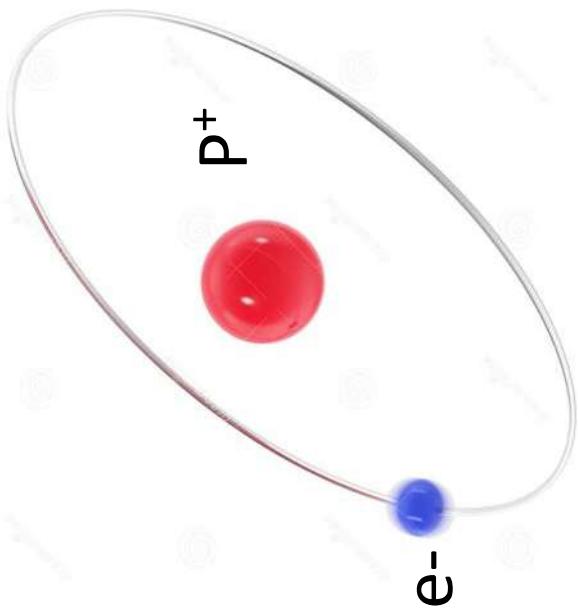


# **CHAPTER III – PART 2**

## **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 the electron's.



## 1.1/ Study of the orbits according to Rutherford's classical model

The electron is subjected to the Coulomb interaction force

$$F_{int} = K \frac{|q_e q_p|}{r^2}$$

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

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

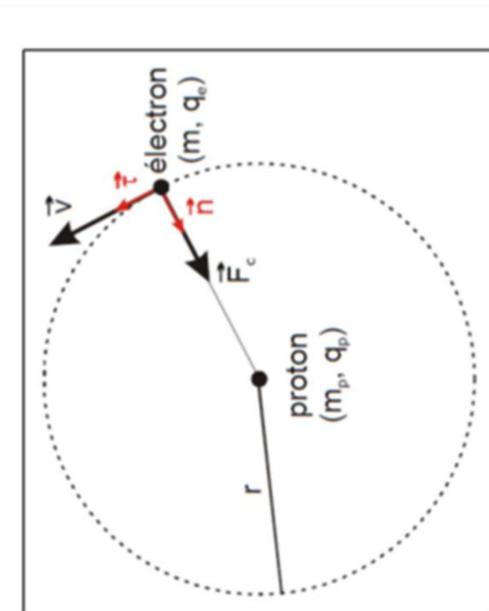
$r$  : Radius of the orbit.

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

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

The electron is subject to a centrifugal force

$m_e$  : Mass of the electron. ( $m_e = 9.1 \cdot 10^{-31}$  kg).  
 $a$  : Acceleration of the electron  
 $v_e$  : Electron velocity.  
 $r$  : Radius of the orbit.



According to Newton's second law

$$\overrightarrow{F}_{int} + \overrightarrow{F}_c = 0$$

$\Rightarrow \sum \vec{F} = 0$

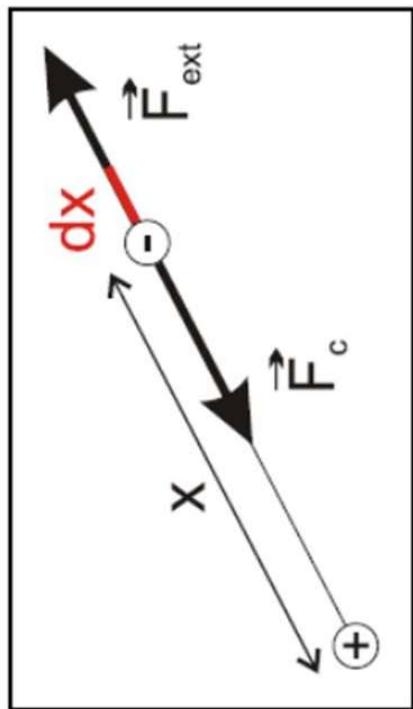
$$r = \frac{K e^2}{m_e v_e^2}$$

## 1.2/ 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.

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



### Total energy

$$E_T = E_K + E_p$$

### 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.

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

$$E_k = \frac{1}{2}$$

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

## III / Bohr's atomic model

### III.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

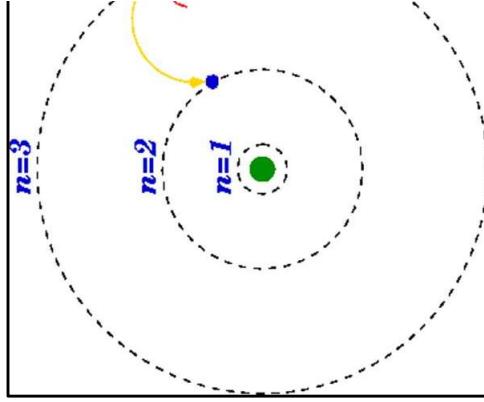
$v_n$ : linear (tangential) velocity of the electron on its  $n$ -th orbit

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

## 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 another, it makes a quantum jump and emits or absorbs a photon with energy:

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

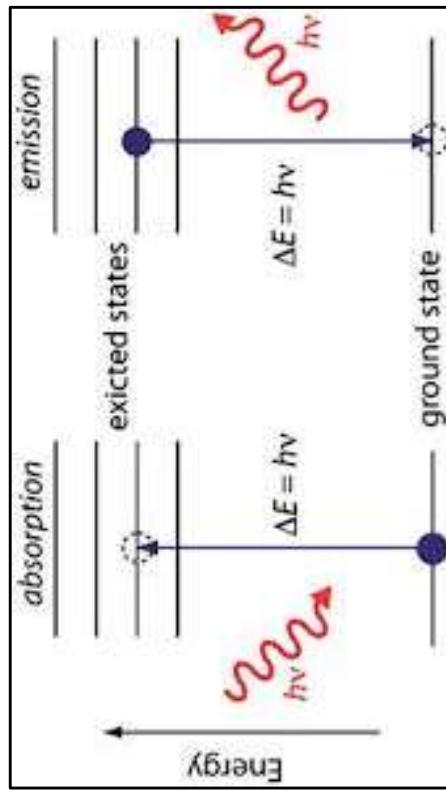


Where:

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

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

$\nu$ : frequency of the emitted or absorbed radiation



## II.3/ Results of Bohr's Theory

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

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

**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 ( $h=6.626\ 070\ 15 \times 10^{-34}\ \text{J.s}$ )  
 $K=10^{10}$ (SI)

For the hydrogen atom and the K shell

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

$$E_1 = -\frac{2\pi^2 m_e K^2 e^4}{h^2} \frac{1}{1^2}$$

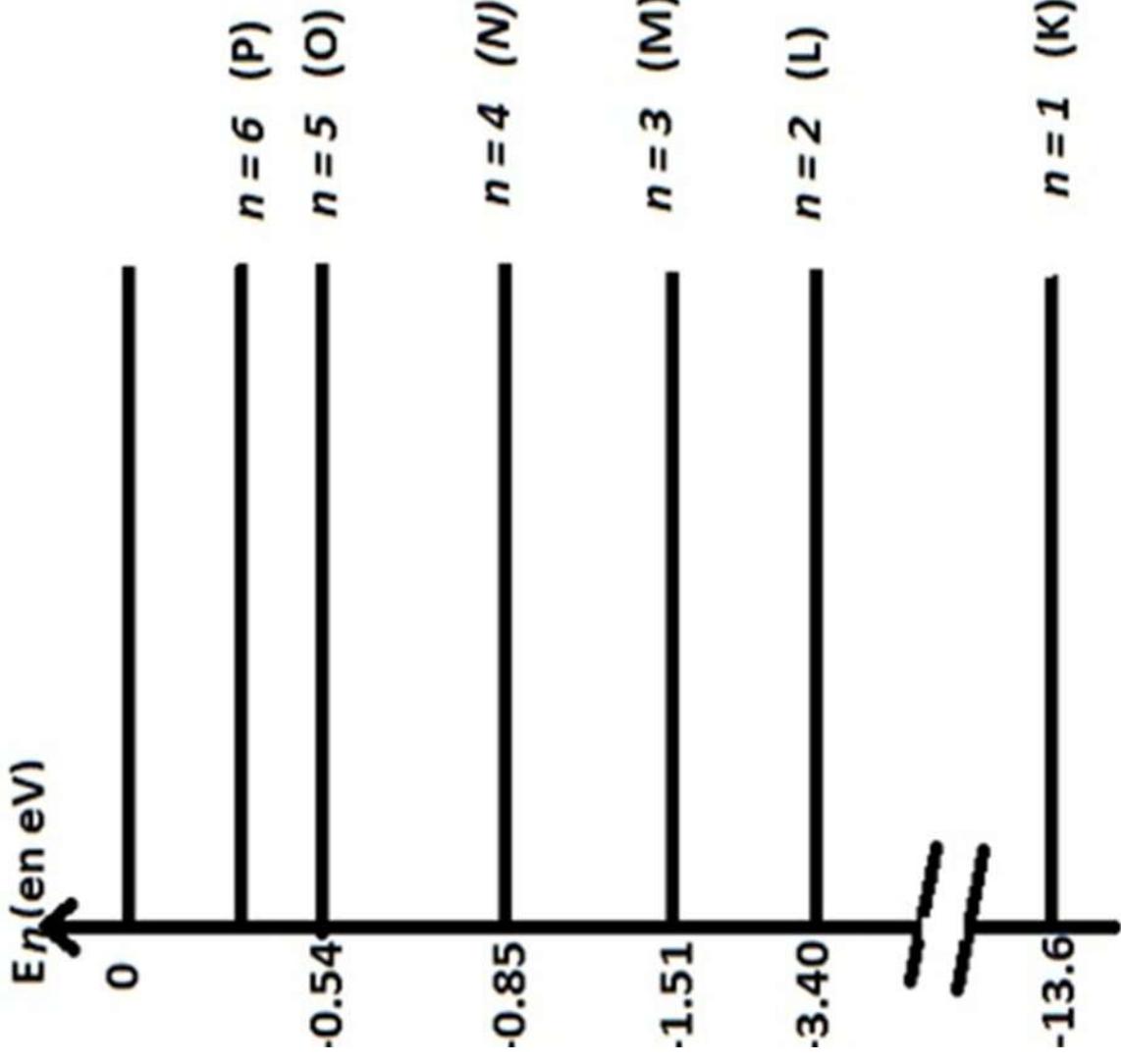
$$= -21,18 \times 10^{-19} J$$

$$= -13,6 \text{ eV}$$

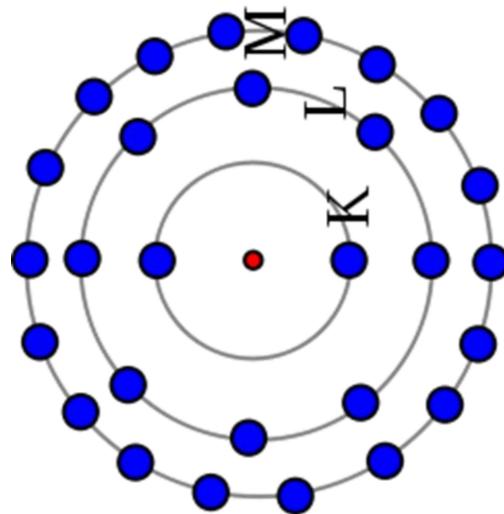
$$E_n = \frac{E_1}{n^2} = \frac{-13.6}{n^2} (\text{eV})$$

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

## 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 n



$n=1$  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

example:  $\text{He}^+$ ,  $\text{Li}^{2+}$ ,  $\text{Be}^{3+}$  ...

In the case of hydrogen-like ions:

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

Accordingly, the extended formulas are:

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

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

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

$Z$ : 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

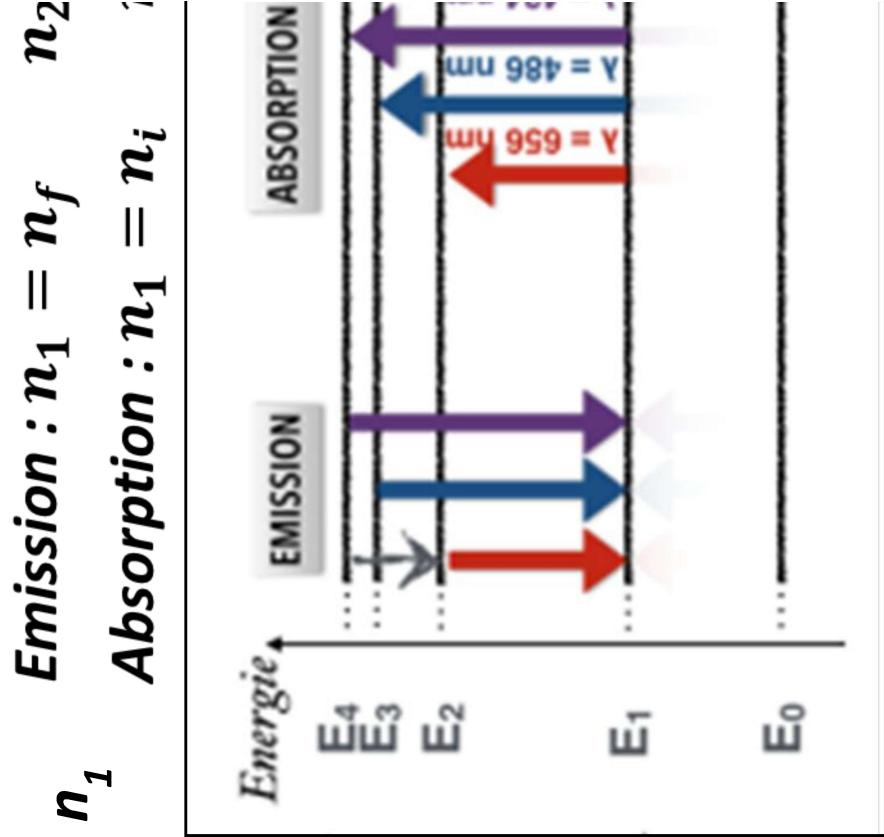
$$\Delta E = |E_f - E_i| = h\nu = h\frac{c}{\lambda}$$

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

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

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

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



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

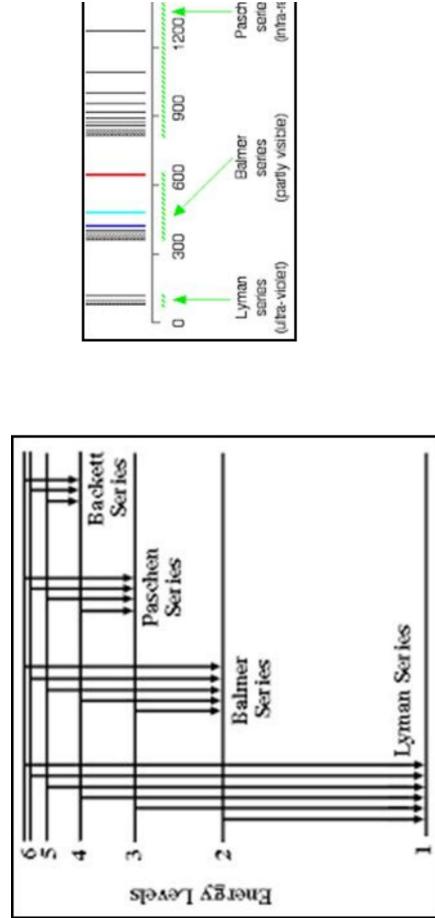
## IV/ The emission spectrum of the hydrogen atom

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

Spectral line → wave → electronic transition

**First spectral line:  $n_2 = n_1 + 1$**

**Limit line:  $n_2 = \infty$**



**IV.1/ The Lyman series**       $n_1 = 1 ; n_2 > 1$

The first spectral line

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

The limit line

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

## 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

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

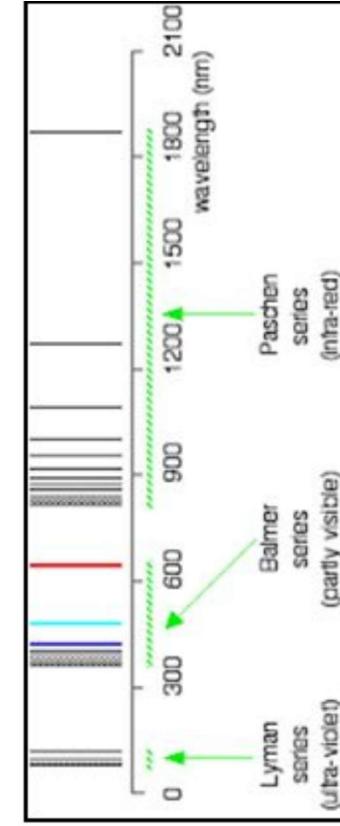
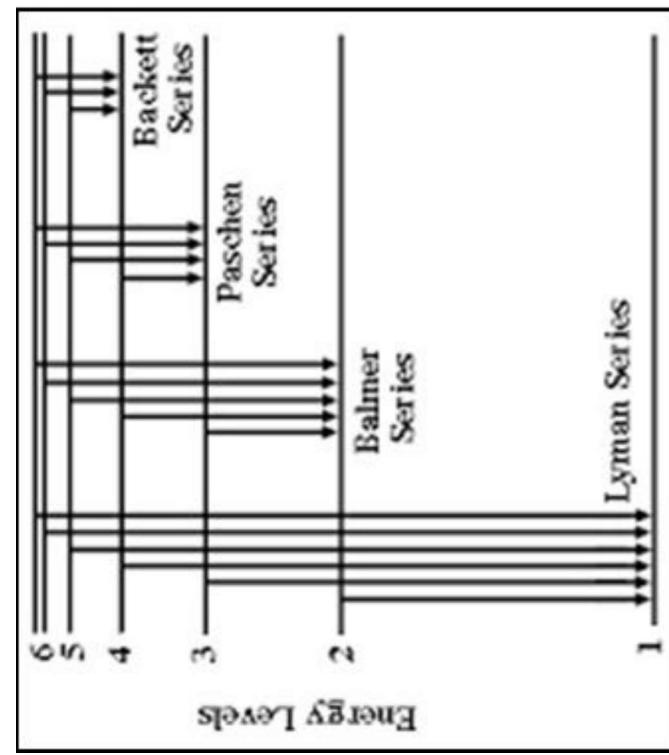
## IV.3/ The Paschen series $n_1 = 3 ; n_2$

The first spectral line

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

The limit line

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



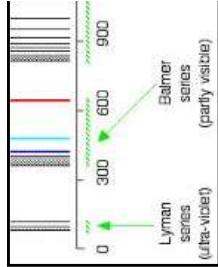
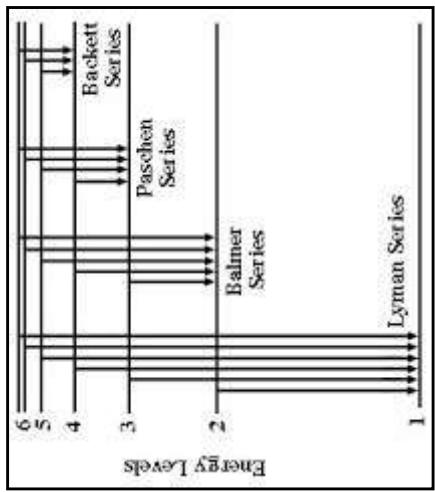
## IV.4/ The Brackett series $n_1 = 4$ ; $n_2 > 4$

The first spectral line

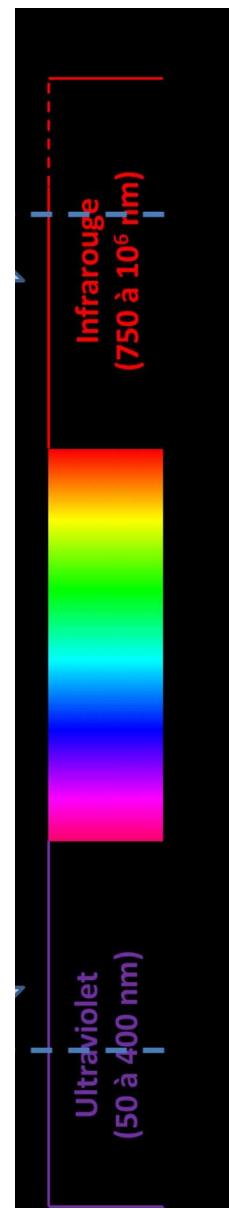
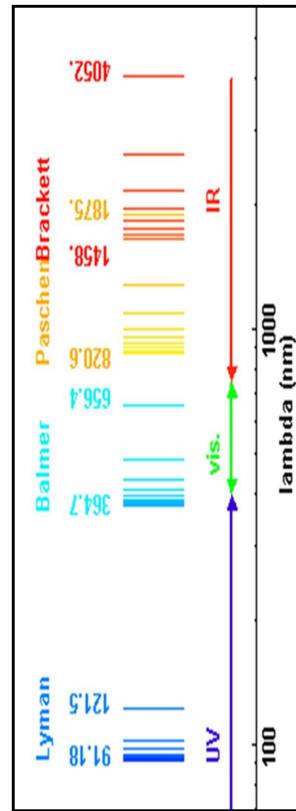
$$\square \quad n_1 = 4 ; n_2 = 5 \quad \lambda_{4 \rightarrow 5} = 4052 \text{ nm.}$$

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 wavelike character becomes evident.

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