From "Atomic Transition Probabilities," 1966, the following transitions correspond to the H-α line of the hydrogen spectrum.

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 for $k \to i$. For H-α, $k = 3$ and $i = 2$. Orbital names correspond to the following azimuthal quantum numbers ℓ.

Name	ℓ
s	0
p	1
d	2

Because of the magnetic quantum number m_ℓ there are multiple ways for each orbital transition to occur. ($m_\ell = 0, \pm 1, \ldots, \pm \ell$)

There are three transitions for $3s \to 2p$.

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

There are three transitions for $3p \to 2s$.

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

Finally, there are fifteen transitions for $3d \to 2p$.

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

For each H-α line, an average A_{ki} is computed by summing over A_{ki} for individual transitions 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.

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

The transition probability (multiplied by a physical constant) is

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

For wave functions ψ in spherical coordinates we have the following transition amplitudes.

$$x_{ki} = \int \psi_k^* \, (r \sin\theta \cos\phi) \, \psi_i \, dV$$
$$y_{ki} = \int \psi_k^* \, (r \sin\theta \sin\phi) \, \psi_i \, dV$$
$$z_{ki} = \int \psi_k^* \, (r \cos\theta) \, \psi_i \, dV$$

Using Eigenmath we obtain the following values for average A_{ki}.

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

These values are essentially identical to the values shown in the table.

Some of the $|r_{ki}|^2$ are zero, indicating forbidden transitions.

The following table shows $|r_{ki}|^2$ for each transition (multiply given values by $a_0^2 = 2.8 \times 10^{-21}$ meter^2).

Initial state	Final state $\psi_{2,0,0}$	Final state $\psi_{2,1,1}$	Final state $\psi_{2,1,0}$	Final state $\psi_{2,1,-1}$
$\psi_{3,0,0}$	–	0.293534	0.293534	0.293534
$\psi_{3,1,1}$	3.13103	–	–	–
$\psi_{3,1,0}$	3.13103	–	–	–
$\psi_{3,1,-1}$	3.13103	–	–	–
$\psi_{3,2,2}$	–	9.01737	0	0
$\psi_{3,2,1}$	–	4.50868	4.50868	0
$\psi_{3,2,0}$	–	1.50289	6.01158	1.50289
$\psi_{3,2,-1}$	–	0	4.50868	4.50868
$\psi_{3,2,-2}$	–	0	0	9.01737