

Let  $A_{nm}$  be the transition rate for the spontaneous emission process  $\psi_n \rightarrow \psi_m$ . In accordance with Heisenberg we have the following formula.

$$A_{nm} = \frac{e^2}{3\pi\epsilon_0\hbar c^3} \omega_{nm}^3 |r_{nm}|^2$$

The transition frequency  $\omega_{nm}$  is given by Bohr's frequency condition.

$$\omega_{nm} = \frac{1}{\hbar}(E_n - E_m)$$

The transition probability (multiplied by a physical constant) is

$$|r_{nm}|^2 = |x_{nm}|^2 + |y_{nm}|^2 + |z_{nm}|^2$$

where

$$\begin{aligned} x_{nm} &= \int \psi_m^* (r \sin \theta \cos \phi) \psi_n dV \\ y_{nm} &= \int \psi_m^* (r \sin \theta \sin \phi) \psi_n dV \\ z_{nm} &= \int \psi_m^* (r \cos \theta) \psi_n dV \end{aligned}$$

Let us compute  $A_{21}$  for hydrogen. The energy levels for hydrogen are

$$E_n = -\frac{\mu}{2n^2} \left( \frac{e^2}{4\pi\epsilon_0\hbar} \right)^2$$

where  $\mu$  is reduced electron mass.

For  $n = 2$  there are four eigenstates.

|     |        |          |
|-----|--------|----------|
| $n$ | $\ell$ | $m_\ell$ |
| 2   | 1      | 1        |
| 2   | 1      | -1       |
| 2   | 1      | 0        |
| 2   | 0      | 0        |

The following table shows the transition probability for every possible transition.

|                | $\psi_{2,1,1} \rightarrow \psi_{1,0,0}$ | $\psi_{2,1,-1} \rightarrow \psi_{1,0,0}$ | $\psi_{2,1,0} \rightarrow \psi_{1,0,0}$ | $\psi_{2,0,0} \rightarrow \psi_{1,0,0}$ |
|----------------|---|--|---|---|
| $x_{21} =$     | $-\frac{128}{243} a_0$                  | $\frac{128}{243} a_0$                    | 0                                       | 0                                       |
| $y_{21} =$     | $-\frac{128}{243} i a_0$                | $-\frac{128}{243} i a_0$                 | 0                                       | 0                                       |
| $z_{21} =$     | 0                                       | 0  | $\frac{128}{243} \sqrt{2} a_0$          | 0                                       |
| $ r_{21} ^2 =$ | $\frac{32768}{59049} a_0^2$             | $\frac{32768}{59049} a_0^2$              | $\frac{32768}{59049} a_0^2$             | 0                                       |

The transition  $\psi_{2,0,0} \rightarrow \psi_{1,0,0}$  has zero probability. For the remaining transitions, the probability  $|r_{21}|^2$  is independent of  $m_\ell$ .

This is the Bohr radius for reduced electron mass  $\mu$ .

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2\mu} = 5.29 \times 10^{-11} \text{ meter}$$

For the transition frequency we have

$$\omega_{21} = \frac{1}{\hbar}(E_2 - E_1) = 1.55 \times 10^{16} \text{ second}^{-1}$$

Hence

$$A_{21} = \frac{e^2}{3\pi\epsilon_0\hbar c^3} \times \omega_{21}^3 \times \frac{32768}{59049} a_0^2 = 6.26 \times 10^8 \text{ second}^{-1}$$

It is interesting to work out  $A_{nm}$  symbolically and see how high the powers get.

$$A_{21} = \frac{e^2}{3\pi\epsilon_0\hbar c^3} \times \underbrace{\left(\frac{3e^4\mu}{128\pi^2\epsilon_0^2\hbar^3}\right)^3}_{\omega_{21}^3} \times \frac{32768}{59049} \underbrace{\left(\frac{4\pi\epsilon_0\hbar^2}{e^2\mu}\right)^2}_{|r_{21}|^2} = \frac{e^{10}\mu}{26244\pi^5\epsilon_0^5\hbar^6c^3}$$

The parameters  $n = 2$  and  $m = 1$  contribute the following numerical factor to  $A_{21}$ .

$$\underbrace{\left(-\frac{1}{2^2} + \frac{1}{1^2}\right)^3}_{\text{from } (E_2 - E_1)^3} \times \underbrace{\frac{32768}{59049}}_{\text{from } |r_{21}|^2} = \frac{512}{2187} = \frac{2^9}{3^7}$$

Multiplying out numerical factors yields the numerical factor shown above in  $A_{21}$ .

$$\frac{1}{3} \times \underbrace{\left(\frac{1}{32}\right)^3}_{\text{from } (E_n - E_m)^3} \times \underbrace{4^2}_{\text{from } a_0^2} \times \frac{512}{2187} = \frac{1}{26244} = \frac{1}{2^2 3^8}$$

Let us analyze the units involved in computing  $A_{nm}$ . For the coefficient of  $A_{nm}$  we have

$$\frac{e^2}{3\pi\epsilon_0\hbar c^3} \propto \frac{\text{ampere}^2 \text{second}^2}{\underbrace{e^2}_{\epsilon_0} \underbrace{\left(\frac{\text{kilogram meter}^2}{\text{second}}\right)}_{\hbar} \underbrace{\left(\frac{\text{meter}^3}{\text{second}^3}\right)}_{c^3}} = \frac{\text{second}^2}{\text{meter}^2}$$

For the transition frequency we have

$$\omega_{21} = \frac{3e^4\mu}{128\pi^2\epsilon_0^2\hbar^3} \propto \frac{\underbrace{(\text{ampere}^4 \text{second}^4)}_{e^4} \underbrace{\text{kilogram}}_{\mu}}{\underbrace{\left(\frac{\text{ampere}^4 \text{second}^8}{\text{kilogram}^2 \text{meter}^6}\right)}_{\epsilon_0^2} \underbrace{\left(\frac{\text{kilogram}^3 \text{meter}^6}{\text{second}^3}\right)}_{\hbar^3}} = \text{second}^{-1}$$

For the Bohr radius we have

$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{e^2\mu} \propto \frac{\underbrace{\left(\frac{\text{ampere}^2 \text{second}^4}{\text{kilogram meter}^3}\right)}_{\epsilon_0} \underbrace{\left(\frac{\text{kilogram}^2 \text{meter}^4}{\text{second}^2}\right)}_{\hbar^2}}{\underbrace{(\text{ampere}^2 \text{second}^2)}_{e^2} \underbrace{\text{kilogram}}_{\mu}} = \text{meter}$$

Hence

$$A_{nm} \propto \frac{\text{second}^2}{\text{meter}^2} \times \underset{\omega_{nm}^3}{\text{second}^{-3}} \times \underset{a_0^2}{\text{meter}^2} = \text{second}^{-1}$$