

Let A_{nm} be the transition rate for the process $\psi_n \rightarrow \psi_m$ where $E_n > E_m$.

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

The transition frequency is

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

The radial density is

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

where

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

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 μ is reduced electron mass.

For $n = 2$ there are four eigenstates.

| n | ℓ | m_ℓ |
|-----|--------|----------|
| 2 | 1 | 1 |
| 2 | 1 | -1 |
| 2 | 1 | 0 |
| 2 | 0 | 0 |

The following table shows the radial density for every possible transition.

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

Note that the transition rate of $\psi_{2,0,0} \rightarrow \psi_{1,0,0}$ is zero. For the allowed transitions, the radial density $|\langle r_{21} \rangle|^2$ is independent of m_ℓ .

This is the Bohr radius for reduced electron mass μ .

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

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.

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

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

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

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

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

For the transition frequency we have

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

For the Bohr radius we have

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

Hence

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