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 $m_\ell = 0, \pm 1, \ldots, \pm\ell$.)

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

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

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

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

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

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

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, $3d \to 2p$ 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.

$$\begin{aligned}
A_{3s2p} &= 6.31358\times 10^6\,\text{second}^{-1} \\
A_{3p2s} &= 2.24483\times 10^7\,\text{second}^{-1} \\
A_{3d2p} &= 6.4651\times 10^7\,\text{second}^{-1}
\end{aligned}$$