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

$$dN_b = -AN_b dt \tag{0.1}$$

which is the ODE for simple exponential decay, so

$$N_b(t) = N_b(0)\,e^{-At} \tag{0.2}$$

The time constant is

$$\tau = \frac{1}{A} \tag{0.3}$$

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

$$\begin{aligned}
e^{-At_{1/2}} &= 0.5 && (0.4)\\
t_{1/2} &= -\frac{\ln 0.5}{A} && (0.5)\\
&= \frac{\ln 2}{A} && (0.6)\\
&\approx 0.693\tau && (0.7)
\end{aligned}$$

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

$$A=\frac{\omega_0^3\left|\mathfrak{p}\right|^2}{3\varepsilon_0\pi\hbar c^3} \tag{0.8}$$

The main calculation is the evaluation of the matrix elements

$$\mathfrak{p}=q\left\langle\psi_b\left|\mathbf{r}\right|\psi_a\right\rangle \tag{0.9}$$

where q is the electron charge and ψ_i is one of the hydrogen wave functions, given by (with $a=4\pi\varepsilon_0\hbar^2/mq^2$ as the Bohr radius)

$$\psi_{nlm}=\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-l-1)!}{2n\left[(n+l)!\right]^3}}e^{-r/na}\left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{na}\right)Y_l^m(\theta,\phi) \tag{0.10}$$

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

$$simplify\left(LaguerreL\left(n-l-1,2*l+1,\frac{2*r}{(n*a)}\right),'LaguerreL'\right) \tag{0.11}$$

The spherical harmonic can be evaluated using

$$simplify\left(convert(SphericalY(l,m,t,p),LegendreP),'LegendreP'\right) \tag{0.12}$$

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

$$x = r\sin\theta\cos\phi \tag{0.13}$$
$$y = r\sin\theta\sin\phi \tag{0.14}$$
$$z = r\cos\theta \tag{0.15}$$

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 0.9 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.

(0.16)
$$\langle \psi_{210} |z| \psi_{100} \rangle = \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^2 \sin\theta \left[r\cos\theta \psi_{210}^* \psi_{100} \right]$$
(0.17)
$$= \int_0^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi r^2 \sin\theta \left(r\cos\theta \right) \left[\frac{\sqrt{2}}{8a^{5/2}\sqrt{\pi}} r e^{-r/2a} \cos\theta \right] \left[\frac{e^{-r/a}}{a^{3/2}\sqrt{\pi}} \right]$$
(0.18)
$$= \frac{128\sqrt{2}}{243} a$$

The other non-zero matrix elements are

$$\langle \psi_{211} |x| \psi_{100} \rangle = \frac{128}{243} ai \tag{0.19}$$
$$\langle \psi_{211} |y| \psi_{100} \rangle = \frac{128}{243} a \tag{0.20}$$
$$\langle \psi_{21-1} |x| \psi_{100} \rangle = \frac{128}{243} ai \tag{0.21}$$
$$\langle \psi_{21-1} |y| \psi_{100} \rangle = -\frac{128}{243} a \tag{0.22}$$

From these we can evaluate 0.9 for each state.

$$\mathfrak{p}_{200} = 0 \tag{0.23}$$
$$\mathfrak{p}_{210} = \frac{128\sqrt{2}}{243} qa\hat{\mathbf{z}} \tag{0.24}$$
$$\mathfrak{p}_{211} = \frac{128}{243} qai\hat{\mathbf{x}} + \frac{128}{243} qa\hat{\mathbf{y}} \tag{0.25}$$
$$\mathfrak{p}_{21-1} = \frac{128}{243} qai\hat{\mathbf{x}} - \frac{128}{243} qa\hat{\mathbf{y}} \tag{0.26}$$

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

$$|\mathfrak{p}_{200}|^2 = 0 \tag{0.27}$$

$$|\mathfrak{p}_{210}|^2 = 2\left(\frac{128}{243}aq\right)^2 \tag{0.28}$$

$$|\mathfrak{p}_{211}|^2 = 2\left(\frac{128}{243}aq\right)^2 \tag{0.29}$$

$$|\mathfrak{p}_{21-1}|^2 = 2\left(\frac{128}{243}aq\right)^2 \tag{0.30}$$

To evaluate the transition rate 0.8 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

$$E_n = -\frac{1}{n^2}\frac{mq^4}{2\hbar^2(4\pi\varepsilon_0)^2} \tag{0.31}$$

We have

$$\omega_0 = \frac{E_2 - E_1}{\hbar} \tag{0.32}$$

$$= \frac{3mq^4}{8\hbar^3(4\pi\varepsilon_0)^2} \tag{0.33}$$

$$= 1.55\times 10^{16}\ \mathrm{s}^{-1} \tag{0.34}$$

Plugging these results into 0.8 we get for all states except ψ_{200}:

$$\tau = \frac{1}{A} = 1.595\times 10^{-9}\ \mathrm{s} \tag{0.35}$$

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

PINGBACKS

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