

Let  $A_{nm}$  be the transition rate for spontaneous emission where the transition is from energy level  $E_n$  to a lower level  $E_m$ . Heisenberg, in his 1925 paper regarded as the origin of modern quantum mechanics, discovered the following formula for  $A_{nm}$ .

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

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

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

For wave functions  $\psi$  in spherical coordinates we have the following transition amplitudes.

$$x_{nm} = \int \psi_m^* (r \sin \theta \cos \phi) \psi_n dV$$

$$y_{nm} = \int \psi_m^* (r \sin \theta \sin \phi) \psi_n dV$$

$$z_{nm} = \int \psi_m^* (r \cos \theta) \psi_n dV$$

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

$$E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}$$

where  $a_0$  is the Bohr radius

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

For the transition frequency we have

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

To compute the transition probability  $|r_{21}|^2$  we need to consider all four eigenstates for  $n = 2$ .

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

The following table shows the probability for every possible transition of  $\psi_2$  to  $\psi_1$ .

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

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  $m_\ell$ .

Now that we have  $|r_{21}|^2$  we can compute a numerical value for  $A_{21}$ .

$$A_{21} = \frac{e^2}{3\pi\epsilon_0\hbar c^3} \times \omega_{21}^3 \times \frac{32768}{59049} a_0^2 = 6.27 \times 10^8 \text{ second}^{-1}$$

Here is  $A_{21}$  as a product of fundamental constants.

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

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 for  $A_{21}$ .

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

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

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

For the transition frequency we have

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

For the Bohr radius we have

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

Hence

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

The coefficients  $B_{12}$  (absorption) and  $B_{21}$  (induced emission) can be computed from  $A_{21}$ .

$$B_{21} = \frac{c^2}{2h\nu^3} A_{21} = \frac{4.25 \times 10^{58}}{\nu^3}$$

$$B_{12} = \frac{g_2}{g_1} B_{21} = \frac{6}{2} B_{21} = \frac{1.28 \times 10^{59}}{\nu^3}$$

Symbol  $g_n$  is the multiplicity associated with energy level  $n$ .

$$g = (2s + 1)(2\ell + 1)$$