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.

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}

A_{ki} is the spontaneous emission rate where i is the lower state and k is the upper state. Orbital names correspond to the following 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 $2p$.

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

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.)

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

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, $3d \rightarrow 2p$ 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.

$$\omega_{ki} = \frac{1}{\hbar}(E_k - E_i)$$

The transition probability (multiplied by a physical constant) is

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

These are the transition amplitudes.

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

Using Eigenmath we obtain the following values for average A_{ki}. The results are essentially identical to the values found in "Atomic Transition Probabilities."

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