

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

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 |