SPONTANEOUS EMISSION RATES FOR HYDROGEN - GENERAL SOLUTION

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The spontaneous emission rate for a charge q (such as an electron in an excited state in an atom) in a starting state $|a\rangle$ decaying to a state $|b\rangle$ is, from Einstein's argument, and averaged over all propagation and polarization directions

$$A=\frac{\omega_0^3|\mathfrak{p}|^2}{3\epsilon_0\pi\hbar c^3} \tag{1}$$

where $\mathfrak{p}$ is the matrix element of the dipole moment

$$\mathfrak{p}=q\langle b|\mathbf{r}|a\rangle \tag{2}$$

For spherically symmetric potentials such as that for the hydrogen atom, we found that transitions are allowed from a state $|n\ell m\rangle$ only for $\ell\to\ell\pm1$ and $m\to m,m\pm1$. The hydrogen wave function in its most general form is

$$\psi_{n\ell m}=R_n(r)Y_\ell^m(\theta,\phi) \tag{3}$$

where R_n is the radial function and Y_ℓ^m is a spherical harmonic. To work out the transition rates we need to work out the matrix elements using these functions, subject to the selection rules given above. That is, we need the matrix elements for each of the three coordinates x, y and z between the starting state $|n\ell m\rangle$ and finishing state $|n'\ell'm'\rangle$. We won't bother working out the R_n part of these matrix elements; rather we'll just leave this bit as an integral.

In order to get the total transition rate from a state $|n\ell m\rangle$ to a state with $\ell'=\ell+1$, we must work out the transition rates to all possible final values of m' and add them up.

Fortunately, there are some formulas for the integrals of spherical harmonics that we will find very useful, so we'll quote them here for reference.

$$\int_0^{2\pi}\int_0^{\pi} Y_\ell^m(\theta\phi)\,Y_0^0(\theta\phi)\,Y_\ell^{-m}(\theta\phi)\,d\theta d\phi = \frac{1}{\sqrt{4\pi}} \tag{4}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_\ell^m(\theta\phi)\,Y_1^0(\theta\phi)\,Y_{\ell+1}^{-m}(\theta\phi)\,d\theta d\phi = \sqrt{\frac{3}{4\pi}}\sqrt{\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}} \tag{5}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_\ell^m(\theta\phi)\,Y_1^1(\theta\phi)\,Y_{\ell+1}^{-(m+1)}(\theta\phi)\,d\theta d\phi = \sqrt{\frac{3}{8\pi}}\sqrt{\frac{(\ell+m+1)(\ell+m+2)}{(2\ell+1)(2\ell+3)}} \tag{6}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_\ell^m(\theta\phi)\,Y_1^1(\theta\phi)\,Y_{\ell-1}^{-(m+1)}(\theta\phi)\,d\theta d\phi = -\sqrt{\frac{3}{8\pi}}\sqrt{\frac{(\ell-m)(\ell-m-1)}{(2\ell-1)(2\ell+1)}} \tag{7}$$

One other formula will come in handy:

$$\int_0^{2\pi}\int_0^{\pi} Y_{\ell_1}^{m_1}(\theta\phi)\,Y_{\ell_2}^{m_2}(\theta\phi)\,Y_{\ell_3}^{-m_3}(\theta\phi)\,d\theta d\phi = 0 \text{ if } m_1+m_2\neq m_3 \tag{8}$$

To make use of these formulas, we note that the matrix elements we need to work out are $\langle n'\ell'm'|x|n\ell m\rangle, \langle n'\ell'm'|y|n\ell m\rangle$ and $\langle n'\ell'm'|z|n\ell m\rangle$. In spherical coordinates, we have

$$x = r\sin\theta\cos\phi \tag{9}$$

$$y = r\sin\theta\sin\phi \tag{10}$$

$$z = r\cos\theta \tag{11}$$

These can be written in terms of spherical harmonics:

$$x+iy = r\sin\theta e^{i\phi} = -r\sqrt{\frac{8\pi}{3}}Y_1^1 \tag{12}$$

$$x-iy = r\sqrt{\frac{8\pi}{3}}Y_1^{-1} \tag{13}$$

$$z = r\sqrt{\frac{4\pi}{3}}Y_1^0 \tag{14}$$

For $\ell' = \ell+1$, the only non-zero matrix elements are (we can eliminate the zero elements using 8):

$$\left\langle n', \ell+1, m \left| z \right| n\ell m \right\rangle = I_{\ell+1} \left\langle \ell+1, m \left| \sqrt{\frac{4\pi}{3}} Y_1^0 \right| \ell m \right\rangle \tag{15}$$

$$= I_{\ell+1} \sqrt{\frac{4\pi}{3}} \int_0^{2\pi} \int_0^{\pi} Y_\ell^m (\theta\phi)\, Y_1^0 (\theta\phi)\, Y_{\ell+1}^{-m} (\theta\phi)\, d\theta d\phi \tag{16}$$

$$= I_{\ell+1} \sqrt{\frac{(\ell+m+1)(\ell-m+1)}{(2\ell+1)(2\ell+3)}} \tag{17}$$

$$\left\langle n', \ell+1, m+1 \left| x+iy \right| n\ell m \right\rangle = -I_{\ell+1} \sqrt{\frac{8\pi}{3}} \int_0^{2\pi} \int_0^{\pi} Y_\ell^m (\theta\phi)\, Y_1^1 (\theta\phi)\, Y_{\ell+1}^{-(m+1)} (\theta\phi)\, d\theta d\phi \tag{18}$$

$$= -I_{\ell+1} \sqrt{\frac{(\ell+m+1)(\ell+m+2)}{(2\ell+1)(2\ell+3)}} \tag{19}$$

$$\left\langle n', \ell+1, m-1 \left| x-iy \right| n\ell m \right\rangle = \left\langle n\ell m \left| x+iy \right| n', \ell+1, m-1 \right\rangle^* \tag{20}$$

$$= -I_{\ell+1} \sqrt{\frac{8\pi}{3}} \left[\int_0^{2\pi} \int_0^{\pi} Y_{\ell+1}^{m-1} (\theta\phi)\, Y_1^1 (\theta\phi)\, Y_\ell^{-m} (\theta\phi)\, d\theta d\phi \right]^* \tag{21}$$

$$= -I_{\ell+1} \sqrt{\frac{(\ell+1-(m-1))(\ell+1-(m-1)-1)}{(2(\ell+1)-1)(2(\ell+1)+1)}} \tag{22}$$

$$= -I_{\ell+1} \sqrt{\frac{(\ell-m+2)(\ell-m+1)}{(2\ell+1)(2\ell+3)}} \tag{23}$$

where

$$I_{\ell+1} \equiv \int_0^\infty r^3 R_{n\ell}(r)\, R_{n'(\ell+1)}(r)\, dr \tag{24}$$

To separate x and y, we note that

$$\left\langle n', \ell+1, m+1 \left| x-iy \right| n\ell m \right\rangle = I_{\ell+1} \sqrt{\frac{8\pi}{3}} \int_0^{2\pi} \int_0^{\pi} Y_\ell^m (\theta\phi)\, Y_1^{-1} (\theta\phi)\, Y_{\ell+1}^{-(m+1)} (\theta\phi)\, d\theta d\phi = 0 \tag{25}$$

because of 8, so adding and subtracting this from 19 we get

$$\left\langle n',\ell+1,m+1\left|x\right|n\ell m\right\rangle = -\frac{1}{2}I_{\ell+1}\sqrt{\frac{(\ell+m+1)(\ell+m+2)}{(2\ell+1)(2\ell+3)}} \tag{26}$$

$$\left\langle n',\ell+1,m+1\left|y\right|n\ell m\right\rangle = \frac{i}{2}I_{\ell+1}\sqrt{\frac{(\ell+m+1)(\ell+m+2)}{(2\ell+1)(2\ell+3)}} \tag{27}$$

Similarly, from 23 we get

$$\left\langle n',\ell+1,m-1\left|x\right|n\ell m\right\rangle = -\frac{1}{2}I_{\ell+1}\sqrt{\frac{(\ell-m+2)(\ell-m+1)}{(2\ell+1)(2\ell+3)}} \tag{28}$$

$$\left\langle n',\ell+1,m-1\left|y\right|n\ell m\right\rangle = -\frac{i}{2}I_{\ell+1}\sqrt{\frac{(\ell-m+2)(\ell-m+1)}{(2\ell+1)(2\ell+3)}} \tag{29}$$

Putting it all together, we get

$$\frac{|\mathfrak{p}|^2}{q^2} = \left|\left\langle n',\ell+1,m\left|z\right|n\ell m\right\rangle\right|^2 + \left|\left\langle n',\ell+1,m+1\left|x\right|n\ell m\right\rangle\right|^2 + \tag{30}$$
$$\left|\left\langle n',\ell+1,m+1\left|y\right|n\ell m\right\rangle\right|^2 + \left|\left\langle n',\ell+1,m-1\left|x\right|n\ell m\right\rangle\right|^2 +$$
$$\left|\left\langle n',\ell+1,m-1\left|y\right|n\ell m\right\rangle\right|^2$$

$$|\mathfrak{p}|^2 = q^2 I_{\ell+1}^2 \frac{(\ell+m+1)(\ell-m+1)+\frac{1}{2}\left[(\ell+m+1)(\ell+m+2)+(\ell-m+2)(\ell-m+1)\right]}{(2\ell+1)(2\ell+3)} \tag{31}$$

$$= q^2 I_{\ell+1}^2 \frac{\ell+1}{2\ell+1} \tag{32}$$

$$A = \frac{q^2 I_{\ell+1}^2 \omega_0^3}{3\epsilon_0 \pi\hbar c^3}\frac{\ell+1}{2\ell+1} \tag{33}$$

For $\ell' = \ell - 1$, we can do the same calculations.

$$\left\langle n',\ell-1,m\left|z\right|n\ell m\right\rangle = \left\langle n',\ell,m\left|z\right|n,\ell-1,m\right\rangle^{*} \tag{34}$$

$$= I_{\ell-1}\sqrt{\frac{(\ell+m)(\ell-m)}{(2\ell-1)(2\ell+1)}} \tag{35}$$

$$\left\langle n',\ell-1,m-1\left|x-iy\right|n\ell m\right\rangle = \left\langle n\ell m\left|x+iy\right|n',\ell-1,m-1\right\rangle^{*} \tag{36}$$

$$= -I_{\ell-1}\sqrt{\frac{(\ell+m-1)(\ell+m)}{(2\ell-1)(2\ell+1)}} \tag{37}$$

$$\left\langle n',\ell-1,m+1\left|x+iy\right|n\ell m\right\rangle = -I_{\ell-1}\sqrt{\frac{(\ell-m-1)(\ell-m)}{(2\ell-1)(2\ell+1)}} \tag{38}$$

Separating x and y as before:

$$\left\langle n',\ell-1,m-1\left|x\right|n\ell m\right\rangle = -\frac{1}{2}I_{\ell-1}\sqrt{\frac{(\ell+m-1)(\ell+m)}{(2\ell-1)(2\ell+1)}} \tag{39}$$

$$\left\langle n',\ell-1,m-1\left|y\right|n\ell m\right\rangle = -\frac{i}{2}I_{\ell-1}\sqrt{\frac{(\ell+m-1)(\ell+m)}{(2\ell-1)(2\ell+1)}} \tag{40}$$

$$\left\langle n',\ell-1,m+1\left|x\right|n\ell m\right\rangle = -\frac{1}{2}I_{\ell-1}\sqrt{\frac{(\ell-m-1)(\ell-m)}{(2\ell-1)(2\ell+1)}} \tag{41}$$

$$\left\langle n',\ell-1,m+1\left|y\right|n\ell m\right\rangle = \frac{i}{2}I_{\ell-1}\sqrt{\frac{(\ell-m-1)(\ell-m)}{(2\ell-1)(2\ell+1)}} \tag{42}$$

Putting it together, we get

$$|\mathfrak{p}|^{2} = q^{2}I_{\ell-1}^{2}\frac{(\ell+m)(\ell-m)+\frac{1}{2}\left[(\ell+m-1)(\ell+m)+(\ell-m-1)(\ell-m)\right]}{(2\ell-1)(2\ell+1)} \tag{43}$$

$$= q^{2}I_{\ell-1}^{2}\frac{\ell}{2\ell+1} \tag{44}$$

$$A = \frac{q^{2}I_{\ell-1}^{2}\omega_{0}^{3}}{3\epsilon_{0}\pi\hbar c^{3}}\frac{\ell}{2\ell+1} \tag{45}$$

This differs from the answer given in Griffiths in that he has $2\ell-1$ in the denominator rather than $2\ell+1$. I'm not sure if his answer is wrong or whether there's something wrong in my calculation. As a check, the matrix elements above all make sense in that from 35 if a state starts $m=\pm\ell$ then m cannot stay the same if $\ell'=\ell-1$, from 37, no transitions are allowed to

$m-1$ if $m=-\ell$ or $m=-\ell+1$, and from 38, no transitions are allowed to $m+1$ if $m=+\ell$ or $m=\ell-1$. So my answer looks sensible, but I can't guarantee it's right.