The following table of hydrogen transition data is from “Atomic Transition Probabilities,” 1966.

Transition	λ(Å)	E_i(cm^{-1})	E_k(cm^{-1})	g_i	g_k	A_{ki}(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 emit the bright red H-α line.

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

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

The orbital names correspond to the following angular momenta.

Letter	Angular momentum 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 $3d \to 2p$.

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

For each H-α line, an average A_{ki} is obtained by summing 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} can be computed using the following Heisenberg 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

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

which is very close 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