The following hydrogen data table is from "Atomic Transition Probabilities," 1966.

Transition	λ(Å)	$E_i(\text{cm}^{-1})$	$E_k(\text{cm}^{-1})$	g_i	g_k	$A_{ki}(\text{sec}^{-1})$
$1s-2p$	1215.67	0	82259	2	6	6.265×10^{8}
$1s-3p$	1025.72	0	97492	2	6	1.672×10^{8}
$1s-4p$	972.537	0	102824	2	6	6.818×10^{7}
$1s-5p$	949.743	0	105292	2	6	3.437×10^{7}
$1s-6p$	937.804	0	106632	2	6	1.973×10^{7}
$2p-3s$	6562.86	82259	97492	6	2	6.313×10^{6}
$2p-4s$	4861.35	82259	102824	6	2	2.578×10^{6}
$2p-5s$	4340.48	82259	105292	6	2	1.289×10^{6}
$2p-6s$	4101.75	82259	106632	6	2	7.350×10^{5}
$2s-3p$	6562.74	82259	97492	2	6	2.245×10^{7}
$2s-4p$	4861.29	82259	102824	2	6	9.668×10^{6}
$2s-5p$	4340.44	82259	105292	2	6	4.948×10^{6}
$2s-6p$	4101.71	82259	106632	2	6	2.858×10^{6}
$2p-3d$	6562.81	82259	97492	6	10	6.465×10^{7}
$2p-4d$	4861.33	82259	102824	6	10	2.062×10^{7}
$2p-5d$	4340.47	82259	105292	6	10	9.425×10^{6}
$2p-6d$	4101.74	82259	106632	6	10	5.145×10^{6}

The $2-3$ 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 we have $k=3$ and $i=2$.

Let us compute A_{ki} for H-α and see if the results match the table.

Orbital names correspond to the following azimuthal quantum numbers.

Name	Azimuthal quantum number 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. $(m_\ell = 0, \pm1, \ldots, \pm\ell)$

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

$$\psi_{3,0,0} \to \psi_{2,1,1}$$
$$\psi_{3,0,0} \to \psi_{2,1,0}$$
$$\psi_{3,0,0} \to \psi_{2,1,-1}$$

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.

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

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

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

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 tables show $|r_{ki}|^2$ for each transition (multiply all by a_0^2).

Each row is an initial state ψ_i and each column is a final state ψ_k.

	$\psi_{2,1,1}$	$\psi_{2,1,0}$	$\psi_{2,1,-1}$
$\psi_{3,0,0}$	0.293534	0.293534	0.293534

	$\psi_{2,0,0}$
$\psi_{3,1,1}$	3.13103
$\psi_{3,1,0}$	3.13103
$\psi_{3,1,-1}$	3.13103

	$\psi_{2,1,1}$	$\psi_{2,1,0}$	$\psi_{2,1,-1}$
$\psi_{3,2,2}$	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