

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

Transition	$\lambda(\text{\AA})$	$E_i(\text{cm}^{-1})$	$E_k(\text{cm}^{-1})$	g_i	g_k	$A_k(\text{sec}^{-1})$
$1s-2p$	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	$\lambda (\text{\AA})$	$A_{ki} (\text{second}^{-1})$
$2p-3s$	6562.86	6.313×10^6
$2s-3p$	6562.74	2.245×10^7
$2p-3d$	6562.81	6.465×10^7

A_{ki} is the spontaneous emission rate for $k \rightarrow i$.

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. ($m_\ell = 0, \pm 1, \dots, \pm \ell$)

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

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

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

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

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

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

For each 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, $3d \rightarrow 2p$ has five distinct initial states, so the divisor is five.

A_{ki} is computed from the following formula.

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

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.

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

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 table shows $|r_{ki}|^2$ for each transition (multiply given values by $a_0^2 = 2.8 \times 10^{-21}$ meter²).

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