Spontaneous Emission in SI Units

Let's compute the lifetime of an excited state of atomic hydrogen. If the transition is to go in the dipole approximation, then the selection rules

$$l_f = l_i \pm 1 \qquad m_f = m_i \text{ or } m_f = m_i \pm 1$$

will apply. To have only one such transition, we will use the state $n=2,\ l=1,\ m=m_i$ as the initial state and $n=1,\ l=0,\ m=0$ plus one photon as the final state.

So we must compute

$$\langle 100k|S(t,0)|21m\rangle = -\frac{i}{\hbar}\int_0^t dt' \langle 100k| e^{i(H_{0m}+H_{0F})t'/\hbar}\left(-\frac{q}{m}\vec{A}(\vec{x},0)\cdot\vec{p}\right) e^{-i(H_{0m}+H_{0F})t'/\hbar}|21m\rangle\,. \qquad (1)$$

The field $A(x,0)$ is

$$\vec{A}(\vec{x},0) = \sum_{k,r}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{\frac{1}{2}}\left[\epsilon_r(k)\,a_r(\vec{k})e^{i\vec{k}\cdot\vec{x}} + \epsilon_r^*(k)\,a_r^\dagger(k)\,e^{-i\vec{k}\cdot\vec{x}}\right]. \qquad (2)$$

Now the photon part of $S(t,0)$ is just

$$\langle k,r|a_{r'}^\dagger(\vec{k}')|0\rangle = \delta_{rr'}\,\delta_{\vec{k},\vec{k}'}\,. \qquad (3)$$

So

$$\langle 100k|S(t,0)|21m\rangle = \frac{iq}{\hbar m}\int_0^t e^{i(E_1+\hbar\omega-E_2)t'/\hbar}\sqrt{\frac{\hbar}{2\epsilon_0 V\omega_k}}\langle 100|\epsilon_r^*(k)\cdot\vec{p}\,e^{-ikx}|21m\rangle\,dt'. \quad (4)$$

Doing the t'-integral, we get

$$\langle 100k|S(t,0)|21m\rangle = \frac{q}{m}\left(\frac{\hbar}{2\epsilon_0 V\omega_k}\right)^{\frac{1}{2}}\left(\frac{e^{i(E_1+\hbar\omega-E_2)t/\hbar}-1}{E_1+\hbar\omega-E_2}\right)\langle 100|\vec{\epsilon}^{\,*}\cdot\vec{p}\,e^{-i\vec{k}\cdot\vec{x}}|21m\rangle. \tag{5}$$

So the probability $P(t)$ is

$$P(t) = |\langle 100k|S(t,0)|21m\rangle|^2$$

$$= \frac{q^2}{m^2}\frac{\hbar}{2\epsilon_0 V\omega_k}\,4\,\frac{\sin^2(E_1+\hbar\omega-E_2)t/2\hbar}{(E_1+\hbar\omega-E_2)^2}\,|\langle 100|\vec{\epsilon}^{\,*}\cdot\vec{p}\,e^{-i\vec{k}\cdot\vec{x}}|21m\rangle. \tag{6}$$

Now our helpful δ-function formula is

$$\lim_{t\to\infty}\frac{\sin^2(E_1+\hbar\omega-E_2)t/2\hbar}{(E_1+\hbar\omega-E_2)^2} = \frac{\pi t}{2\hbar}\,\delta(E_1+\hbar\omega-E_2). \tag{7}$$

So apart from a sum over final states, the transition rate is

$$\hat{w} = \frac{dP}{dt} = \frac{\pi q^2}{m^2}\frac{|\langle 100|\vec{\epsilon}_r^{\,*}(k)\cdot\vec{p}\,e^{-i\vec{k}\cdot\vec{x}}|21m\rangle|^2}{\epsilon_0 V\omega_k}\,\delta(E_1+\hbar\omega-E_2). \tag{8}$$

Using $q^2 = \alpha\hbar c 4\pi\epsilon_0$ with $\alpha \approx 1/137.04$, we have

$$\hat{w} = \frac{4\pi^2\alpha\hbar c}{m^2 V\omega_k}\,|\langle 100|\vec{\epsilon}_r^{\,*}(k)\cdot\vec{p}\,e^{-i\vec{k}\cdot\vec{x}}|21m\rangle|^2\,\delta(E_1+\hbar\omega-E_2). \tag{9}$$

Recall now that $\vec{p} = \frac{m}{i\hbar}[\vec{x}, H_{0m}]$. (10)

So by making the dipole approximation

$$e^{-i\vec{k}\cdot\vec{x}} = 1 - ik\cdot x + \cdots \approx 1 \qquad (11)$$

which is valid to about 1 part in 1000, we find

$$\hat{w} = \frac{4\pi^2 \alpha \hbar c}{m^2 V \omega_k} \left| \langle 100 | \frac{m}{i\hbar} [\vec{\epsilon}_n^{\,*}(k)\cdot\vec{x}, H_{0M}] | 21m \rangle \right|^2 \delta(E_1 + \hbar\omega - E_2) \qquad (12)$$

$$= \frac{4\pi^2 \alpha c}{\hbar V \omega_k} (E_2 - E_1)^2 \left| \langle 100 | \vec{\epsilon}_n^{\,*}(k)\cdot\vec{x} | 21m \rangle \right|^2 \delta(E_1 + \hbar\omega - E_2) \qquad (13)$$

Since the δ-function keeps $E_2 - E_1 = \hbar\omega_k$, we have

$$\hat{w} = \frac{4\pi^2 \alpha c}{V} (E_2 - E_1) \left| \langle 100 | \vec{\epsilon}_n^{\,*}(k)\cdot\vec{x} | 21m \rangle \right|^2 \delta(E_1 + \hbar\omega - E_2). \qquad (14)$$

We may choose our coordinate system so that the magnetic quantum number $m=0$. In this case, only the z-component of $\vec{x}$ survives

$$\langle 100 | x_i | 210 \rangle = \delta_{i3} \langle 100 | z | 210 \rangle, \qquad (15)$$

We will now show that

$$\langle 100 | z | 210 \rangle = \frac{2^7\sqrt{2}}{3^5} a_0 = \frac{2^7\sqrt{2}}{3^5} \frac{\hbar}{\alpha m c} \qquad (16)$$

in which $a_0 = \hbar / (\alpha m c) \cong 0.53 \mathring{A}$ is the Bohr radius.

We use

$$R_{10}(r) = \frac{2}{a_0^{3/2}} e^{-r/a_0} \tag{a}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{r}{a_0} e^{-r/(2a_0)} \tag{b}$$

and $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ and $Y_1^0(\theta,\phi) = \sqrt{\frac{3}{4\pi}} \cos\theta$. (c)

So

$$\langle 100|z|210\rangle = \int d\Omega \int_0^\infty r^2 dr \frac{2}{a_0^{3/2}} \frac{e^{-r/a_0}}{\sqrt{4\pi}} r\cos\theta \frac{e^{-r/(2a_0)}}{\sqrt{3}\,(2a_0)^{3/2}} \frac{r}{a_0} \sqrt{\frac{3}{4\pi}} \cos\theta$$

$$= \frac{2\pi}{4\pi}\, \frac{1}{a_0^4\sqrt{2}} \int_{-1}^{1} d\cos\theta \int_0^\infty dr\, r^4 e^{-3r/2a_0} \cos^2\theta$$

$$= \frac{1}{3\sqrt{2}} \frac{1}{a_0^4} \int_0^\infty dr\, r^4 e^{-3r/2a_0}$$

$$= \frac{1}{3\sqrt{2}\, a_0^4} \frac{4!}{\left(\frac{3}{2a_0}\right)^5} = \frac{4\cdot 3\cdot 2\cdot 2^5}{3^6\sqrt{2}} = \frac{2^7}{3^5}\sqrt{2}\, a_0$$

$$= \frac{2^7}{3^5}\sqrt{2}\, \frac{\hbar}{\alpha m c}. \tag{d}$$

Using this value for the matrix element
$\langle 100|z|210\rangle = 2^7\sqrt{2}\,\hbar/(3^5\alpha mc)$

we find for the transition rate

$$\hat{w} = \frac{4\pi^2\alpha c}{V}(E_2 - E_1)\,|\epsilon_r(k)_3|^2\,\frac{2^{15}}{3^{10}}\,\frac{\hbar^2}{\alpha^2 m^2 c^2}\,\delta(E_1 + \hbar\omega - E_2) \qquad (17)$$

in which $\epsilon_r(k)_3 = \epsilon_r(k)\cdot\hat{z}$ is the 3-component of the polarization vector $\vec{\epsilon}_r(k)$. So

$$\hat{w} = \frac{2^{17}}{3^{10}}\,\frac{\pi^2\hbar^2}{\alpha c m^2}\,\frac{(E_2 - E_1)}{V}\,|\epsilon_r(\vec{k})_3|^2\,\delta(E_1 + \hbar\omega - E_2). \qquad (18)$$

The polarization vectors $\epsilon_1(k)$ and $\epsilon_2(k)$ span the subspace of $\mathbb{R}^3$ orthogonal to the vector $\vec{k}$. Thus

$$\sum_{r=1}^{2}\epsilon_r(k)\,\epsilon_r^{\dagger}(k) = 1 - \hat{k}\hat{k}^T. \qquad (19)$$

To sum $\hat{w}$ over r, we will use

$$\sum_{r=1}^{2}|\epsilon_r(k)_3|^2 = \left(\sum_{r=1}^{2}\epsilon_r(k)\,\epsilon_r^{\dagger}(k)\right)_{33}$$
$$= \left(1 - \hat{k}\hat{k}^T\right)_{33} = \delta_{33} - \hat{k}_3\hat{k}_3$$
$$= 1 - \hat{k}_3^2. \qquad (20)$$

If the vector $\vec{k}$ has polar angles θ and ϕ, then

$$\hat{k}_3 = \cos\theta \tag{21}$$

and the sum over polarizations is

$$\sum_{r=1}^{2} |\epsilon_r(k)_3|^2 = 1 - \cos^2\theta. \tag{22}$$

We now must sum over the momenta and spins of the emitted photon. Since

$$\vec{k} = \frac{2\pi}{L}\vec{n} \tag{23}$$

and

$$\vec{n} = \frac{L}{2\pi}\vec{k} \tag{24}$$

we may approximate the sum as the integral

$$\sum_{\vec{n}} = \left(\frac{L}{2\pi}\right)^3 \int d^3k = V\int\frac{d^3k}{(2\pi)^3} \tag{25}$$

$$w = \frac{2^{17}}{3^{10}}\frac{\pi^2\hbar^2(E_2-E_1)}{\alpha c m^2}\int\frac{d^3k}{(2\pi)^3}(1-\cos^2\theta)\,\delta(E_1+\hbar\omega-E_2)$$

$$= \frac{2^{17}}{3^{10}}\frac{\pi^2\hbar^2(E_2-E_1)}{\alpha c m^2}\int_0^\infty\frac{k^2\,d\hbar\omega}{\hbar c}\int_{-1}^{1}dx\,\frac{(1-x^2)}{(2\pi)^2}\,\delta(E_1+\hbar\omega-E_2)$$

$$= \frac{2^{15}}{3^{10}}\frac{\hbar(E_2-E_1)}{\alpha c^2 m^2}\,\frac{(E_2-E_1)^2}{\hbar^2c^2}\int_{-1}^{1}dx\,(1-x^2). \tag{26}$$

Since
$$\int_{-1}^{1} dx\,(1-x^2) = 2 - \left[\frac{x^3}{3}\right]_{-1}^{1} = 2\left(1-\frac{1}{3}\right) = \frac{4}{3} \tag{27}$$
the rate is
$$w = \frac{2^{17}}{3^{11}} \frac{(E_2-E_1)^3}{\alpha \hbar c^4 m^2}. \tag{28}$$

Now in atomic hydrogen
$$E_n = -\frac{1}{2} mc^2 \frac{\alpha^2}{n^2} \tag{29}$$
So
$$E_2 - E_1 = \frac{1}{2} mc^2\alpha^2\left(1-\frac{1}{4}\right) = \frac{3}{8} mc^2\alpha^2. \tag{30}$$
So the rate is
$$w = \frac{2^{17}}{3^{11}} \frac{3^3}{2^9} \frac{m^3 c^6 \alpha^6}{\alpha \hbar c^4 m^2}$$
$$= \left(\frac{2}{3}\right)^8 \frac{mc^2\alpha^5}{\hbar}. \tag{31}$$
The lifetime $\tau = 1/w$ then is
$$\tau = \frac{1}{w} = \left(\frac{3}{2}\right)^8 \frac{\hbar}{mc^2} \alpha^{-5}. \tag{32}$$

Numerically $\quad mc^2 = 0.511 \text{ MeV}$

$$\hbar = 6.582 \times 10^{-22} \text{ MeV s}$$

$$\alpha = 1/137.036 \tag{33}$$

so the lifetime of the 2p state of atomic hydrogen is

$$\tau = \left(\frac{3}{2}\right)^8 \frac{6.582 \times 10^{-22}}{0.511} (137.036)^5 \text{ s}$$

$$= 1.6 \times 10^{-9} \text{ s} = 1.60 \text{ ns}. \tag{34}$$

This $2p \to 1s$ transition is said to be an "allowed transition" because it proceeds through the first term in

$$e^{ik\cdot x} = 1 + ik\cdot x + \cdots, \tag{35}$$

They have lifetimes of nanoseconds. The $2s \to 1s$ transition must use the $k\cdot x$ term which is smaller by a factor of about 10^{-3}. When squared, this suppression is 10^{-6}. Such transitions take milliseconds. They are called "magnetic-dipole" or "electric-quadrupole" transitions according to whether the anti-symmetric or symmetric part of $e\cdot p\, k\cdot x$ causes the decay of the excited state.