SPONTANEOUS EMISSION RATES FOR THE HYDROGEN ATOM

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 9.10, 9.11.

A collection of atoms an excited state will decay over time into the ground state by spontaneous emission of radiation. If the rate of decay is A (this is the rate at which a single atom decays, defined as the derivative of the transition probability with respect to time), then over a time dt a fraction $A\,dt$ of the number N_b of atoms still in the excited state will decay (on average). That is

$$dN_b = -AN_b dt \tag{1}$$

which is the ODE for simple exponential decay, so

$$N_b(t) = N_b(0)\,e^{-At} \tag{2}$$

The time constant is

$$\tau = \frac{1}{A} \tag{3}$$

and is the time required for the original population to be reduced to $1/e \approx 0.368$ of its size at $t = 0$. An often-quoted, related quantity is the *half-life* $t_{1/2}$ which is the time required for the population to be reduced to half its original size. That is

$$\begin{aligned} e^{-At_{1/2}} &= 0.5 && (4)\\ t_{1/2} &= -\frac{\ln 0.5}{A} && (5)\\ &= \frac{\ln 2}{A} && (6)\\ &\approx 0.693\tau && (7) \end{aligned}$$

As an example, we can calculate the lifetimes of the four $n = 2$ states of the hydrogen atom. The transition rate is

$$A = \frac{\omega_0^3 |\mathfrak{p}|^2}{3\epsilon_0 \pi \hbar c^3} \tag{8}$$

The main calculation is the evaluation of the matrix elements

$$\mathfrak{p} = q \langle \psi_b | \mathbf{r} | \psi_a \rangle \tag{9}$$

where q is the electron charge and ψ_i is one of the hydrogen wave functions, given by (with $a = 4\pi\epsilon_0\hbar^2/mq^2$ as the Bohr radius)

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right) Y_l^m(\theta,\phi) \tag{10}$$

where L is an associated Laguerre polynomial and Y is a spherical harmonic. Doing these integrals by hand gets quite tedious and error-prone, so it's easier to use Maple to do them. The Maple code for evaluating the Laguerre polynomial is

$$simplify\left(LaguerreL\left(n-l-1, 2*l+1, \frac{2*r}{(n*a)}\right), 'LaguerreL'\right) \tag{11}$$

The spherical harmonic can be evaluated using

$$simplify\left(convert(SphericalY(l,m,t,p), LegendreP), 'LegendreP'\right) \tag{12}$$

The t stands for θ and the p stands for ϕ.

With these definitions, we can get expressions for ψ_{200}, ψ_{21-1}, ψ_{210}, ψ_{211} and ψ_{100} and use the rectangular to spherical conversion formulas

$$x = r\sin\theta\cos\phi \tag{13}$$

$$y = r\sin\theta\sin\phi \tag{14}$$

$$z = r\cos\theta \tag{15}$$

With $\psi_a = \psi_{100}$ and ψ_b set to each of the four $n = 2$ wave functions in turn, we have a total of 12 integrals to work out to evaluate 9 in all cases. We can do all these in Maple, but here's the explicit formula for one of the integrals so you can see what they look like.

$$\langle\psi_{210}|z|\psi_{100}\rangle = \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^2 \sin\theta\,[r\cos\theta\psi_{210}^*\psi_{100}] \tag{16}$$

$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^2 \sin\theta\,(r\cos\theta)\left[\frac{\sqrt{2}}{8a^{5/2}\sqrt{\pi}} r e^{-r/2a}\cos\theta\right]\left[\frac{e^{-r/a}}{a^{3/2}\sqrt{\pi}}\right] \tag{17}$$

$$= \frac{128\sqrt{2}}{243}a \tag{18}$$

The other non-zero matrix elements are

$$\langle\psi_{211}|x|\psi_{100}\rangle = \frac{128}{243}ai \tag{19}$$

$$\langle\psi_{211}|y|\psi_{100}\rangle = \frac{128}{243}a \tag{20}$$

$$\langle\psi_{21-1}|x|\psi_{100}\rangle = \frac{128}{243}ai \tag{21}$$

$$\langle\psi_{21-1}|y|\psi_{100}\rangle = -\frac{128}{243}a \tag{22}$$

From these we can evaluate 9 for each state.

$$\mathfrak{p}_{200} = 0 \tag{23}$$

$$\mathfrak{p}_{210} = \frac{128\sqrt{2}}{243}qa\hat{\mathbf{z}} \tag{24}$$

$$\mathfrak{p}_{211} = \frac{128}{243}qai\hat{\mathbf{x}} + \frac{128}{243}qa\hat{\mathbf{y}} \tag{25}$$

$$\mathfrak{p}_{21-1} = \frac{128}{243}qai\hat{\mathbf{x}} - \frac{128}{243}qa\hat{\mathbf{y}} \tag{26}$$

From this we get $|\mathfrak{p}|^2 = |\mathfrak{p}_x|^2 + |\mathfrak{p}_y|^2 + |\mathfrak{p}_z|^2$.

$$|\mathfrak{p}_{200}|^2 = 0 \tag{27}$$

$$|\mathfrak{p}_{210}|^2 = 2\left(\frac{128}{243}aq\right)^2 \tag{28}$$

$$|\mathfrak{p}_{211}|^2 = 2\left(\frac{128}{243}aq\right)^2 \tag{29}$$

$$|\mathfrak{p}_{21-1}|^2 = 2\left(\frac{128}{243}aq\right)^2 \tag{30}$$

To evaluate the transition rate 8 we need ω_0 which is the energy of the emitted photon, which we can get from the difference in energy between the $n=2$ and $n=1$ levels in the Bohr formula

$$E_n = -\frac{1}{n^2}\frac{mq^4}{2\hbar^2(4\pi\epsilon_0)^2} \tag{31}$$

We have

$$\omega_0 = \frac{E_2 - E_1}{\hbar} \tag{32}$$
$$= \frac{3mq^4}{8\hbar^3(4\pi\epsilon_0)^2} \tag{33}$$
$$= 1.55\times 10^{16}\text{ s}^{-1} \tag{34}$$

Plugging these results into 8 we get for all states except ψ_{200}:

$$\tau = \frac{1}{A} = 1.595\times 10^{-9}\text{ s} \tag{35}$$

For ψ_{200}, the lifetime is $1/A = \infty$ so this state is stable.

PINGBACKS

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