

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

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

The  $2-3$  transitions correspond to the H- $\alpha$  line of the hydrogen spectrum.

Transition	$\lambda (\text{\AA})$	$A_{ki} (\text{second}^{-1})$
$2p-3s$	6562.86	$6.313 \times 10^6$
$2s-3p$	6562.74	$2.245 \times 10^7$
$2p-3d$	6562.81	$6.465 \times 10^7$

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

For H- $\alpha$  we have  $k=3$  and  $i=2$ .

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

Orbital names correspond to the following azimuthal quantum numbers.

Name	Azimuthal quantum number $\ell$
$s$	0
$p$	1
$d$	2

Because of the magnetic quantum number  $m_\ell$  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- $\alpha$  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  $\omega_{ki}$  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  $\psi$  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  $a_0^2 = 2.8 \times 10^{-21}$  meter<sup>2</sup>).

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