

Hydrogen alpha line

The following transitions correspond to the H- α line of the hydrogen spectrum. See “Atomic Transition Probabilities Volume I,” issued May 20, 1966, page 2. A_{ki} is the spontaneous emission rate where k is the upper state and i is the lower state.

Transition	λ (Å)	A_{ki} (second $^{-1}$)
$2p - 3s$	6562.86	6.313×10^6
$2s - 3p$	6562.74	2.245×10^7
$2p - 3d$	6562.81	6.465×10^7

Orbital names correspond to azimuthal quantum numbers ℓ .

Orbital	ℓ
s	0
p	1
d	2

Each transition in the table has multiple processes due to the magnetic quantum number m_ℓ . (Recall that $m_\ell = 0, \pm 1, \dots, \pm \ell$.)

There are three ways to transition from $3s$ to $2p$.

$$\begin{aligned}\psi_{3,0,0} &\rightarrow \psi_{2,1,1} \\ \psi_{3,0,0} &\rightarrow \psi_{2,1,0} \\ \psi_{3,0,0} &\rightarrow \psi_{2,1,-1}\end{aligned}$$

There are three ways to transition from $3p$ to $2s$.

$$\begin{aligned}\psi_{3,1,1} &\rightarrow \psi_{2,0,0} \\ \psi_{3,1,0} &\rightarrow \psi_{2,0,0} \\ \psi_{3,1,-1} &\rightarrow \psi_{2,0,0}\end{aligned}$$

Finally, there are fifteen ways to transition from $3d$ to $2p$. (Some of these transitions have zero amplitude.)

$$\begin{array}{lll}\psi_{3,2,2} \rightarrow \psi_{2,1,1} & \psi_{3,2,2} \rightarrow \psi_{2,1,0} & \psi_{3,2,2} \rightarrow \psi_{2,1,-1} \\ \psi_{3,2,1} \rightarrow \psi_{2,1,1} & \psi_{3,2,1} \rightarrow \psi_{2,1,0} & \psi_{3,2,1} \rightarrow \psi_{2,1,-1} \\ \psi_{3,2,0} \rightarrow \psi_{2,1,1} & \psi_{3,2,0} \rightarrow \psi_{2,1,0} & \psi_{3,2,0} \rightarrow \psi_{2,1,-1} \\ \psi_{3,2,-1} \rightarrow \psi_{2,1,1} & \psi_{3,2,-1} \rightarrow \psi_{2,1,0} & \psi_{3,2,-1} \rightarrow \psi_{2,1,-1} \\ \psi_{3,2,-2} \rightarrow \psi_{2,1,1} & \psi_{3,2,-2} \rightarrow \psi_{2,1,0} & \psi_{3,2,-2} \rightarrow \psi_{2,1,-1}\end{array}$$

For each H- α line, an average A_{ki} is computed by summing over A_{ki} for individual processes and dividing by the number of distinct initial states. For example, $3d \rightarrow 2p$ has five distinct initial states, so the divisor is five.

A_{ki} is computed from the following formula.

$$A_{ki} = \frac{e^2}{3\pi\varepsilon_0\hbar c^3} \omega_{ki}^3 |r_{ki}|^2$$

The transition frequency ω_{ki} is given by Bohr's frequency condition

$$\omega_{ki} = \frac{E_k - E_i}{\hbar}$$

The transition probability is

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

These are the transition amplitudes.

$$\begin{aligned} x_{ki} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} r \sin \theta \cos \phi \psi_i^* \psi_k r^2 \sin \theta dr d\theta d\phi \\ y_{ki} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} r \sin \theta \sin \phi \psi_i^* \psi_k r^2 \sin \theta dr d\theta d\phi \\ z_{ki} &= \int_0^\infty \int_0^\pi \int_0^{2\pi} r \cos \theta \psi_i^* \psi_k r^2 \sin \theta dr d\theta d\phi \end{aligned}$$

Using Eigenmath, the results are essentially identical to the book values.

$$A_{3s2p} = 6.31358 \times 10^6 \text{ second}^{-1}$$

$$A_{3p2s} = 2.24483 \times 10^7 \text{ second}^{-1}$$

$$A_{3d2p} = 6.4651 \times 10^7 \text{ second}^{-1}$$