangle}{(E_d - E_x)(E_c - E_x)}$$

Then $\langle a|\beta\rangle \simeq \dfrac{\langle a|H|x\rangle}{E_x - E_a}$

$$\langle\beta|b\rangle \simeq \sum_c \frac{\langle x|H|c\rangle\langle c|H|b\rangle}{(E_x - E_c)(E_x - E_b)}$$

Then, with $\langle a|\alpha\rangle^* = \langle b|\beta\rangle = 1$,

$$P_{a\to b} = \frac{2\pi}{\hbar^2}\sum_{x,c}\frac{\langle b|H|a\rangle\langle a|H|x\rangle\langle x|H|c\rangle\langle c|H|b\rangle\,\omega_{ax}}{(E_b - E_a)(E_x - E_a)(E_x - E_c)(E_x - E_b)}$$

$$\times\,\delta(\omega_{ax})$$

The factor $\omega_{ax}^2\,\delta(\omega_{ax})$ picks out $c = a$ from the sum. Then

$$P_{a\to b} = \frac{2\pi}{\hbar^2}\,\frac{|\langle b|H|a\rangle|^2}{(E_a - E_b)}\,\sum_x \frac{|\langle x|H|a\rangle|^2}{(E_x - E_b)}\,\delta(\omega_{ax}$$

$$= \frac{2\pi}{\hbar^2}\,|\langle b|H|a\rangle|^2 \cdot \frac{1}{\pi}\,\frac{\Gamma_a/2}{\omega_{ab}^2}$$

where $\Gamma_a = \dfrac{2\pi}{\hbar^2}\sum_x |\langle x|H|a\rangle|^2\,\delta(\omega_{ax})$

= resonance width.