SPONTANEOUS EMISSION FROM N=3 TO N=1 IN HYDROGEN

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References: Griffiths, David J. (2005), Introduction to Quantum Mechanics, 2nd Edition; Pearson Education - Problem 9.14.

Suppose we have a hydrogen atom with its electron in the state $|300\rangle$. If it is to decay to the ground state $|100\rangle$ the possible transition paths are constrained by the selection rules. We must have $\Delta l = \pm 1$ and $\Delta m = \pm 1, 0$ at each step. Therefore the possible paths are

$$|300\rangle \rightarrow |210\rangle \rightarrow |100\rangle \tag{1}$$

$$|300\rangle \rightarrow |211\rangle \rightarrow |100\rangle \tag{2}$$

$$|300\rangle \rightarrow |21-1\rangle \rightarrow |100\rangle \tag{3}$$

We can't decay from $|300\rangle \rightarrow |200\rangle$ since $\Delta l = 0$ for this transition, and this is forbidden (for a transition involving the electric dipole $\mathfrak{p}$, at any rate).

To work out the decay rates for each path, we need to work out

$$A = \frac{\omega_0^3 |\mathfrak{p}|^2}{3\epsilon_0 \pi \hbar c^3} \tag{4}$$

where the dipole moment matrix element is

$$\mathfrak{p} = q \left\langle n'l'm' \left| \mathbf{r} \right| nlm \right\rangle \tag{5}$$

We can use the same technique that we used earlier. Doing this by hand gets very tedious, so it's best to turn it over to Maple. We need to work out only the rates for the first step in each path to find the relative rates for the three paths. We get (with $a = 4\pi\epsilon_0\hbar^2/mq^2$ as the Bohr radius)

$$\langle 300 | \mathbf{r} | 210 \rangle = \frac{3456}{15625}\sqrt{6}a\hat{\mathbf{z}} \tag{6}$$

$$\langle 300 | \mathbf{r} | 211 \rangle = \frac{3456}{15625}\sqrt{3}ai\hat{\mathbf{x}} + \frac{3456}{15625}\sqrt{3}a\hat{\mathbf{y}} \tag{7}$$

$$\langle 300 | \mathbf{r} | 21-1 \rangle = \frac{3456}{15625}\sqrt{3}ai\hat{\mathbf{x}} - \frac{3456}{15625}\sqrt{3}a\hat{\mathbf{y}} \tag{8}$$

Since $|\mathfrak{p}|^2 = 6\left(\frac{3456}{15625}aq\right)^2$ is the same for all three transitions, the probability of decay is the same for all three paths.

To work out the lifetime of the $|300\rangle$ state, we need the frequency ω_0 of the emitted photon which we can get from the Bohr energy levels in hydrogen.

$$E_n = -\frac{1}{n^2}\frac{mq^4}{2\hbar^2(4\pi\epsilon_0)^2} = -\frac{q^2}{8\pi\epsilon_0 a n^2} \tag{9}$$

The transition from $n = 3$ to $n = 2$ has frequency

$$\omega_0 = \frac{E_3 - E_2}{\hbar} \tag{10}$$

$$= \frac{5q^2}{4\pi\epsilon_0 (72\hbar a)} \tag{11}$$

$$= 2.87 \times 10^{15}\ \mathrm{s}^{-1} \tag{12}$$

The total decay rate is the sum of the individual rates given by 4 (assuming the paths are independent), so the total decay rate is $3A$ and the lifetime is

$$\tau = \frac{1}{3A} = 1.583 \times 10^{-7}\ \mathrm{s} \tag{13}$$