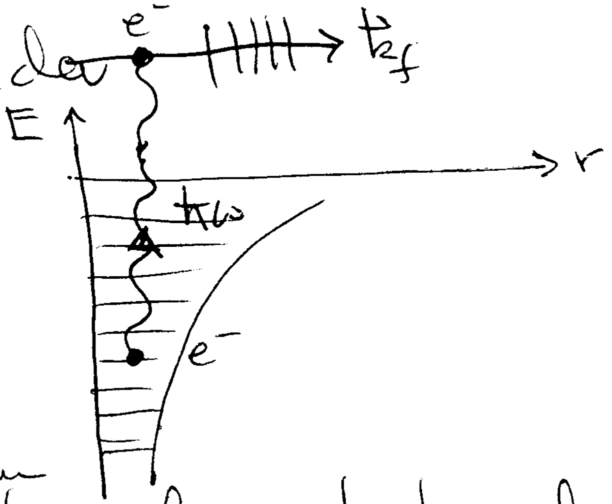
As an example concider

<u>Photoionization</u>:



Suppose the external E-M pumps enough energy into the atom to liberate an electron from its bound state into the continuum. Since the electron is in the continuum, we must sum over the e^- states within the resolution of the detector. So

$$d\sigma_{fi}^{\text{dipole}}\Big|_{\text{abs}} = (2\pi)^2 \alpha \hbar\omega \frac{\partial n}{\partial E_f} \left| \vec{\epsilon}(k,\lambda) \cdot \langle \varphi_f | \vec{R} | \varphi_i \rangle \right|^2$$

$E_f = E_i + \hbar\omega$

Now the final electron is in a plane wave state, so

$$\varphi_f(\vec{r}) = \frac{1}{\sqrt{\Omega}} e^{i\vec{k}_f\cdot\vec{r}}$$

(assume plane wave dominates φ_f matrix el. though not eigenstate of H_0!)

with $E_f = \frac{\hbar^2 k_f^2}{2m}$. As usual for plane waves, the density of final states is

$$\frac{\partial n}{\partial E_f} = d\Omega_f \frac{\Omega}{(2\pi\hbar)^3} m\hbar k_f \quad , \quad \text{where}$$

$$dn = \frac{L^3}{(2\pi)^3} d^3k = \left(\frac{L}{2\pi}\right)^3 d\Omega_f \, k^2 \frac{dk}{dE} dE$$

we have not included the spin of the electron since the interaction is spin independent. Hence we find

$$\left.\frac{d\sigma_{fi}}{d\Omega_f}\right|^{\text{Dipole}}_{\text{abs.}} = \frac{\alpha}{2\pi}\,\frac{m\omega k_f}{\hbar}\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\int d^3r\,\vec{r}\,e^{-i\vec{k}_f\cdot\vec{r}} \times \varphi_i(\vec{r})\right|^2$$

$$\frac{\hbar^2 k_f^2}{2m} = E_i + \hbar\omega$$

As <u>another example</u>, consider the <u>de-excitation of an atom</u> with the <u>emission of a photon</u>. Recalling the dipole approximation golden rule transition rate, we have

$$\left.R_{fi}\right|^{\text{Dipole}}_{\text{emis.}} = 2\pi\alpha\omega^2\,|A_0|^2\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times 4\pi\epsilon_0 c \times \delta(E_f - E_i + \hbar\omega).$$

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Since we are interested in the emission of a single photon(*) when the atom makes the $|\varphi_i\rangle \rightarrow |\varphi_f\rangle$ transition, we use (page — [illegible] —) the relation

(*) this is spontaneous emission (really should quantized γ also)

Note that for the atom in the presence of an external electromagnetic field, we have by our semi-classical viewpoint that $|A_0|^2$ is related to the photon number density or, more appropriately, the classical energy density of the wave

$$|A_0|^2 = \frac{\text{[illegible]}\hbar c^2}{\text{[illegible]}\omega}\rho_\gamma \qquad (\text{page} - \text{[illegible]} -)$$

$$= \text{[illegible]} \langle u \rangle \qquad (\text{page} - \text{[illegible]} -).$$

Hence the emission rate is

$$R\Big|^{\text{Dipole}}_{fi\ \text{emis.}} = \frac{2\pi\alpha\omega^2}{\text{[illegible]}} \frac{\text{[illegible]}\hbar c^2}{\text{[illegible]}\omega}\rho_\gamma \left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\psi_f|\vec{R}|\psi_i\rangle\right|^2 \times \delta(E_f - E_i + \hbar\omega)$$

$$= 4\pi^2\alpha\,(\underbrace{\hbar\omega\rho_\gamma}^{=\langle u\rangle} c)\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\psi_f|\vec{R}|\psi_i\rangle\right|^2 \times \delta(E_f - E_i + \hbar\omega)$$

$$= 4\pi^2\alpha\langle u\rangle c\left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\psi_f|\vec{R}|\psi_i\rangle\right|^2 \times \delta(E_f - E_i + \hbar\omega),$$

Thus the atom, when stimulated by the classical electromagnetic field, gives up energy to the field (in the form of photons with $\hbar\omega$ energy). Even though we have derived this result for the stimulated case we can imagine that after the atom de-excites it gives up one additional photon when there were no photons present to start with. This is just the spontaneous emission of a γ by the atom (decay of atom by spontaneous emission). Since there is just one photon present $\rho_\gamma = \frac{1}{\Omega}$ in the above formula to obtain the spontaneous emission case

$$R_{fi}^{\text{Dipole}}\Big|_{\text{emis}} = \frac{4\pi^2 \alpha \hbar \omega c}{\Omega} \left| \vec{\epsilon}(\vec{k},\lambda) \cdot \langle \psi_f | \vec{R} | \psi_i \rangle \right|^2 \cdot \times \delta(E_f - E_i + \hbar\omega) .$$

To be correct, we should "quantize" the electromagnetic field as we did the atom. This can be done by considering the "field" as an infinite collection of point mechanical particles and then apply the rules of Q.M. to them (i.e. this is Quantum Field Theory and in the case of E-M field, Quantum Electrodynamics QED). Then H_0 will contain an additional unperturbed photon energy piece. Hence the atomic level wavefunctions are not stationary states of H_0 anymore, we need also the photon wavefunctions, hence we can have transition between atomic states. The interaction Hamiltonian H' is still of the same $\vec{J}_{emfi} \cdot \vec{A}$ form and we obtain the same result as we will below when we apply Fermi's Golden Rule to this QED system. That is the QED calculation reduces to our $\rho_\gamma = \frac{1}{\Omega}$ condition in the stimulated emission rate formula for the spontaneous emission case we now study.

$$|\vec{A}_0|^2 = |A_0|^2 = \frac{1}{\Omega}\frac{\hbar c^2}{\omega} .$$

Hence the "spontanious" emission rate of the atom is

$$R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = \frac{(2\pi)^2 \alpha \hbar \omega c}{\Omega} \left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times \delta(E_f - E_i + \hbar\omega) .$$

Now the energy of the emitted photon is

$$E_\gamma = \hbar\omega = \hbar|\vec{k}|c = \hbar k c , \quad \text{so}$$

$$R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = \frac{(2\pi)^2 \alpha E_\gamma c}{\Omega} \left|\vec{\epsilon}(\vec{k},\lambda)\cdot\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 \times \delta(E_f - E_i + E_\gamma) .$$

Further, the emitted photon in the final state of the system is in the continuum, hence we must sum over the number of γ-states in the resolution of the detector. The density of final states for the photon is

$$\frac{\partial n}{\partial E_\gamma} = d\Omega_\gamma \frac{\Omega}{(2\pi)^3} \underbrace{g(E_\gamma)}_{=\sum_{\lambda=1}^{2}} k^2 \frac{\partial k}{\partial E_\gamma} ,$$

Since $E_\gamma = \hbar k c$; $\frac{\partial k}{\partial E_\gamma} = \frac{1}{\hbar c}$, so

$$\boxed{\frac{\partial n}{\partial E_\gamma} = d\Omega_\gamma \frac{\Omega}{(2\pi\hbar)^3} \frac{E_\gamma^2}{c^3} \sum_{\lambda=1}^{2} .}$$

Summing over the energy resolution of the detector, we get

$$\delta R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = \int dE_\gamma \frac{\partial n}{\partial E_\gamma} R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}}$$

$$= d\Omega_\gamma \int dE_\gamma\, \delta(E_f - E_i + E_\gamma) \frac{\Omega}{(2\pi\hbar)^3} \frac{E_\gamma^2}{c^3} \times$$

$$\times \sum_{\lambda=1}^{2} \frac{(2\pi)^2 \alpha E_\gamma c}{\Omega} \left| \vec{\epsilon}(\vec{k},\lambda) \cdot \langle \varphi_f | \vec{R} | \varphi_i \rangle \right|^2$$

$$= d\Omega_\gamma \frac{\alpha}{2\pi} \frac{E_\gamma^3}{\hbar^3 c^2} \sum_{\lambda=1}^{2} \left| \vec{\epsilon}(\vec{k},\lambda) \cdot \langle \varphi_f | \vec{R} | \varphi_i \rangle \right|^2 \Bigg|_{E_\gamma = E_i - E_f}$$

$$= d\Omega_\gamma \frac{\alpha}{2\pi} \frac{(E_i - E_f)^3}{\hbar^3 c^2} \sum_{\lambda=1}^{2} \epsilon_i(\vec{k},\lambda)\, \epsilon_j(\vec{k},\lambda) \times$$

$$\times \langle \varphi_f | X^i | \varphi_i \rangle \langle \varphi_f | X^j | \varphi_i \rangle^* \Big|_{E_\gamma = E_i - E_f}$$

Recall that $\sum_{\lambda=1}^{2} \epsilon_i(\vec{k},\lambda)\epsilon_j(\vec{k},\lambda) = \delta_{ij} - \hat{k}_i \hat{k}_j$

$$= \delta_{ij} - \frac{k_i k_j}{\vec{k}^2}$$

$\Rightarrow$

$$\delta R_{fi}^{\text{Dipole}}\Big|_{\text{emis.}} = d\Omega_\gamma \frac{\alpha}{2\pi} \left(\frac{E_i - E_f}{\hbar}\right)^3 \frac{1}{c^2} \left(\delta_{ij} - \hat{k}_i \hat{k}_j\right) \times$$

$$\times \langle \varphi_f | X^i | \varphi_i \rangle \langle \varphi_f | X^j | \varphi_i \rangle^* \Big|_{E_\gamma = E_i - E_f} .$$

The <u>total</u> <u>rate</u> for the emission process is found by integrating over all angles for the emitted photon, using

$$\int_{4\pi} d\Omega_\gamma\, \delta_{ij} = 4\pi\, \delta_{ij} \quad \text{and}$$

$$\int_{4\pi} d\Omega_\gamma \hat{k}_i \hat{k}_j = \underset{\uparrow \text{ constant}}{C} \delta^{ij},$$

since for $i \neq j$ the integral vanishes by symmetry i.e. summing over all directions of vectors cancels, when $i=j$, summing the same quantity over all angles.

To find the constant, take the ij trace

$$\int_{4\pi} d\Omega_\gamma \underbrace{\hat{k}_i \hat{k}_i}_{=1} = C\delta_{ii} = 3C$$

$$\Rightarrow \quad 4\pi = 3C \quad \Rightarrow \quad C = \frac{4\pi}{3}.$$

So $\int_{4\pi} d\Omega_\gamma \hat{k}_i \hat{k}_j = \frac{4\pi}{3}\delta_{ij}$, hence we find

the total rate

$$\Gamma^{\text{Dipole}}_{fi\,\text{emis.}} \equiv \int_{4\pi} d\Omega_\gamma \, \delta R^{\text{Dipole}}_{fi}\Big|_{\text{emis.}}$$

$$= \frac{\alpha}{2\pi}\left(\frac{E_i - E_f}{\hbar}\right)^3 \frac{1}{c^2}\left(4\pi - \frac{4\pi}{3}\right)\delta_{ij} \langle \varphi_f | X^i | \varphi_i \rangle \times$$

$$\times \langle \varphi_f | X^j | \varphi_i \rangle^*$$

$$\boxed{\Gamma^{\text{Dipole}}_{fi\ \text{emis.}} = \frac{4}{3}\alpha\left(\frac{E_i-E_f}{\hbar}\right)^3\frac{1}{c^2}\left|\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 .}$$

We can further simplify the matrix element by expanding x,y,z in terms of spherical polar coordinates

$$\left|\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 = \langle\varphi_f|X^i|\varphi_i\rangle\langle\varphi_f|X^i|\varphi_i\rangle^*$$

$$= \langle\varphi_f|X^i|\varphi_i\rangle\langle\varphi_i|X^i|\varphi_f\rangle$$

$$= \langle\varphi_f|X|\varphi_i\rangle\langle\varphi_i|X|\varphi_f\rangle + \langle\varphi_f|Y|\varphi_i\rangle\langle\varphi|Y|\varphi_f\rangle$$

$$+ \langle\varphi_f|Z|\varphi_i\rangle\langle\varphi|Z|\varphi\rangle$$

Defining $X_\pm \equiv \frac{1}{\sqrt{2}}(X \pm iY)$, this becomes

$$\left|\langle\varphi_f|\vec{R}|\varphi_i\rangle\right|^2 = \langle\varphi_f|X_+|\varphi_i\rangle\underbrace{\langle\varphi_i|X_-|\varphi_f\rangle}_{=\langle\varphi_f|X_+|\varphi_i\rangle^*}$$

$$+ \langle\varphi_f|X_-|\varphi_i\rangle\langle\varphi_i|X_+|\varphi_f\rangle^*$$

$$+ \langle\varphi_f|Z|\varphi_i\rangle\underbrace{\langle\varphi_i|Z|\varphi_f\rangle}_{=\langle\varphi_f|Z|\varphi_i\rangle^*}$$

So $$|\langle \varphi_f|\vec{R}|\varphi_i\rangle|^2 = |\langle \varphi_f|\underline{X}_+|\varphi_i\rangle|^2 + |\langle \varphi_f|\underline{X}_-|\varphi_i\rangle|^2 + |\langle \varphi_f|Z|\varphi_i\rangle|^2.$$

Now introducing spherical coordinates

$$Z = r\cos\theta = \sqrt{\tfrac{4\pi}{3}}\, r Y_1^0(\theta,\varphi)$$

$$\underline{X}_\pm = \tfrac{1}{\sqrt{2}} r\sin\theta\, e^{\pm i\varphi} = \mp\sqrt{\tfrac{4\pi}{3}}\, r Y_1^{\pm 1}(\theta,\varphi)$$

we have

$$|\langle \varphi_f|\vec{R}|\varphi_i\rangle|^2 = \frac{4\pi}{3}\Big\{ |\langle \varphi_f|rY_1^1(\theta,\varphi)|\varphi_i\rangle|^2 + |\langle \varphi_f|rY_1^{-1}(\theta,\varphi)|\varphi_i\rangle|^2 + |\langle \varphi_f|rY_1^0(\theta,\varphi)|\varphi_i\rangle|^2 \Big\}$$

$$= \frac{4\pi}{3}\sum_{m=-1}^{+1} |\langle \varphi_f|rY_1^m(\theta,\varphi)|\varphi_i\rangle|^2 .$$

Then the total rate for photon emission becomes

$$\Gamma^{\text{Dipole}}_{fi\ \text{emis.}} = \frac{16\pi}{9}\alpha\left(\frac{E_i-E_f}{\hbar}\right)^3 \frac{1}{c^2}\sum_{m=-1}^{+1} |\langle \varphi_f|rY_1^m(\theta,\varphi)|\varphi_i\rangle|^2$$

For initial and final hydrogenic atom bound states we have

$$|\varphi_i\rangle = |n_i, l_i, m_i\rangle$$

$$|\varphi_f\rangle = |n_f, l_f, m_f\rangle$$ with the

corresponding bound state energies

$$E_i = -\frac{mc^2\alpha^2}{2n_i^2}Z^2 \;,\; E_f = -\frac{mc^2\alpha^2}{2n_f^2}Z^2$$

yielding $$E_i - E_f = Z^2\frac{mc^2\alpha^2}{2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

As well, since we do not detect the final state hydrogen atom azimuthal quantum number we must sum over these states. Also we do not specify the initial hydrogen atom azimuthal quantum number, hence we must average over these. This implies

$$\Gamma^{\text{Dipole}}_{fi\,\text{emis.}} = \frac{2\pi}{9}\frac{\alpha^7 m^3 c^4}{\hbar^3}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)^3 Z^6$$

$$\sum_{m=-1}^{+1} \underbrace{\sum_{m_f=-l_f}^{+l_f}}_{\text{sum over final m-q\#}} \underbrace{\left(\frac{1}{2l_i+1}\right)\sum_{m_i=-l_i}^{+l_i}}_{\text{average initial m-q\#}} \left|\langle n_f, l_f, m_f | r Y_1^m(\theta,\varphi) | n_i, l_i, m_i\rangle\right|^2$$

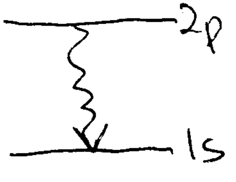
Now we can write

$$\langle n_f, l_f, m_f | r Y_1^m(\theta,\varphi) | n_i, l_i, m_i\rangle$$
$$= \langle n_f, l_f | r | n_i, l_i\rangle \langle l_f, m_f | Y_1^m(\theta,\varphi) | l_i, m_i\rangle$$

So we finally obtain the total dipole transition rate

$$\Gamma^{\text{Dipole}}_{fi\text{ emis.}} = \frac{2\pi}{9}\,\frac{\alpha^7 m^3 c^4}{\hbar^3}\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)^3 \left|\langle n_f, l_f | r | n_i, l_i\rangle\right|^2$$
$$\times Z^6 \times \sum_{m=-1}^{+1}\sum_{m_f=-l_f}^{+l_f}\left(\frac{1}{2l_i+1}\right)\sum_{m_i=-l_i}^{+l_i}\left|\langle l_f, m_f | Y_1^m(\theta,\varphi) | l_i, m_i\rangle\right|^2 .$$

Example: Hydrogen 2p-1s transition rate



$$R_{10} = \frac{1}{\sqrt{2}}\left(\frac{2Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$
$$R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2} e^{-Zr/a_0}\left(\frac{Zr}{a_0}\right)$$

$$\Rightarrow \langle 1s | r | 2p\rangle = \frac{1}{\sqrt{6}}\,\frac{2^8}{3^4}\left(\frac{a_0}{Z}\right)$$

& recall $\frac{a_0}{Z} = \frac{1}{\alpha Z}\left(\frac{\hbar}{mc}\right)$.

The angular integral becomes

$$\langle 1s | Y_1^m | 2p \rangle = \int d\Omega \, Y_0^0 Y_1^m Y_{l_i}^{m_i}$$

$$= \frac{1}{\sqrt{4\pi}} (-1)^m \int Y_1^{-m\,*} Y_{l_i}^{m_i} \, d\Omega$$

$$= \frac{(-1)^m}{\sqrt{4\pi}} \delta_{l_i,1} \delta_{m_i,-m} .$$

(This is a selection rule for Electric dipole transitions, Only $l=1$, the p-state, can decay via the dipole mode to 1s state.)

So

$$\underbrace{\frac{1}{2l_i+1}}_{2+1} \sum_{m_i=-1}^{+1} \sum_{m_f=0} \sum_{m=-1}^{+1} \delta_{m_i,-m} = \frac{1}{3} \sum_{m_i=-1}^{+1} = \frac{1}{3} \cdot 3 = 1$$

So

$$\Gamma_{2p\to 1s} = \frac{2\pi}{9} \frac{Z^6 \alpha^7 m^3 c^4}{\hbar^3} \underbrace{\left(\frac{1}{1} - \frac{1}{2^2} \right)^3}_{\left(\frac{3}{4} = \frac{3}{2^2}\right)^3} \left(\frac{1}{\sqrt{6}} \frac{2^8}{3^4} \left(\frac{a_0}{Z} \right) \right)^2 \times \frac{1}{4\pi}$$

$$= \frac{2\pi}{9} \frac{Z^6 \alpha^7 m^3 c^4}{\hbar^3} \left(\frac{3^3}{2^6} \right) \frac{1}{6} \frac{2^{16}}{3^8} \underbrace{\left(\frac{a_0}{Z} \right)^2}_{=\left(\frac{1}{\alpha Z}\right)^2 \left(\frac{\hbar}{mc}\right)^2} \frac{1}{4\pi}$$

$$= \left(\frac{2}{3} \right)^8 Z^4 \alpha^5 \left(\frac{mc^2}{\hbar} \right)$$

So the 2p→1s total transition rate is

$$\boxed{\Gamma_{2p\to 1s} = \left(\frac{3}{8}\right)^8 Z^4 \alpha^5 \left(\frac{mc^2}{\hbar}\right)}$$

Suppose we have N-atoms in the initial state $|\varphi_i\rangle$. $\Gamma_{fi}^{\text{Dipole}}$ is the transition rate $= \frac{\text{probability of transition}}{\text{unit time}}$. The number of atoms dN that make the transition in time dt is

$$dN = -N\Gamma_{fi}^{\text{Dipole}}\, dt$$

$$\Rightarrow \qquad N = N_0 e^{-\Gamma_{fi}^{\text{Dip.}} t} \equiv N_0 e^{-\frac{t}{\tau}}$$

$$\tau = \text{mean lifetime} = \frac{1}{\Gamma_{fi}^{\text{Dipole}}}.$$

For 2p→1s we have for H-atom

$$\Gamma_{2p\to 1s} = 6.3\times 10^{8}\ \text{sec}^{-1}$$

$$\Rightarrow \boxed{\tau_{2p\to 1s} = 1.6\times 10^{-9}\ \text{sec}.}$$

If the atom can decay to many states we must sum over these to find the total rate, then.

$$dN = -N \sum_f^i \Gamma_{fi}^{\text{Dipole}}\, dt$$

so (to lowest order in α) $\Rightarrow$

$$N = N_0 e^{-\left(\sum_f^i \Gamma_{fi}^{\text{Dip.}}\right)t} \equiv N_0 e^{-\frac{t}{\tau}}$$

$$\Rightarrow \quad \boxed{\tau = \frac{1}{\sum_f^i \Gamma_{fi}^{\text{Dip.}}}}$$

add transition rates to find lifetime.