

DOING PHYSICS WITH PYTHON

QUANTUM MECHANICS

HYDROGEN ATOM

Selection Rules, Transition Rates, lifetimes

Ian Cooper

matlabvisualphysics@gmail.com

DOWNLOAD DIRECTORY FOR PYTHON SCRIPTS

qmHTR.py Solution to the [3D] Schrodinger equation for the hydrogen atom: eigenvalues and eigenfunctions for an initial state and final state. Calculation of the transition rates and lifetimes for the transition between two states.

qmSpectrum.py The visible hydrogen spectrum for the Balmer series.

[GitHub](#)

[Google Drive](#)

Excited states and transition rates in a hydrogen atom

If a hydrogen atom is excited to a higher energy level, it will at some later time spontaneously make transitions to successively lower energy levels. In a transition from a higher energy state n_2 to a lower energy state n_1 , the frequency and wavelength of the emitted photon are

$$(1) \quad f = \left| \frac{E_{n_2} - E_{n_1}}{h} \right| \quad \lambda = \frac{c}{f}$$

The discrete wavelengths emitted in all transitions that take place constitute the lines in the emission spectrum. But **not** all possible transitions take place. Photons are observed only with frequencies corresponding to transitions between states whose quantum numbers satisfy the **selection rules**

$$(2) \quad \Delta l = \pm 1 \quad \Delta m_l = 0 \text{ or } \pm 1$$

These selection rules are found to apply to all one-electron atoms.

Why are some transitions forbidden?

We can answer this question by using a mix of classical and quantum physics.

A **transmission rate** R_t is the probability per second that an atom in a certain energy level will make a transition to a lower energy level.

Typical allowed transition rates are $\sim 10^8 \text{ s}^{-1}$. This means that in about 10^{-8} s , the probability that the transition has occurred is about one.

This time interval is called the **lifetime** t_L .

$$(3) \quad t_L = \frac{1}{R_t}$$

The eigenfunctions represent stationary states, that is, they do not vary with time. However, for compound states where the wavefunction is a combination of two stationary states of energies E_{n1} and E_{n2} , then, the probability density function contains a term that oscillates in time at frequency

$$(4) \quad f_{n1n2} = \left| \frac{E_{n2} - E_{n1}}{h} \right|$$

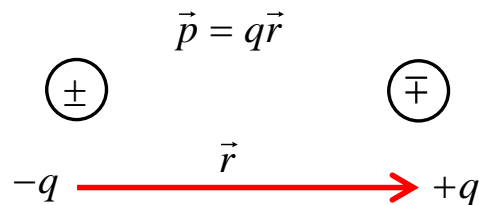
Hence, the electron charge distribution must also oscillate at a frequency f_{n1n2} and this is precisely the frequency of the emitted photon in the transition between the states.

View animations of compound states at

<https://d-arora.github.io/Doing-Physics-With-Matlab/pyDocs/qm049an.htm>

Oscillating electric dipole

The atom's evolving charge distribution can be modeled as an **oscillating electric dipole**.



The **electric dipole moment** \vec{p} for the oscillating charge distribution is the product of the electron charge e and the expectation value of its displacement $\langle \vec{r} \rangle$ value from the nucleus.

A charge distribution that is constant in time will not emit electromagnetic radiation, while a charge distribution with an oscillating electric dipole moment emits radiation at the frequency of the oscillator. The oscillating electric dipole is the most efficient radiator of electromagnetic radiation.

We can use a semi-classical formula for the rate of emission of energy by an oscillating electric dipole

$$(5) \quad R_t = \frac{4\pi^3 f^3}{3\epsilon_0 h c^3} p^2$$

where p is the amplitude of its oscillating electric dipole moment and f is the frequency of the oscillation. R_t is the **atomic transition rate**.

Relative to the Origin at the nucleus, the atomic electric dipole moment is

$$(6) \quad \vec{p} = -e \vec{r}$$

where \vec{r} is the position vector from the nucleus at the Origin.

We can calculate the expectation value of \vec{p} to obtain an expression for the amplitude p of the oscillating electric dipole moment of the atom in a compound state as shown in the following arguments:

$$(7) \quad \Psi_{n_1} = \psi_{n_1} \exp(i E_{n_1} t / \hbar) \quad \Psi_{n_2} = \psi_{n_2} \exp(i E_{n_2} t / \hbar)$$

$$(8) \quad \Psi = \Psi_{n_1} + \Psi_{n_2}$$

where Ψ_{n_1} and Ψ_{n_2} are the wavefunctions for the two states.

The time independent wavefunction for the eigenstate (n, l, m_l) is

$$(9) \quad \psi_{n l m_l}(\vec{r}, \theta, \phi) = R_{n l}(\vec{r}) \Theta_{l m_l}(\theta) \Phi_{m_l}(\phi)$$

$$n = 1, 2, 3, \dots \quad l = 0, 1, 2, \dots, n-1 \quad m_l = 0, \pm 1, \pm 2, \dots, \pm l$$

where n is the principal quantum number, l is the orbital angular momentum quantum number, and m_l is the magnetic quantum number.

The **azimuthal wavefunction** $\Phi_{m_l}(\phi)$ is

$$(10) \quad \begin{aligned} \Phi_{m_l}(\phi) &= \left(\frac{1}{\sqrt{2\pi}} \right) \exp(-i m_l \phi) \\ \int_0^{2\pi} \Phi_{m_l}^* \Phi_{m_l} d\phi &= 1 \end{aligned}$$

The **polar wavefunctions** $\Theta_{l,m_l}(\theta)$ are the *associated Legendre functions* and the normalization condition is

$$\int_0^\pi \Theta_{l,m_l}^* \Theta_{l,m_l} \sin \theta d\theta = 1$$

The spherical harmonics $Y_{l,m_l}(\theta, \phi)$ can be calculated in Python using the function

`Y = sph_harm(mL, L, theta, phi)`

and by setting $\phi = 0$ (phi = 0) then you get the associated Legendre function Θ_{l,m_l}

`THETA = sph_harm(mL, L, theta, 0)`

Radial wavefunction $R(r)$

We can define the **reduced radial wavefunction** $g_{n,l}(\vec{r})$ which is the solution of the **reduced radial Schrodinger Equation**

$$(11) \quad \left[-\left(\frac{\hbar^2}{2m} \right) \frac{d^2}{dr^2} - \frac{Z e^2}{4\pi\epsilon_0 r} + \frac{l(l+1)\hbar^2}{2m_e} \right] g_{nl}(r) = E_n g_{nl}(r)$$

where $g_{nl}(r) = R_{nl}(r) / r$

$$\int_0^{\infty} R_{nl}^*(r) R_{nl}(r) dr = \int_0^{\infty} g_{nl}^*(r) g_{nl}(r) r^2 dr = 1$$

For our normalized wavefunction

$$\int_0^{\infty} g_{nl}^*(r) g_{nl}(r) r^2 dr \int_0^{\pi} \Theta_{lm_l}^* \Theta_{lm_l} \sin \theta d\theta \int_0^{2\pi} \Phi_{m_l}^* \Phi_{m_l} d\phi = 1$$

since the probability of finding the electron is 1. The integration is done over the volume element $dV = r^2 dr d\theta d\phi$

The electric dipole moment can be expressed as

(12)

$$\vec{p} = \int \psi_{n1}^* (-e\vec{r}) \psi_{n1} dV = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \psi_{n1}^* (-e\vec{r}) \psi_{n1} r^2 \sin \theta d\phi d\theta dr$$

This is a vector quantity and has components (p_x, p_y, p_z) where

$$(13) \quad x = r \sin \theta \cos \phi \quad y = r \sin \theta \sin \phi \quad z = r \cos \theta$$

(14)

$$p_x = e \left| \int_0^{\infty} r g_{n1}^* g_{n2} dr \int_0^{\pi} \Theta_{l_1 m_{11}}^* \Theta_{l_2 m_{12}} \sin^2 \theta d\theta \int_0^{2\pi} \Phi_{m_{11}}^* \Phi_{m_{12}} \cos \phi d\phi \right|$$

$$p_y = e \left| \int_0^{\infty} r g_{n1}^* g_{n2} dr \int_0^{\pi} \Theta_{l_1 m_{11}}^* \Theta_{l_2 m_{12}} \sin^2 \theta d\theta \int_0^{2\pi} \Phi_{m_{11}}^* \Phi_{m_{12}} \sin \phi d\phi \right|$$

$$p_z = e \left| \int_0^\infty r g_{n1}^* g_{n2} dr \int_0^\pi \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \cos \theta \sin \theta d\theta \int_0^{2\pi} \Phi_{m_1}^* \Phi_{m_2} d\phi \right|$$

Let

(15)

$$I_{Ax} = \int_0^{2\pi} \Phi_{m_1}^* \Phi_{m_2} \cos \phi d\phi \quad f_{Ax} = \Phi_{m_1}^* \Phi_{m_2} \cos \phi$$

$$I_{Ay} = \int_0^{2\pi} \Phi_{m_1}^* \Phi_{m_2} \sin \phi d\phi \quad f_{Ay} = \Phi_{m_1}^* \Phi_{m_2} \sin \phi$$

$$I_{Az} = \int_0^{2\pi} \Phi_{m_1}^* \Phi_{m_2} d\phi = 1 \quad f_{Az} = 1/2\pi$$

$$I_{Sx} = \int_0^\pi \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \sin^2 \theta d\theta \quad f_{Sx} = \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \sin^2 \theta$$

$$I_{Sy} = \int_0^\pi \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \sin^2 \theta d\theta \quad f_{Sy} = \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \sin^2 \theta$$

$$I_{Sz} = \int_0^\pi \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \cos \theta \sin \theta d\theta \quad f_{Sz} = \Theta_{l_1 m_1}^* \Theta_{l_2 m_2} \cos \theta \sin \theta$$

$$I_R = \int_0^\infty r g_{n1}^* g_{n2} dr \quad f_R = r g_{n1}^* g_{n2}$$

Hence,

$$(16) \quad \begin{aligned} p_x &= e I_R I_{Sx} I_{Ax} = e I_x \\ p_y &= e I_R I_{Sy} I_{Ay} = e I_y \end{aligned}$$

$$p_z = e I_R I_{Sz} I_{Az} = e I_z$$

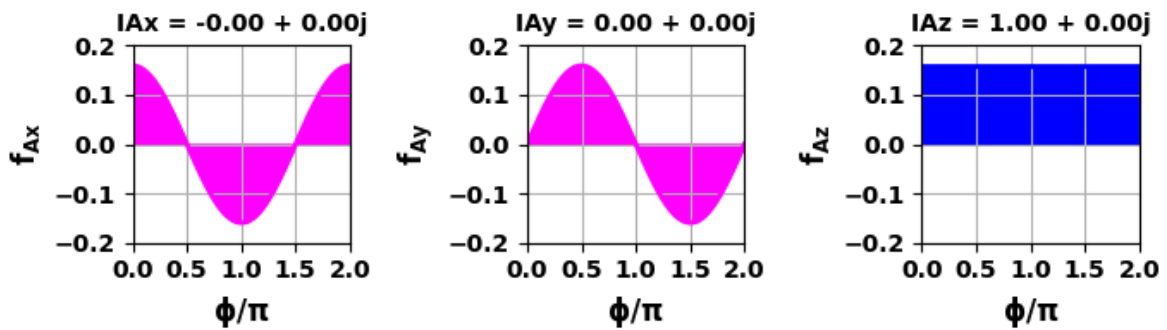
$$(17) \quad p^2 = p_x^2 + p_y^2 + p_z^2$$

$$(18) \quad p = \sqrt{p_x^2 + p_y^2 + p_z^2}$$

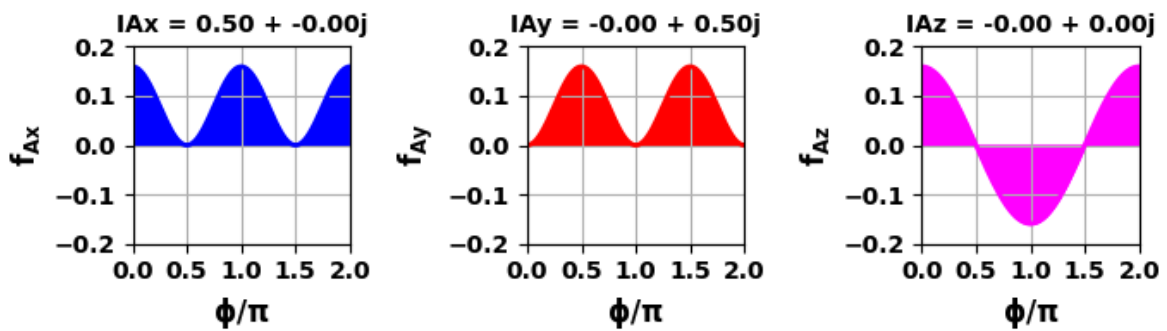
The radial wavefunction $g_{n,l}(r)$ can be found numerically by solving the radial equation by the [Matrix Method](#) and the associated Legendre functions $\Theta_{l,m_l}(\theta)$ can be evaluated in Python from the [spherical harmonics](#). The normalization constants can be found by numerical integration using Simpson's rule. The integrals in the set of equations (15) are computed numerically to find the numerical value of the amplitude of the oscillating electric dipole moment p . Then from equation (3) and equation (4) the transition rate R_t and the lifetime t_L can be calculated respectively. A summary of the calculations is given in Table 1.

Selection rules for m_l (Azimuthal equations)

$$mL_1 = 0 \quad mL_2 = 0 \quad \Delta mL = 0$$



$$mL_1 = 0 \quad mL_2 = 1 \quad \Delta mL = 1$$



$$mL_1 = 0 \quad mL_2 = 2 \quad \Delta mL = 2$$

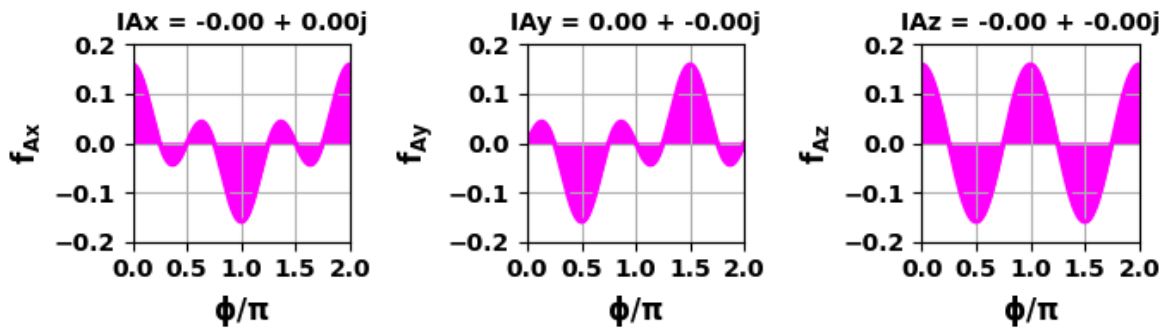


Fig. 1. Azimuthal function equations 15. I_A functions: blue \rightarrow real f_A , red \rightarrow imaginary f_A , and magenta \rightarrow zero f_A . Area under the curves for f_A vs ϕ gives the value of I_A .

Table 1. Components of the overlap integral I_A for the azimuthal wavefunction.

| Δm_l | I_{Ax} | I_{Ay} | I_{Az} |
|--------------------|----------|----------|----------|
| $\Delta m_l = 0$ | 0 | 0 | 1 |
| $\Delta m_l = +1$ | 0.5 | 0.5j | 0 |
| $\Delta m_l = -1$ | 0.5 | -0.5j | 0 |
| $ \Delta m_l > 1$ | 0 | 0 | 0 |

Selection rules on m_l for allowed spontaneous transitions by electric dipole radiation

$$\Delta m_l = 0 \quad \Delta m_l = \pm 1$$

The selection rules also define the polarization of the radiation emitted. For $\Delta m_l = \pm 1$, the components I_{Ax} and I_{Ay} have the same magnitude but I_{Ay} is complex while I_{Ax} is real. In terms of SHM, it signifies that the oscillations of I_{Ay} either lead or lag those of I_{Ax} . The combination of two such perpendicular oscillations of equal magnitude differing in phase by yield an electric dipole moment rotating in the XY-plane when $\Delta m_l = \pm 1$. For $\Delta m_l = 0$ the polarization is linear with the oscillations long the Z-axis.

[linear polarized light](#)

[circular and elliptical polarized light](#)

Consider a radiating atom in a magnetic field aligned in the Z direction. Then, states with different m_l values will have slightly different energies of orientation in the magnetic field. Therefore, the three selection rules means that that photons of three different energies are emitted. So, a single spectral line will be split into three lines with slightly different wavelengths and polarizations when the radiating atoms are the magnetic field. This splitting of the spectral lines in a magnetic field is known as the Zeeman Effect (P. Zeeman, 1890).

Table 2. Zeeman Effect

| Frequency | Emitted light |
|--|--|
| Highest frequency $\Delta m_l = -1$ | Circular polarization in plane perpendicular to the magnetic field |
| Intermediate frequency $\Delta m_l = 0$ | Linearly polarized line parallel to the magnetic field |
| Lowest frequency $\Delta m_l = +1$ | Circular polarization in plane perpendicular to the magnetic field, but opposite sense to the case for $\Delta m_l = -1$ |

An oscillating linear electric dipole emits no radiation along the direction of its axis of oscillation. Thus, looking along the field direction, one observes only two oppositely circular-polarized components. Looking perpendicularly to the field, one observes

only the radiation due to I_{Az} which is linearly polarized to the field, and also a pair of lines polarized perpendicular to the field as a result of viewing the circularly polarized components in their own plane.

Selection rules: orbital angular momentum quantum number l

The selection rules for l depend upon the value of the integral in equation 15, I_{Sx} , I_{Sy} , and I_{Sz} . It is found that allowed transitions for electric dipole radiation must satisfy the relationship

$$\Delta l = \pm 1$$

This selection rule embodies a very basic property of electric dipole radiation: transitions can only take place between quantum states of opposite parity. In a central potential, the complete wavefunctions $\psi_{nlm_l}(\vec{r})$ have either even or odd parity according to whether the orbital angular momentum quantum number l is even or odd. The integral defining the magnitude of the electric dipole moment for a transition from state 1 to state 2 is

$$\vec{p}_{12} = -e \int \psi_{n_1 l_1 m_{l_1}}^* \vec{r} \psi_{n_2 l_2 m_{l_2}} dV$$

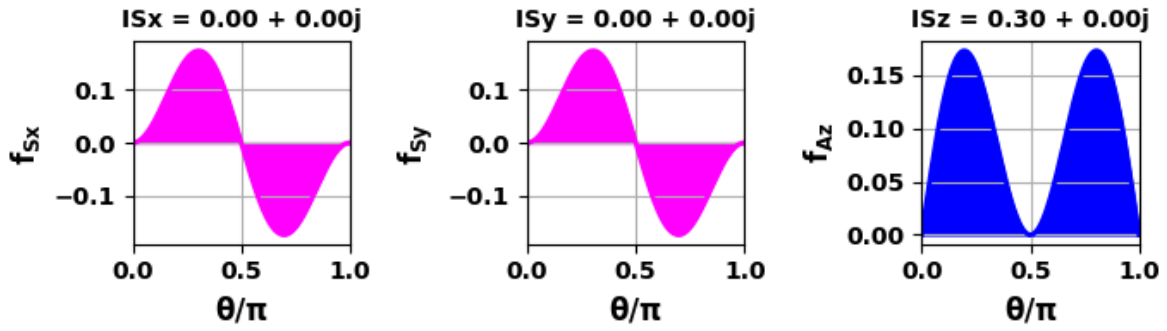
If the electric dipole \vec{p}_{12} is non-zero, then the total integrand must be even. If the integrand is odd, then the product of the angular components of the integrand must be odd. Hence if l_1 is even, then l_2 must be odd and vice versa for the transition to be allowed.

We will consider the transitions for the polar equations given in equation 15

$$l_1 = 1 \quad m_{l_1} = 0 \rightarrow l_2 = 0 \quad m_{l_2} = 0 \quad \Delta l = -1 \quad \Delta m_l = 0$$

$$\text{and } l_1 = 1 \quad m_{l_1} = \pm 1 \rightarrow l_2 = 0 \quad m_{l_2} = 0 \quad \Delta l = -1 \quad \Delta m_l = \mp 1$$

$$L_1 = 1 \quad L_2 = 0 \quad \Delta L = -1 \quad mL_1 = 0 \quad mL_2 = 0 \quad \Delta mL = 0$$



$$L_1 = 1 \quad L_2 = 0 \quad \Delta L = -1 \quad mL_1 = 1 \quad mL_2 = 0 \quad \Delta mL = -1$$

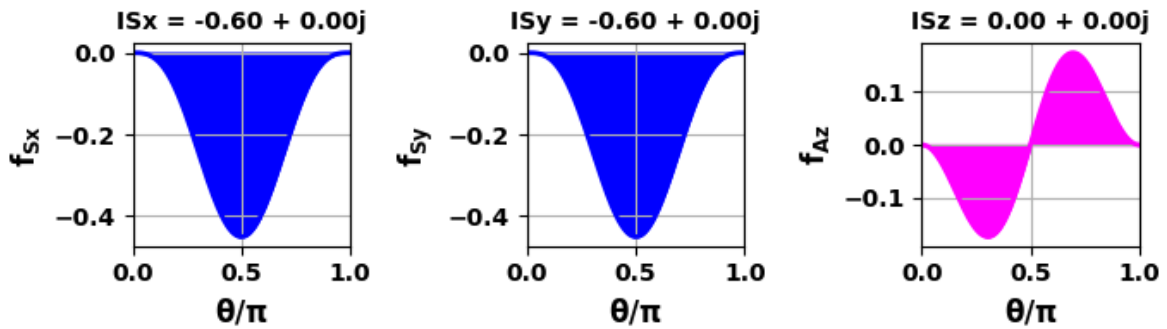


Fig. 2. Polar function equations 17. I_S functions: blue \rightarrow real f_S red \rightarrow imaginary f_S , and magenta \rightarrow zero f_S . Area under the curves for f_{AS} vs θ gives the value of I_S .

Table 3 gives a summary of the x,y,z components of the overlap integrals (equation 15) for the angular dependence for the transitions

$l = 1 \rightarrow l = 0$ where

$$I_{ASx} = I_{Ax} I_{Sx} \quad I_{ASy} = I_{Ay} I_{Sy} \quad I_{ASz} = I_{Az} I_{Sxz}$$

Table 3. The x,y,z components of the overlap integrals (equation 17) for the angular dependence for the transitions $l = 1 \rightarrow l = 0$

| m_l | I_{ASx} | I_{ASy} | I_{ASz} | Polarization |
|-------|-----------|-----------|-----------|--------------|
| -1 | -0.408 | 0.408 i | 0 | elliptical |
| 0 | 0 | 0 | 0.577 | linear |

BALMER SERIES

We can calculate for the Balmer series, the rates of transition and lifetimes for the transitions to the state $n = 2$ from higher energy states where $n = 3, 4, 5, 6,$ and 7 . Each state is specified by the vector

(n, l, m_l) . The value of **rMax** is incremented as the value of n is increased.

Final state 2s (2,0,0) $E = 1.51$ eV

Final state 3p (3,1,0) $E = 3.40$ eV

$$p_x = 0 \quad p_y = 0 \quad p_z = 1.50 \times 10^{-29} \quad p = 1.503 \times 10^{-29}$$

$$\text{Transition rate } R = 2.25 \times 10^7 \text{ s}^{-1}$$

$$\text{Lifetime } t_{avg} = 45 \text{ ns} \quad (\text{web } 44.6 \text{ ns})$$

$$\text{Photon } dE = 1.89 \text{ eV} \quad \lambda = 657 \text{ nm} \quad \text{linear polarized}$$

Final state 4p (4,1,0) $E = 1.51$ eV

$$p_x = 0 \quad p_y = 0 \quad p_z = 6.27 \times 10^{-30} \quad p = 6.27 \times 10^{-30}$$

$$\text{Transition rate } R = 9.62 \times 10^6 \text{ s}^{-1}$$

$$\text{Lifetime } t_{avg} = 104 \text{ ns} \quad (\text{web } 10.3.5 \text{ ns})$$

$$\text{Photon } dE = 2.55 \text{ eV} \quad \lambda = 486 \text{ nm} \quad \text{linear polarized}$$

Final state 5p (5,1,0) $E = 0.849$ eV

$$p_x = 0 \quad p_y = 0 \quad p_z = 3.80 \times 10^{-30} \quad p = 3.80 \times 10^{-30}$$

$$\text{Transition rate } R = 4.95 \times 10^6 \text{ s}^{-1}$$

$$\text{Lifetime } t_{avg} = 202 \text{ ns}$$

$$\text{Photon } dE = 2.85 \text{ eV} \quad \lambda = 434 \text{ nm} \quad \text{linear polarized}$$

Final state 6p (6,1,0) $E = 0.849$ eV

$$p_x = 0 \quad p_y = 0 \quad p_z = 2.70 \times 10^{-30} \quad p = 2.70 \times 10^{-30}$$

$$\text{Transition rate } R = 2.98 \times 10^6 \text{ s}^{-1}$$

$$\text{Lifetime } t_{avg} = 336 \text{ ns})$$

$$\text{Photon } dE = 3.02 \text{ eV} \quad \lambda = 410 \text{ nm} \quad \text{linear polarized}$$

Final state 7d (7,1,0) $E = 0.277$ eV

$$p_x = 0 \quad p_y = 0 \quad p_z = 2.54 \times 10^{-30} \quad p = 2.02 \times 10^{-30}$$

$$\text{Transition rate } R = 1.83 \times 10^6 \text{ s}^{-1}$$

$$\text{Lifetime } t_{avg} = 547 \text{ ns}$$

$$\text{Photon } dE = 3.12 \text{ eV} \quad \lambda = 398 \text{ nm} \quad \text{linear polarized}$$

For the Balmer series, the brightness of the visible spectral lines decreases as the average lifetime increases.

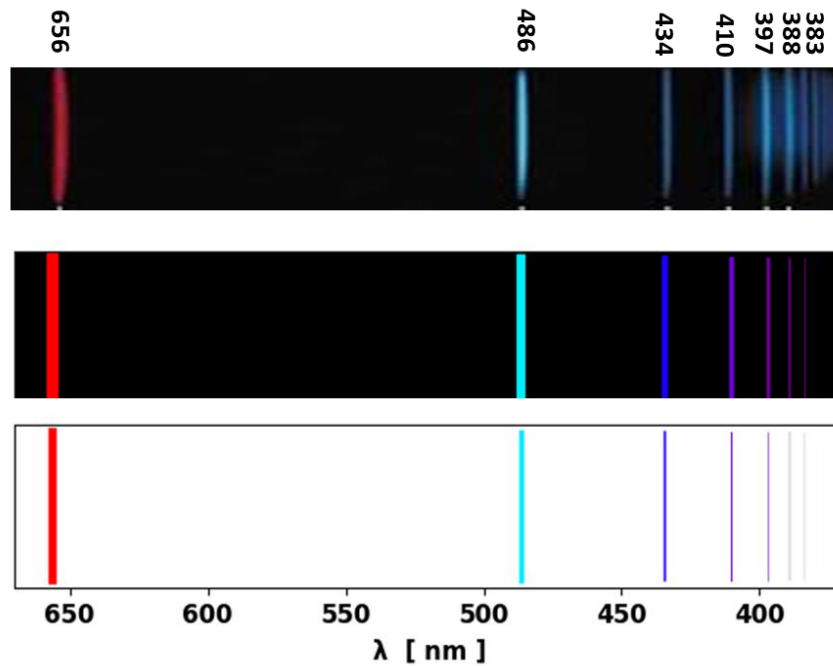


Fig. 3. Balmer series spectrum for the visible components. Top is an image of the spectrum and the lower two spectrum are created using the code [qmSpectrum.py](#).

Table 4. Blamer series: transitions from initial state to final state, wavelength, lifetime and experimental relative intensity of the spectral lines.

| | $3 \rightarrow 2$ | $4 \rightarrow 2$ | $5 \rightarrow 2$ | $6 \rightarrow 2$ | $7 \rightarrow 2$ |
|-----------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| λ [nm] | 656 | 486 | 434 | 410 | 397 |
| lifetime [ns] | 45 | 104 | 202 | 336 | 547 |
| relative intensity | 180 | 80 | 60 | 30 | 8 |

TRANSITION LIFETIMES

Table 5: Data for the transition from a higher energy level to a lower level. The initial and final states are given by the set of quantum numbers ($n l m_l$). Published values are given for the lifetime so that the model results can be compared to accepted values.

| final state $n_2 l_2 m_{l2}$ | initial state $n_1 l_1 m_{l1}$ | lifetime t_L (ns) web* | lifetime t_L (ns) simulati on | E_{B2} (eV) | EB_1 (eV) | λ (nm) |
|------------------------------------|--------------------------------------|--------------------------------|--|------------------|----------------|-------------------|
| 1s (1 0 0) | 2s (2 0 0) | $\sim \infty$ | $\sim \infty$ | 13.58 | 3.40 | |
| 1s (1 0 0) | 3s (3 0 0) | $\sim \infty$ | $\sim \infty$ | 13.58 | 1.51 | |
| 1s (1 0 0) | 3d (3 2 0) | $\sim \infty$ | $\sim \infty$ | 13.58 | 1.51 | |
| 1s (1 0 0) | 3d (3 2 1) | $\sim \infty$ | $\sim \infty$ | 13.58 | 1.51 | |
| 1s (1 0 0) | 3d (3 2 2) | $\sim \infty$ | $\sim \infty$ | 13.58 | 1.51 | |
| 3p (3 1 1) | 4f (4 3 0) | $\sim \infty$ | $\sim \infty$ | 1.51 | 0.85 | |
| 3d (3 2 0) | 4d (4 3 2) | $\sim \infty$ | $\sim \infty$ | 1.51 | 0.85 | 1877 |
| 1s (1 0 0) | 2p (2 1 0) | 1.60 | 1.60 | 13.58 | 3.40 | 122 |
| 1s (1 0 0) | 2p (2 1 1) | | 1.60 | 13.58 | 3.40 | 122 |
| 1s (1 0 0) | 3p (3 1 0) | 5.98 | 6.00 | 13.58 | 1.51 | 102 |
| 1s (1 0 0) | 3p (3 1 1) | | 6.00 | 13.58 | 1.51 | 102 |
| 1s (1 0 0) | 4p (4 1 0) | 14.5 | 12.1 | 13.58 | 0.85 | 97 |
| 2s (2 0 0) | 3p (3 1 0) | 44.5 | 44.6 | 3.40 | 1.51 | 658 |
| 2s (2 0 0) | 3p (3 1 1) | | 44.6 | 3.40 | 1.51 | 658 |
| 2s (2 0 0) | 4p (4 1 0) | 103.4 | 103.5 | 3.40 | 0.85 | 487 |
| 2s (2 0 0) | 4p (4 1 1) | | 103.5 | 3.40 | 0.85 | 487 |
| 2p (2 1 0) | 3s (3 0 0) | 475 | 478 | 3.40 | 1.51 | 657 |
| 2p (2 1 1) | 3s (3 0 0) | | 478 | 3.40 | 1.51 | 657 |
| 2p (2 1 0) | 3d (3 2 0) | | 23.3 | 3.40 | 1.51 | 657 |
| 2p (2 1 0) | 3d (3 2 1) | | 31.0 | 3.40 | 1.51 | 657 |

| | | | | | | |
|------------|------------|------|------|------|------|-----|
| 2p (2 1 1) | 3d (3 2 0) | | 93.1 | 3.40 | 1.51 | 657 |
| 2p (2 1 1) | 3d (3 2 1) | | 31.0 | 3.40 | 1.51 | 657 |
| 2p (2 1 0) | 4s (4 0 0) | 1171 | 1168 | 3.40 | 0.85 | 487 |
| 2p (2 1 1) | 4s (4 0 0) | | 1168 | 3.40 | 0.85 | 487 |

From Table 5, it is quite clear that not all transitions give rise to spectral emissions where spectral lines are not observed or very weak. For the case of electric dipole radiation, the transition rates are zero when the dipole matrix elements are zero. This gives rise to a set of **selection rules** which are conditions on the quantum numbers of the eigenfunctions of the initial state (state 1) and the final state (state 2) energy levels. For the electric dipole radiation, allowed transitions (electric dipole moment, $p \neq 0$) are given by the selection rules

$$\text{Allowed transitions} \quad (\Delta l = \pm 1) \quad \text{and} \quad (\Delta m_l = 0 \quad \text{or} \quad \Delta m_l = \pm 1)$$

Transitions rates of atom are typically $R_t \sim 10^8 \text{ s}^{-1}$.

If these conditions are **not** satisfied, the electric dipole moment, $p = 0$ and the transitions is called **forbidden**.

Selection rules arise because of the symmetry properties of the oscillating charge distribution of the atom. The compound state formed by the superposition of two stationary states must have an oscillating charge distribution which oscillates as the same frequency

of the emitted photon. Also, for the system of the atom and the emitted photon, angular momentum must be conserved. The angular momentum of the emitted photon in units of \hbar is one, hence the change in the angular momentum quantum number of the atom should be $\Delta l = \pm 1$.

Selection rules do not absolutely prohibit transitions that violate them, but only make such transitions very unlikely. The transition may occur through some other mechanism such as magnetic dipole moment radiation or electric quadrupole moment radiation.

View animations of the oscillations between states:

[ANIMATIONS](#)

References

<https://www.chem.uci.edu/~unicorn/old/H2A/handouts/PDFs/LectureA5.pdf>

<http://www.nist.gov/srd/upload/jpcrd382009565p.pdf>