

From “Atomic Transition Probabilities,” the following 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 $k \rightarrow i$. For H- α , $k = 3$ and $i = 2$. Orbital names correspond to the following azimuthal quantum numbers ℓ .

Orbital	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 $a_0^2 = 2.8 \times 10^{-21} \text{ meter}^2$).

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