

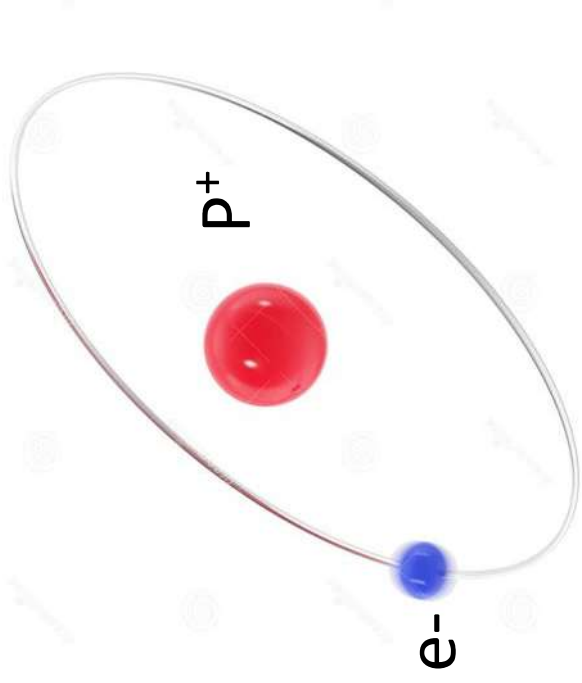
CHAPTER III – PART 2

THE HYDROGEN SPECTRUM

AND BOHR'S MODEL

I/ Rutherford's classical atomic model

We consider a hydrogen atom where the electron, with charge $q_e = -e$ and mass m_e around the proton with a linear velocity v . The proton's mass m_p is much larger than electron's.



I.1/ Study of the orbits according to Rutherford's classical model

The electron is subjected to the Coulomb interaction force

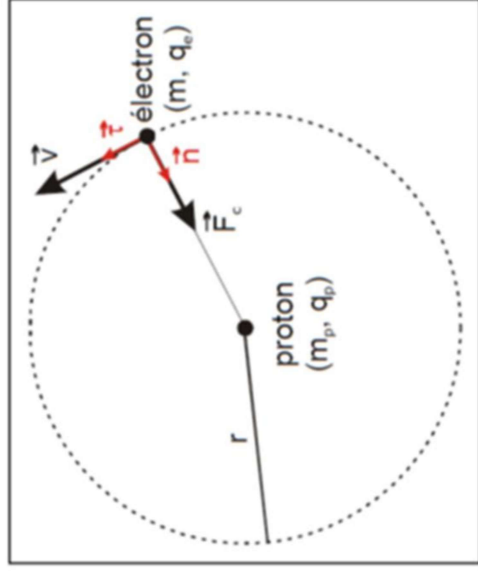
$$\vec{F}_{int} = K \frac{|q_e q_p|}{r^2}$$

q_e : Charge of the electron ($q_e = -1.6 \cdot 10^{-19} \text{ C}$).

q_p : Charge of the proton ($q_p = +1.6 \cdot 10^{-19} \text{ C}$).

r : Radius of the orbit.

$$K = 9.987 \times 10^9 \text{ kg} \cdot \text{m}^3 \cdot \text{A}^{-2} \cdot \text{s}^{-4} \approx 10^{10} (\text{SI})$$



According to Newton's second law

$$\vec{F}_{int} + \vec{F}_c = \mathbf{0}$$

The electron is subject to a centrifugal force

$$F_c = m_e a = m_e \frac{v_e^2}{r}$$

m_e : Mass of the electron. ($m_e = 9.1 \cdot 10^{-31} \text{ kg}$).

a : Acceleration of the electron

v_e : Electron velocity.

r : Radius of the orbit.

$$\rightrightarrows \sum \vec{F} = \mathbf{0}$$

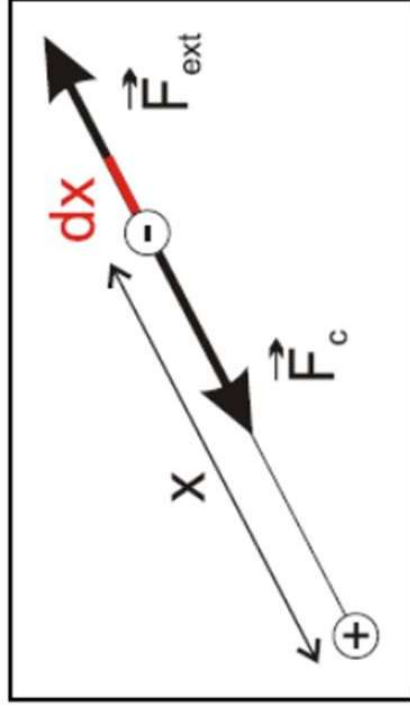
$$r = \frac{K e^2}{m_e v_e^2}$$

I.2/ Energy study of the hydrogen atom according to Rutherford's model

Electrostatic potential energy of the proton–electron system

We consider a hydrogen atom made up of a proton and an electron.

$$E_p = \int_{\infty}^r \overrightarrow{f_r} dr \qquad E_p = -K \frac{e^2}{r}$$



Total energy

$$E_T = E_K + E_p$$



$$E_T = -\frac{1}{2} K \frac{e^2}{r}$$

Kinetic energy

Because the proton's mass is much greater than the electron's mass, the proton is considered stationary.

As a result, all the kinetic energy is due to the motion of the electron around the proton.

$$E_k = \frac{1}{2} m_e v_e^2$$

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II/ Bohr's atomic model

II.1/ First Postulate (The Orbit Postulate)

Electrons can move around the nucleus without emitting radiation only in certain orbits. These orbits are defined by the following quantization rule:

$$m_e v_e r = n \frac{h}{2\pi}$$

With:

n : principal quantum number, $n \in \{1, 2, 3, \dots\}$

m_e : mass of the electron

r : radius of the electron's orbit around the nucleus

v_n : linear (tangential) velocity of the electron on its $n_{\text{-th}}$ orbit

h : Planck's constant ($h = 6.626\,070\,15 \times 10^{-34}$ J.s)



II.2/ Postulate N°2 (The Postulate of Energy Emission and Absorption)

Each allowed orbit has a specific energy level. When an electron moves from one to another, it makes a quantum jump and emits or absorbs a photon with energy:

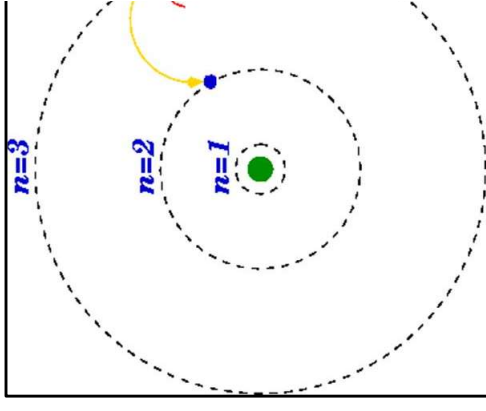
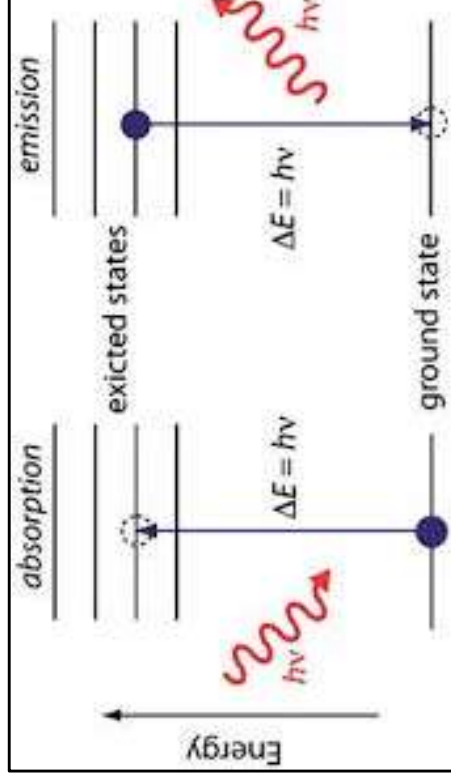
$$E = |E_f - E_i| = h\nu.$$

Where:

E_i : energy corresponding to the initial orbit (initial energy level)

E_f : energy corresponding to the final orbit (final energy level)

ν : frequency of the emitted or absorbed radiation



II.3/ Results of Bohr's Theory

$$r = \frac{h^2}{4\pi^2 K m e^2} n^2$$

$$v_e = \frac{2\pi m K e^2}{nh}$$

$$E_T = -\frac{2\pi^2 m_e K^2 e^4}{h^2} \frac{1}{n^2}$$

n : principal quantum number, $n \in \{1, 2, 3, \dots\}$

m_e : mass of the electron

r : radius of the electron's orbit around the nucleus

v_n : linear (tangential) velocity of the electron on its n_{th} orbit

h : Planck's constant ($h = 6.626\,070\,15 \times 10^{-34} \text{ J}\cdot\text{s}$)
 $K = 10^{10} \text{ (SI)}$

For the hydrogen atom and the K shell

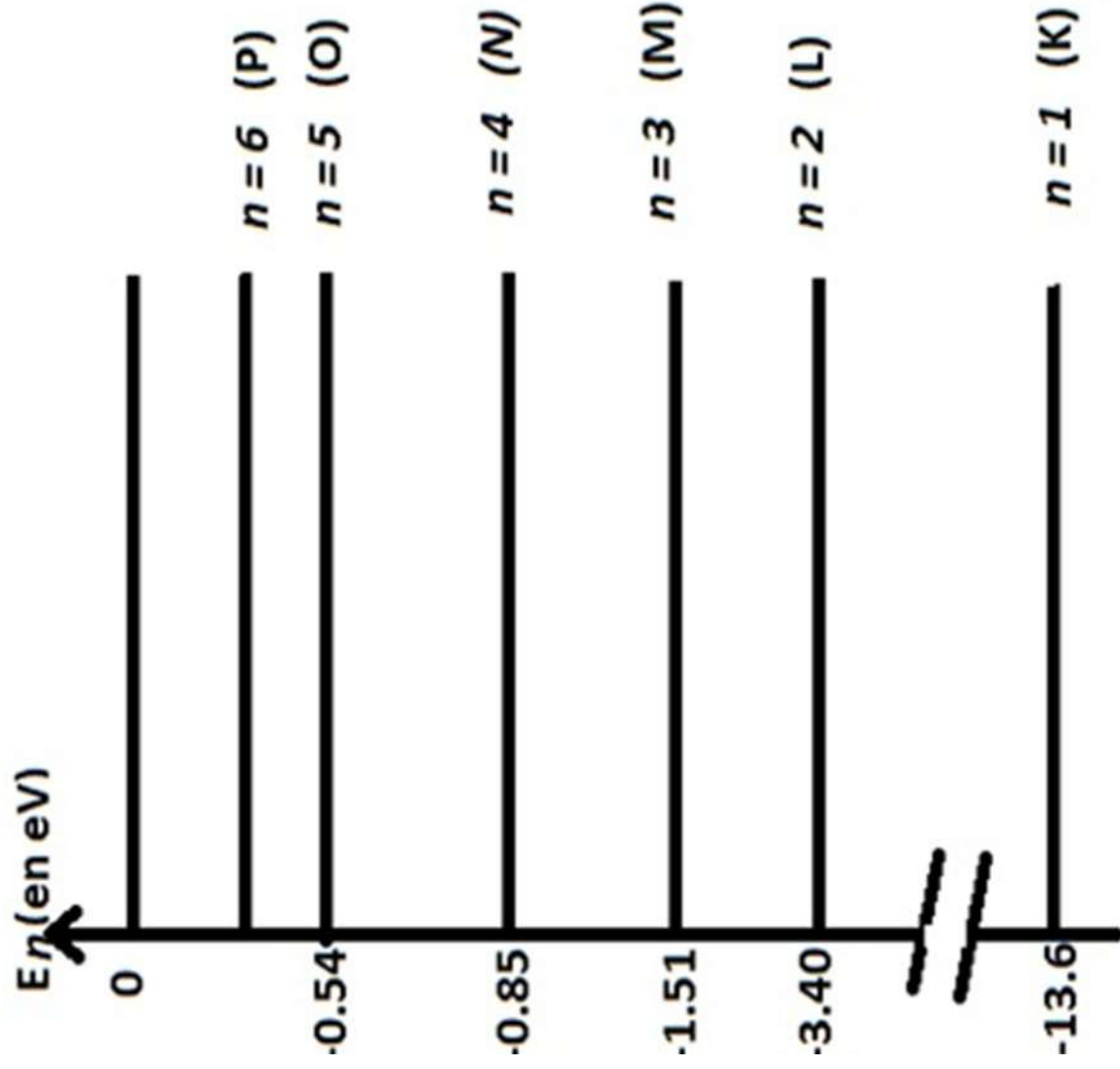
$$r_1 = \frac{h^2}{4\pi^2 K m e^2} = 0,529 \cdot 10^{-10} m \approx 0,529 \text{ \AA}$$

$$\begin{aligned} E_1 &= -\frac{2\pi^2 m_e K^2 e^4}{h^2} \frac{1}{1^2} \\ &= -21,18 \times 10^{-19} J \\ &= -13,6 \text{ eV} \end{aligned}$$

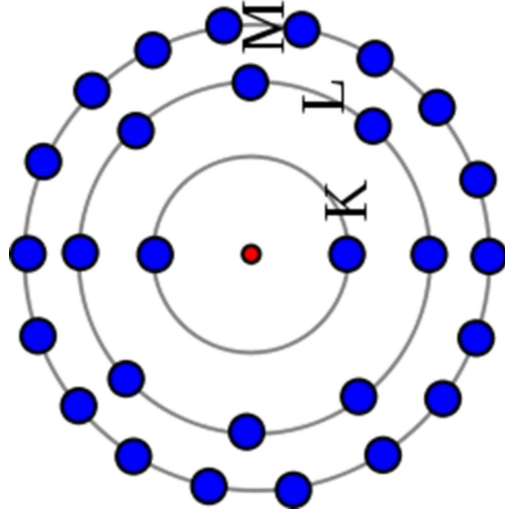
$$r_n = r_1 n^2 = 0.53 n^2 (\text{\AA})$$

$$E_n = \frac{E_1}{n^2} = \frac{-13.6}{n^2} \text{ (eV)}$$

Energy level diagram of the hydrogen atom



Bohr's atomic model is called the "s" because electrons are arranged in energy levels, or shells, around the nucleus.



$n=1$ Shell K.

$n=2$ Shell L.

$n=3$ Shell M.

II.4/ Extension of the Bohr model to hydrogen-like atoms

Hydrogen-like species are ions containing only one electron, similar to the hydrogen atom.
example: He^+ , Li^{2+} , Be^{3+} ...

In the case of hydrogen-like ions:

$$q(\text{nucleus}) = +Z \cdot e$$
$$q(\text{electron}) = -e$$

Accordingly, the extended formulas are:

$$r_n = r_1 \frac{n^2}{Z} = 0.53 \frac{n^2}{Z} (\text{\AA})$$

$$v_n = 2,19 \cdot 10^6 \frac{Z}{n} (m \cdot s^{-1})$$

$$E_n = \frac{E_1 Z^2}{n^2} = \frac{-13.6 Z^2}{n^2} (eV)$$

Z : The number of protons

n : The principal quantum number (or

II.5/ Definition of Ionization Energy

The ionization energy is the minimum energy required to remove an electron from an atom in its ground state ($n = 1$) to a point infinitely far from the nucleus ($n = \infty$, where the electron is no longer bound to the atom).

Mathematically, for a hydrogen-like atom:

$$E_{ion} = E_{\infty} - E_1 = \frac{E_1 Z^2}{\infty^2} - \frac{E_1 Z^2}{1^2} = 0 - \frac{-13.6 Z^2}{n^2} = \frac{13.6 Z^2}{n^2}$$

$$E_{ion} = \frac{13.6 Z^2}{n^2} (eV)$$

III/ Balmer formula

In the case of hydrogen-like atoms

$$\Delta E = |E_f - E_i| = h\nu = h \frac{c}{\lambda}$$

$$|E_f - E_i| = -\frac{2\pi^2 m e^2 K^2 e^4}{h^2 n_f^2} - \left(-\frac{2\pi^2 m e^2 K^2 e^4}{h^2 n_i^2} \right) = h \frac{c}{\lambda}$$

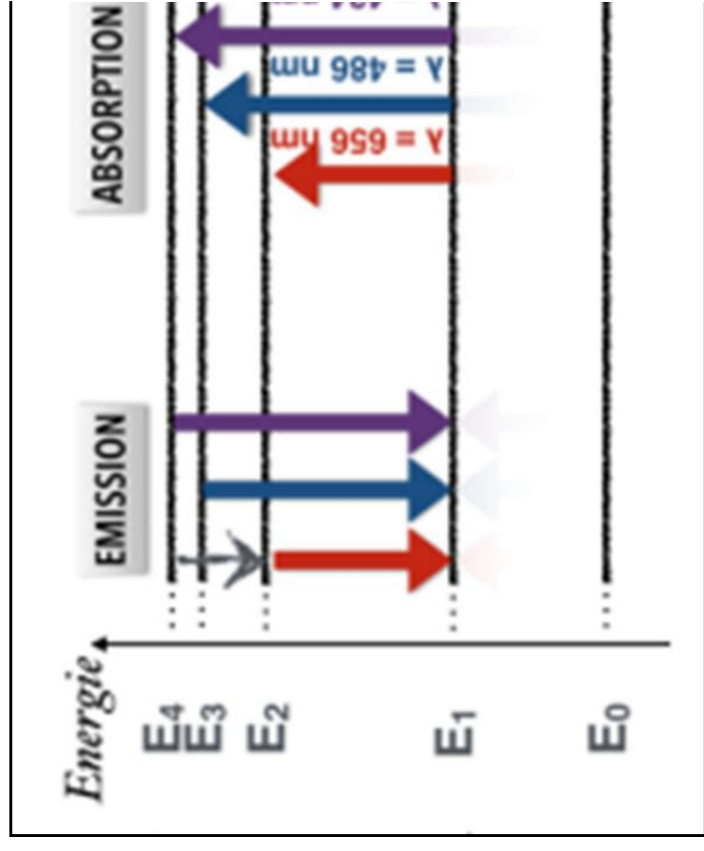
$$\frac{1}{\lambda} = \left| -\frac{2\pi^2 m e^2 K^2 e^4}{h^3 c} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right|$$

$$\frac{1}{\lambda} = \left| -R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right|$$

$$R_H = 1,096775 \cdot 10^7 \text{ m}^{-1}$$

$$\frac{1}{\lambda} = R_h Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\begin{array}{l} \text{Emission : } n_1 = n_f \quad n_2 \\ \text{Absorption : } n_1 = n_i \end{array}$$



IV/ The emission spectrum of the hydrogen atom

Each absorbed or emitted wave corresponds to a spectral line, therefore:

Spectral line \rightarrow wave \rightarrow electronic transition

First spectral line: $n_2 = n_1 + 1$

Limit line: $n_2 = \infty$

IV.1/ The Lyman

$$n_1 = 1 ; n_2 > 1$$

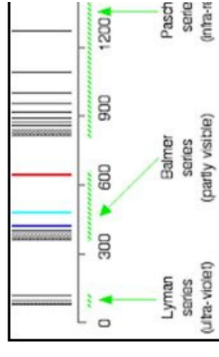
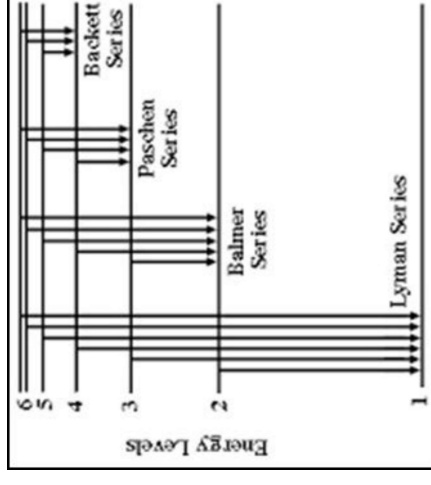
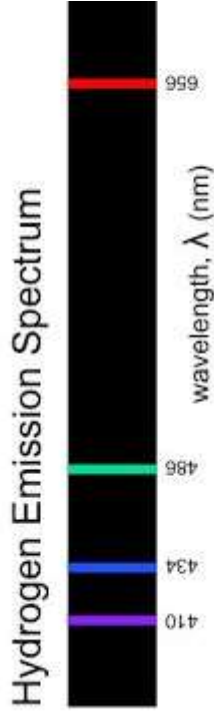
series

The first spectral line

$$\square \quad n_1 = 1 ; n_2 = 2 \quad \lambda_{1 \rightarrow 2} = 121.6 \text{ nm}$$

The limit line

$$\triangleright \quad n_1 = 1 ; n_2 = + \infty \quad \lambda_{1 \rightarrow \infty} = 91.2 \text{ nm}$$



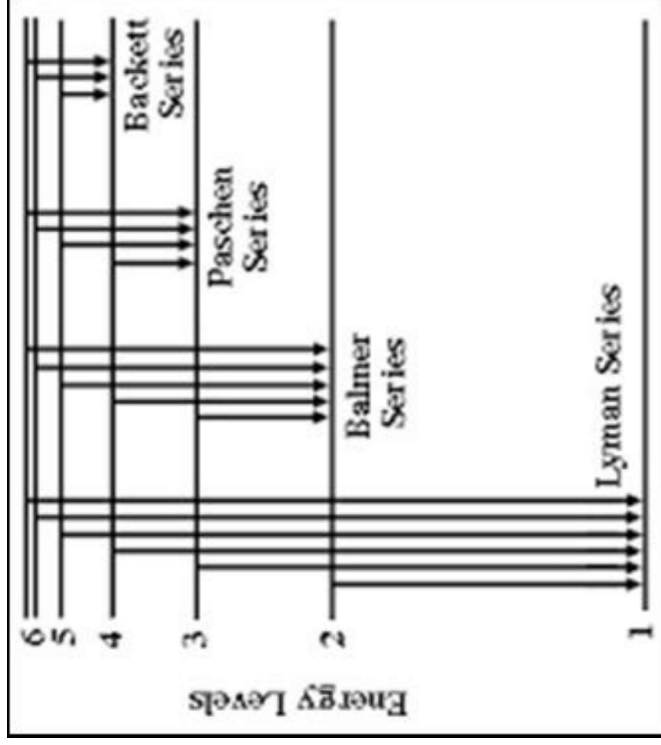
IV.2/ The Balmer series $n_1 = 2 ; n_2 > 2$

The first spectral line

$$\square \quad n_1 = 2 ; n_2 = 3 \quad \lambda_{2 \rightarrow 3} = 656.3 \text{ nm}$$

The limit line

$$\triangleright \quad n_1 = 2 ; n_2 = +\infty \quad \lambda_{2 \rightarrow \infty} = 364.7 \text{ nm}$$



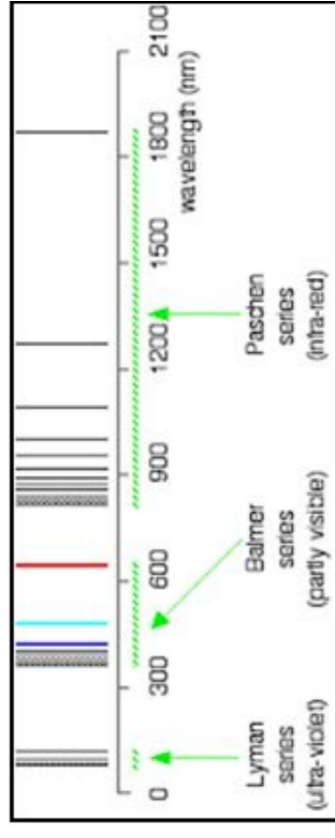
IV.3/ The Paschen series $n_1 = 3 ; n_2$

The first spectral line

$$\square \quad n_1 = 3 ; n_2 = 4 \quad \lambda_{3 \rightarrow 4} = 1876 \text{ nm}$$

The limit line

$$\triangleright \quad n_1 = 3 ; n_2 = +\infty \quad \lambda_{3 \rightarrow \infty} =$$



IV.4/ The Brackett series $n_1 = 4 ; n_2 > 4$

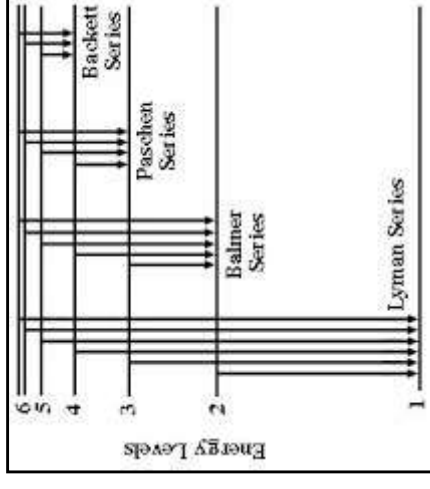
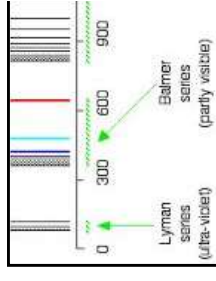
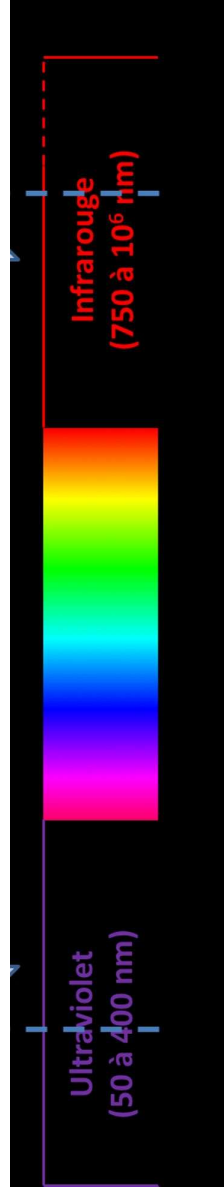
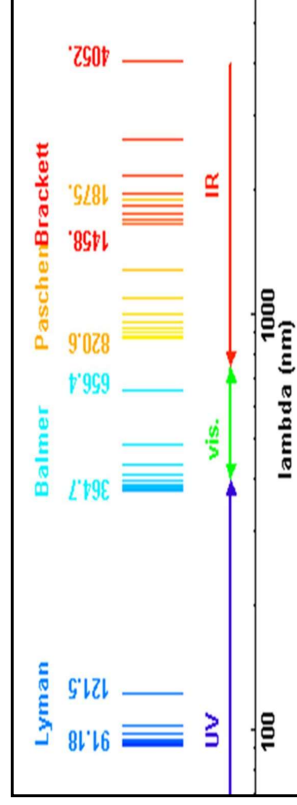
The first spectral line

$$\square \quad n_1 = 4 ; n_2 = 5 \quad \lambda_{4 \rightarrow 5} = 4052 \text{ nm.}$$

The limit line

$$\triangleright \quad n_1 = 4 ; n_2 = +\infty \quad \lambda_{4 \rightarrow \infty} = 1458 \text{ nm}$$

V/ The electromagnetic spectrum



V/ Limitations of the Bohr Model

The Bohr model correctly predicts the energy levels of the hydrogen atom and other single-electron systems.

However, the depiction of an electron moving in well-defined orbits, like in a "miniature solar system," is incompatible with the wave-like nature of the electron.

In fact, when an electron is confined within a space comparable in size to its wavelength, **wave character** becomes evident.

It is this **wave nature of matter** that leads to the concept of **atomic orbitals**, which explain the **geometric structure** of the atom.