

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     | $6.265 \times 10^8$       |
| $1s-3p$    | 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 emit the bright red H- $\alpha$  line.

| 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                | $6.465 \times 10^7$           |

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

The orbital names correspond to the following angular momenta.

| Letter | Angular momentum $\ell$ |
|--------|-------------------------|
| $s$    | 0                       |
| $p$    | 1                       |
| $d$    | 2                       |

Because of the magnetic quantum number  $m_\ell$  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  $\omega_{ki}$  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.

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

The average  $A_{ki}$  is obtained by summing over  $m_\ell$  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.

These are the  $|r_{ki}|^2$  for  $3s \rightarrow 2p$  (multiply all by  $a_0^2$ ).

$$\begin{array}{llll}
& \psi_{2,1,1} & \psi_{2,1,0} & \psi_{2,1,-1} \\
\psi_{3,0,0} & 0.293534 & 0.293534 & 0.293534
\end{array}$$

These are the  $|r_{ki}|^2$  for  $3p \rightarrow 2s$ .

|                 |                |
|-----------------|----------------|
|                 | $\psi_{2,0,0}$ |
| $\psi_{3,1,1}$  | 3.13103        |
| $\psi_{3,1,0}$  | 3.13103        |
| $\psi_{3,1,-1}$ | 3.13103        |

These are the  $|r_{ki}|^2$  for  $3d \rightarrow 2p$ .

|                 |                |                |                 |
|-----------------|----------------|----------------|-----------------|
|                 | $\psi_{2,1,1}$ | $\psi_{2,1,0}$ | $\psi_{2,1,-1}$ |
| $\psi_{3,2,2}$  | 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         |