

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

Transition	$\lambda(\text{\AA})$	$E_i(\text{cm}^{-1})$	$E_k(\text{cm}^{-1})$	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 emit the bright red H- α line.

Transition	$\lambda (\text{\AA})$	$A_{ki} (\text{second}^{-1})$
$2p-3s$	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 processes for each transition.

There are three processes for the transition $3s \rightarrow 2p$.

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

There are three processes for the transition $3p \rightarrow 2s$.

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

Finally, there are fifteen processes for the transition $3d \rightarrow 2p$.

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

For each process, A_{ki} can be computed using the following Heisenberg formula.

$$A_{ki} = \frac{e^2}{3\pi\epsilon_0\hbar c^3} \omega_{ki}^3 |r_{ki}|^2$$

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.

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

The average A_{ki} is obtained by summing over m_ℓ states and dividing by the number of distinct initial states.

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.