## 3.1. Wave-Particle Duality of Light:

### a/ Wave nature of light

Light behaves as an electromagnetic wave that propagates through space at a constant speed of around $3.10^8$ m/s. This wave is characterized by :

***Wavelength (λ):** is the distance between two consecutive crests (or two troughs)

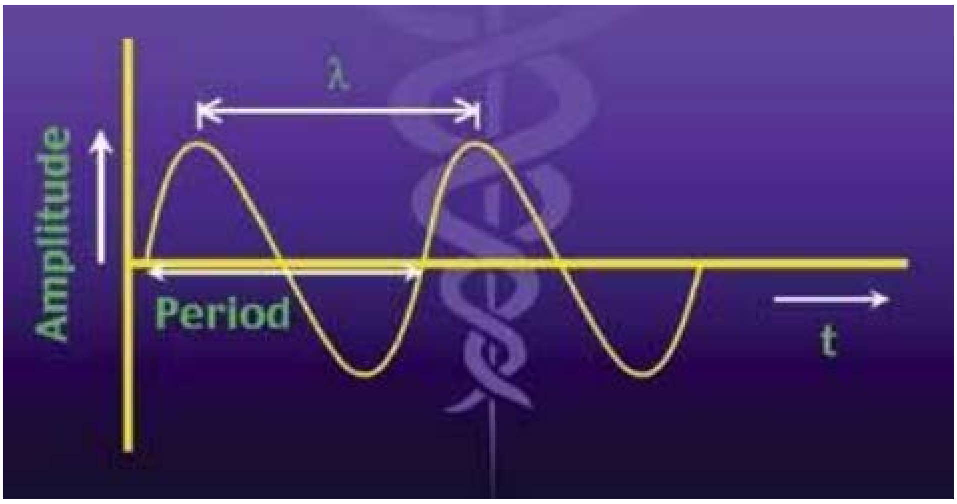
***Period (T):** is the time it takes for a wave to complete one wave cycle (wavelength).

***Frequency** ($\nu$) **:** is the number of waves that pass by each second, and is measured in Hertz (Hz). $\nu = \frac{C}{\lambda}$

***Amplitude (A):** is the distance from the center line (or the still position) to the top of a crest or to the bottom of a trough.

***Speed (C):** speed at which light waves propagate through the vacuum is defined as **$3.10^8$ m/s**.

***Wave number ($\bar{\upsilon}$) :** is the number of waves present per meter. $\bar{\upsilon} = \frac{1}{\lambda}$



### b/ particle nature of light

Light can be visualised as a stream of particles of electromagnetic energy. These 'particles' of light are called **photons**. The energy held by a photon is related to the frequency of the light via **Planck's equation**. $\mathbf{E = h\,\nu = \frac{h.C}{\lambda}}$ **(1)**

According to Einstein's mass-energy equivalence, energy can be expressed as: $\mathbf{E = m.C^2}$ **(2)**

Setting equation 2 equal to 1: $\mathbf{\frac{h.C}{\lambda} = m.C^2}$

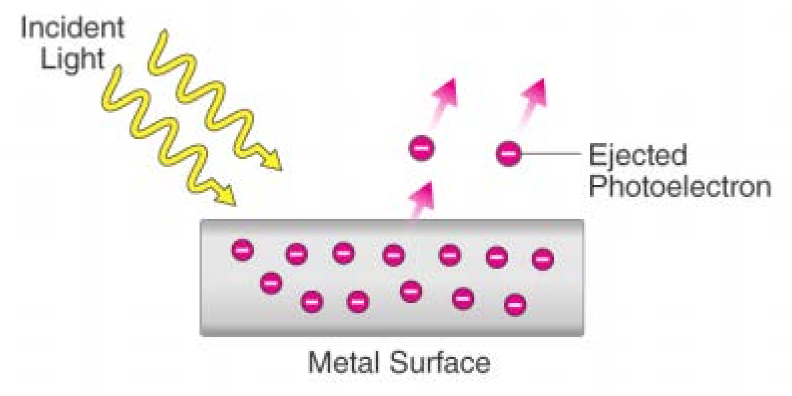
From this, the photon that propagates at the speed of light has a wavelength given by:

$$\lambda = \frac{h}{m.C}$$

Where :

- h : Planck's constant ($h = 6{,}62\ 10^{-34}$ J.s).
- $\nu$ : frequency of the light
- c : speed of light in the vacuum
- λ : wavelength of the light
- m : apparent mass of the photon

## 3.2. Photoelectric Effect:

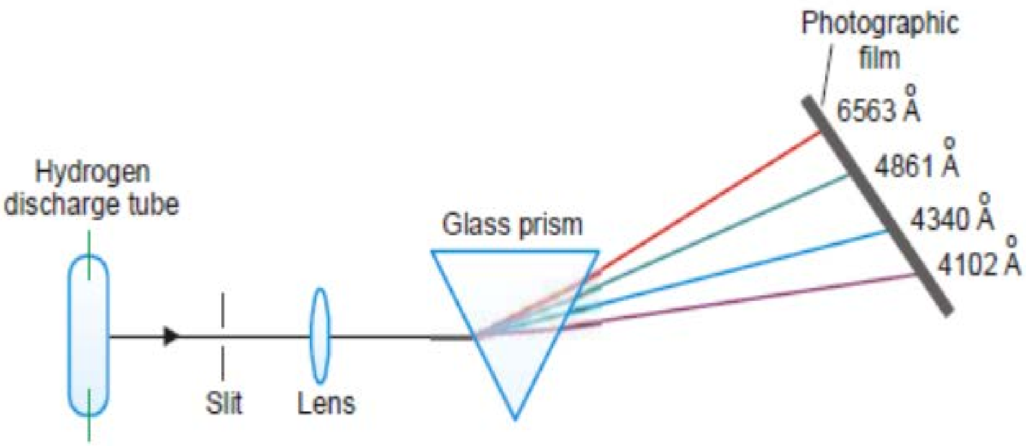


hν: irradiation energy or incident energy.
$h\nu_0$: electron extraction energy or photoelectric threshold energy.

The light energy sent (hν) is absorbed by the metal, which then releases electrons; this phenomenon is the **photoelectric effect**. Three cases can be observed depending on the irradiated metal, if :

- **$h\nu < h\nu_0$**: The radiation sent is insufficient to extract electrons from the metal.
- **$h\nu = h\nu_0$**: The radiation sent is just sufficient to extract electrons from the metal.
- **$h\nu > h\nu_0$**: The radiation sent extracts electrons from the metal, and the excess energy is used by the electrons as kinetic energy (**$E_c$**). In this case, there is a photoelectric effect, and we can write the relationship: **$h\nu = h\nu_0 + \frac{1}{2} mv^2$**

## 3.3. Emission spectrum of the hydrogen atom



When hydrogen contained in a cathode tube at low pressure is excited by high voltage, it emits electromagnetic radiation that can be analyzed using a prism. The spectrum observed on the photographic plate consists of very fine lines of various colors, separated by large dark spaces (discontinuous line spectrum). Each line corresponds to a well-defined wavelength λ (frequency ν).

**(1)** a red line with a wavelength λ = 6563 Å.
**(2)** a blue-green line with a wavelength λ = 4861 Å.

**(3)** a blue line with a wavelength $\lambda = 4340$ Å.
**(4)** a violet line with a wavelength $\lambda = 4102$ Å.

- **Balmer's formula**

The above series of four lines in the visible spectrum of hydrogen was named as the Balmer Series. By studying the wavelengths of the observed lines, **Balmer** was able to give the following empirical formula :

$$\bar{\nu} = \frac{\nu}{C} = \frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right)$$ With : $n > 2$

Where:
$\bar{\nu}$ : wavenumber.
$\lambda$ : wavelength of the emitted light.
$R_H$ :Rydberg constant for hydrogen ($R_H \approx 1.096777 \times 10^7$ m$^{-1}$).
n : is an integer (principal quantum number).
$\nu$ : frequency of light.
C : speed of light.

In addition to Balmer Series, four other spectral series were discovered in the infrared (IR) and ultraviolet (UV) regions of the hydrogen spectrum.

- **Rydberg's formula**

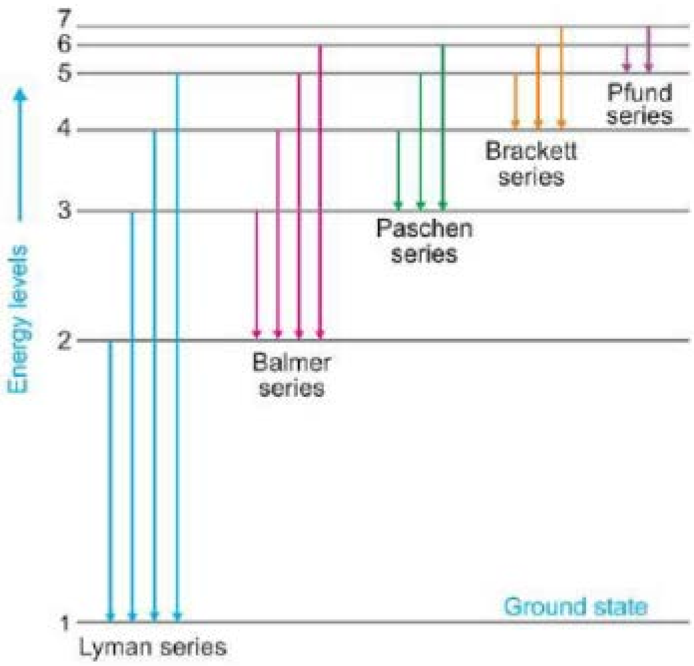
This equation is a generalisation of the Balmer's formula for all hydrogen transitions.

$$\bar{\nu} = \frac{\nu}{C} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$ With : $n_2 > n_1$

***Notion of a series of spectral lines**

A series of spectral lines corresponds to the set of all lines that result from an electron returning to a given, fixed level "$n_1$". These series bear the names of the discoverers.

| Series name | $n_1$ | $n_2$ | Spectral range (region) | Wavelength ($\lambda$) |
|---|---|---|---|---|
| **Lyman** | 1 | $\geq 2$ | Ultraviolet | < 400 nm |
| **Balmer** | 2 | $\geq 3$ | Visible | $400\text{nm} \leq \lambda \leq 800\text{nm}$ |
| **Paschen** | 3 | $\geq 4$ | Infrared | > 800 nm |
| **Brackett** | 4 | $\geq 5$ | | |
| **Pfund** | 5 | $\geq 6$ | | |



**Note**

Each series is bounded by two lines:

- **The first line** corresponds to the **transition $n_2 \rightarrow n_1$** with **$n_2 = n_1+1$**. It is characterized by a **smaller energy difference** and **greater wavelength** ($\lambda_{max}$).

$$\frac{1}{\lambda_{max}} = Z^2 R_H \left(\frac{1}{{n_1}^2} - \frac{1}{(n_1+1)^2}\right)$$

$$\frac{1}{\lambda_{max}} = Z^2 R_H \left(\frac{(n_1+1)^2 - {n_1}^2}{{n_1}^2 (n_1+1)^2}\right)$$

$$\frac{1}{\lambda_{max}} = Z^2 R_H \left(\frac{2n_1+1}{{n_1}^2 (n_1+1)^2}\right) \Rightarrow \boxed{\lambda_{max} = \frac{{n_1}^2 (n_1+1)^2}{Z^2 R_H (2n_1+1)}}$$

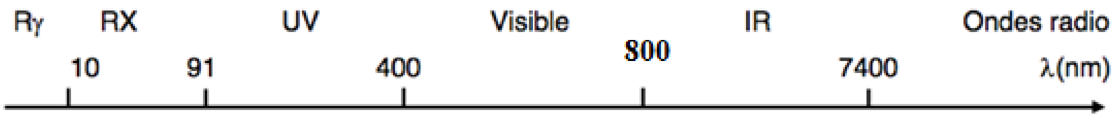
- **The final line** corresponds to the **transition $n_2 = \infty \rightarrow n_1$**. It is characterized by **greater energy difference** and **smaller wavelength** ($\lambda_{min}$)

$$\frac{1}{\lambda_{\min}} = Z^2 R_H\left(\frac{1}{{n_1}^2} - \frac{1}{\infty^2}\right)$$

$$\frac{1}{\lambda_{\min}} = Z^2 R_H\left(\frac{1}{{n_1}^2}\right) \Rightarrow \boxed{\lambda_{\min} = \frac{{n_1}^2}{Z^2 R_H}}$$

## Electromagnetic ray spectrum:

The entire electromagnetic spectrum, from the lowest to the highest frequency (longest to shortest wavelength), includes all radio waves (e.g., commercial radio and television, microwaves, radar), infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays.



## 4.3. Atomic Model of Bohr : Hydrogen atom

This model is limited to the study of systems with a single electron, including hydrogen and hydrogenoids.

### 4.3.1. Bohr model postulates

### a/ Postulate I

***"The electron in the atom moves along a stationary circular orbit (of constant energy) around the nucleus"***

### b/ Postulate II

***"The angular momentum of the electron is calculated by the following relationship :*** $m.v.r = \frac{n.h}{2\pi}$ ***"***

### c/ Postulate III

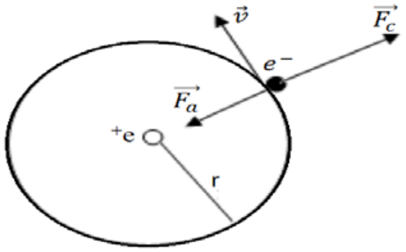
***" The atom emits or absorbs energy only when the electron moves from one stationary orbit to another"***

- **Determination of the orbits radius**

An electron with **m** mass moves at $\mathbf{v_n}$ speed and draws a stable orbit with a radius of $\mathbf{r_n}$, this electron is subject to two forces equal in intensity and opposite in direction: the ***attraction force*** $\vec{F_a}$ and the ***centrifugal force*** $\vec{F_c}$ .

$$F_a = -\frac{K.e^2}{r^2}$$

$$F_c = \frac{m.v^2}{r}$$



According to postulate I of Bohr, the system is in eqilibrium :

$\overrightarrow{F_a} + \overrightarrow{F_c} = 0 \leftrightarrow \|\overrightarrow{F_a}\| = \|\overrightarrow{F_c}\|$

$\frac{\mathbf{m.v^2}}{\mathbf{r}} = \frac{\mathbf{K\,e^2}}{\mathbf{r^2}} \leftrightarrow \mathbf{m\,v^2} = \frac{\mathbf{K\,e^2}}{\mathbf{r}}$ **(1)**

with :

m : masse of the electron

e : charge of the electron

v : speed of the electron

r : orbit radius

$K = \frac{1}{4\pi\,\varepsilon_0} = 9.10^9$ MKSA

$\varepsilon_0$ : Permittivity of a vaccum ($\varepsilon_0 = 8{,}85.10^{-12}$)

By postulate II of Bohr :

$m.v.r = \frac{n.h}{2\pi} \leftrightarrow v = \frac{n.h}{2\pi.m.r} \leftrightarrow \mathbf{v^2} = \frac{\mathbf{n^2h^2}}{\mathbf{4\pi^2r^2m^2}}$ **(2)**

We compensate (2) in (1) we find:

$\boldsymbol{r_n = \left(\frac{h^2}{4\,\pi^2 m\,k\,e^2}\right)n^2}$ **(3)**

($r_1$) is the hydrogen atom radius in its basic state:

$\boldsymbol{r_1 = a_0 = \frac{h^2}{4\,\pi^2 m\,k\,e^2} = 0{,}53.10^{-10}\ \mathrm{m} = 0{,}53\ \mathrm{A°}}$

We deduce that : $\boldsymbol{r_n = r_1.n^2 = a_0.n^2}$ **(4)**

- **Determination of the electron speed on a stationary orbit**

By postulate II of Bohr :

$m.v.r = \frac{n.h}{2\pi} \leftrightarrow v_n = \frac{n.h}{2\pi.m.\boldsymbol{r_n}}$

And we have : $\boldsymbol{r_n} = \left(\frac{\boldsymbol{h^2}}{\boldsymbol{4\,\pi^2 m\,k\,e^2}}\right)\boldsymbol{n^2}$

We compensate $\boldsymbol{r_n}$ in $\mathbf{v_n}$ we find:

$v_n = \frac{n.h}{2\pi.m}\left(\frac{\boldsymbol{4\,\pi^2 m\,k\,e^2}}{h^2n^2}\right) \leftrightarrow v_n = \left(\frac{\mathbf{2\pi}.k.e^2}{\mathbf{h}}\right).\frac{\mathbf{1}}{\mathbf{n}}$

($v_1$) is the speed of hydrogen atom electron in its basic state:

$\mathbf{v_1} = \frac{\mathbf{2\pi.k.e^2}}{\mathbf{h}} = \mathbf{2{,}18.10^6\ m/s}$

We deduce that : $v_n = \frac{\mathbf{v_1}}{\mathbf{n}}$ **(5)**

- **Determination of the electron energy on a stationary orbit**

The total energy of the electron consisting of kinetic energy $\boldsymbol{E_c}$ and latent energy $\boldsymbol{E_P}$ where :

$E_T = E_C + E_P$ **(6)**

$E_C = \frac{1}{2}mv^2$

According to equation (1): $m\,v^2 = \frac{K\,e^2}{r}$; so : $\mathbf{E_C} = \frac{\mathbf{K\,e^2}}{\mathbf{2\,r}}$ **(7)**

$E_P = -\int_\infty^r F_a\,dr = \int_\infty^r \frac{K\,e^2}{r^2}dr = -\frac{K\,e^2}{r}$; $\mathbf{E_P} = -\frac{\mathbf{K\,e^2}}{\mathbf{r}}$ **(8)**

By substituting equations (7) and (8) into (6), we obtain the expression for the total energy of the electron in a stationary orbit:

$$E_T = \frac{K\,e^2}{2\,r} - \frac{K\,e^2}{r} \quad \leftrightarrow \quad \mathbf{E_T = -\frac{K\,e^2}{2\,r}} \qquad \textbf{(9)}$$

The substitution of equation (3) into (9) gives:

$$E_T = E_n = -\frac{K\,e^2}{2\,r} = -\frac{K\,e^2}{2}\left(\frac{4\,k\,\pi^2 e^2 m}{n^2 h^2}\right)$$

$$\mathbf{E_n} = \left(-\frac{2\,\pi^2 K^2 e^4 m}{h^2}\right)\frac{1}{n^2} \qquad \textbf{(10)}$$

($E_1$) is the energy of hydrogen atom electron in its basic state:

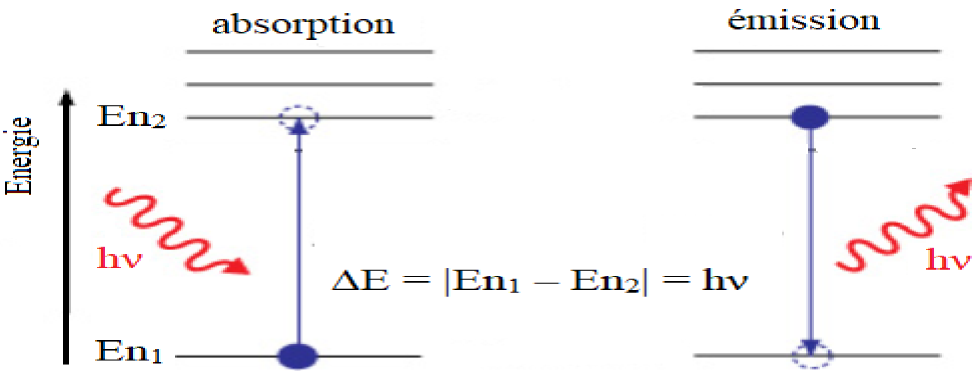
$$E_1 = \frac{-2\,\pi^2 K^2 e^4 m}{h^2} = -21{,}76\,.10^{-19} J = -13{,}6\ eV$$

$$\mathbf{E_n = \frac{E_1}{n^2} = \frac{-13{,}6}{n^2}\ (eV)} \qquad \textbf{(11)}$$

**Note:**

**n = 1**: the atom is in the **ground state**.
**n > 1**: the electron of the atom is in an **excited state**.
**n = ∞**: the atom is **ionized** (the electron has left the atom).

- **Determination of the wavenumber**



According to postulate III of Bohr, when the electron of an atom moves from an energy level $E_{n1}$ to an energy level $E_{n2}$, the energy involved is given by the expression:

$$\Delta E = E_{n2} - E_{n1} = \frac{2\,\pi^2 K^2 e^4 m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\Delta E = h\nu = \frac{h\,c}{\lambda}$$

So :

$$\frac{h\,c}{\lambda} = \frac{2\,\pi^2 K^2 e^4 m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The wavenumber ($\bar{\nu}$) corresponding to this radiation is given by:

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{hc}.\frac{2\,\pi^2 K^2 e^4 m}{h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\boldsymbol{\bar{\nu} = \frac{1}{\lambda} = \frac{2\,\pi^2 K^2 e^4 m}{h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$$

$$\boldsymbol{\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)} \qquad \textbf{(12)}$$

$$R_H = \frac{2\,\pi^2 K^2 e^4 m}{h^3 c} = 1{,}097.10^7\ m^{-1}$$

**Note :**

• An absorption of radiation occurs when an electron transitions from level $n_1$ to level $n_2$ with $n_1 < n_2$ and $\Delta E = +h\nu = E_{n2} - E_{n1} > 0$.

• An emission of radiation occurs when an electron transitions from level $n_2$ to level $n_1$ with $n_1 > n_2$ and $\Delta E = -h\nu = E_{n1} - E_{n2} < 0$.

### 4.3.2. Application of the Bohr model to hydrogenoids

Hydrogenoids are cations that have only one electron and Z protons.

Examples : ${}^4_2He^+$; ${}^6_3Li^{2+}$; ${}^9_4Be^{3+}$…

The general formula of the hydrogenoid is: $\mathbf{{}^A_ZX^{(Z-1)+}}$

The application of Bohr's theory to hydrogenoid ions leads to:

***Attraction force :*** $\mathbf{F_a = -\frac{Z.K.e^2}{r^2}}$

***Latent energy :*** $\mathbf{E_P = -\frac{Z.K.e^2}{r}}$

The radius of the orbit, the total energy, the speed, and the wave number will then be:

- $r_n(\text{hydrognoid}) = \frac{r_n(\text{hydrogen})}{Z} = r_1.\frac{n^2}{Z} = \mathbf{a_0}.\frac{n^2}{Z}$ $\mathbf{r_n = r_1\frac{n^2}{Z} = a_0\frac{n^2}{Z}}$
- $V_n(\text{hydrognoid}) = Z.V_n(\text{hydrogen}) = \mathbf{V_1\frac{Z}{n}}$ $\mathbf{V_n = V_1\frac{Z}{n}}$
- $E_n(\text{hydrognoid}) = Z^2.E_n(\text{hydrogen}) = E_1\frac{Z^2}{n^2} = -13{,}6\,\frac{Z^2}{n^2}$ $\mathbf{E_n = -13{,}6\,\frac{Z^2}{n^2}\ (eV)}$
- $\bar{\nu}(\text{hydrognoid}) = Z^2.\bar{\nu}(\text{hydrogen}) = R_H Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ $\mathbf{\bar{\nu} = R_H Z^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)}$

### 4.3.3. Ionization energy of hydrogen atom and hydrogenoids

The energy that is needed to remove the electron from the atom is called the ionization energy.

$E_i = \Delta E_{n\to\infty} = E_\infty - E_n$ Where : $1 \le n < \infty$

For hydrogen atom in its basic state :

$E_i = \Delta E_{1\to\infty} = E_\infty - E_1$

$E_\infty = 0$

$E_i = -E_1 = -\frac{(-13{,}6)}{n^2} = -\frac{(-13{,}6)}{1^2} = 13.6\ eV$

Ionization energy is always positive.

### 4.3.4. Shortcomings of the Bohr model

**(1)** It was unsuccessful for every atom containing more than one electron (${}_2He$, ${}_3Li$, ${}_4Be$...).

**(2)** It could not explain the effect of magnetic and electric fields on the spectra of atoms (splitting of spectral lines).

**(3)** It could not account for the ability of atoms to form molecules through chemical bonds.

### 4.4. Electronic structure of hydrogen tom by wave mechanics

### a/ Wave-particle duality of matter and De Broglie relation

In 1924, De Broglie proposed the hypothesis that wave-particle duality is a general property of physics. He stated that:

**« To any particle of mass « m » moving at a speed « v », we can associate a wave with a wavelength « λ », such that: $\lambda = \frac{h}{m.v}$ »**

**Note:**

* The particle can be microscopic (exp: electron, proton, atom...) or macroscopic (exp: car, projectile).

*The wave (λ) has no physical meaning unless applied at the microscopic scale.

**Example:** calculation of the wavelengths λ associated with the following particles:

**Macroscopic particle:** A tennis ball with mass 0.05 kg and speed 40 m/s.

$\lambda = \frac{h}{m.v} = \frac{6{,}62.10^{-34}}{0{,}05*40} = 3{,}31.10^{-34}$ m (Insignificant value)

This wavelength is entirely negligible and has no meaning.

**Microscopic particle:** An electron with mass m=9,1. $10^{-31}$kg and speed v=$10^{7}$m/s.

$\lambda = \frac{h}{m.v} = \frac{6{,}62.10^{-34}}{9{,}1.\ 10^{-31}*10^{7}} = 0{,}727.10^{-10}$ m (Significant value)

This value is measurable and corresponds to the wavelength λ of X-rays.

### b/ Heisenberg's uncertainty principle

The principle stated by Werner Heisenberg in 1927 stipulates that:

« **It is impossible to simultaneously know, with precision, the position (x) and the momentum (p = m.v) of a moving particle**". This is expressed by the following inequality:

$\Delta x.\Delta p \geq \frac{h}{2\pi}$ ; Where ; $\Delta p = \Delta(m.v) = m.\Delta v$

Thus, we have: $\Delta x.\Delta v \geq \frac{h}{2\pi.m}$

Δx : Uncertainty in position.

Δv : Uncertainty in speed.

**Note:**

Heisenberg's uncertainty principle has significance only at the microscopic scale.

**Example:** Applying Heisenberg's uncertainty principle to calculate Δv for the following two systems:

- An electron moving in a straight line with Δx=1 A°
- A small ball of mass 10 g (0.01 kg) moving in a straight line with Δx=1 µm

**Macroscopic scale: A small ball**

m = 0,01 Kg ; Δx = 1µm = $10^{-6}$ m

$\Delta v \geq \frac{6{,}62.10^{-34}}{2.(3{,}14).(10^{-2}).(10^{-6})} = 1{,}05.10^{-26}\text{m/s}$

**Microscopic scale: an electron**

m = 9,1. $10^{-31}$ Kg Δx = 1Å = $10^{-10}$ m

$\Delta v \geq \frac{6{,}62.10^{-34}}{2.(3{,}14).(9{,}1\ .10^{-31}).(10^{-10})} = 1{,}16.10^{6}\text{m/s}$

**Summary of Results**

For the electron: $\Delta v \geq 1{,}16.10^{6}\text{m/s}$

For the ball: $\Delta v \geq 1{,}05.10^{-26} m/s$
This shows that the uncertainty in velocity (speed) for the electron is significantly greater than that for the larger mass (the ball), which is consistent with the Heisenberg uncertainty principle.

## c/ Wave function and Schrödinger equation

In wave mechanics, an electron located at a point with coordinates (x, y, z) at time "t" is described by a function **Ψ(x, y, z)** called the **"wave function"**

To study the movement of the electron in the atom, Schrödinger provided the following equation:

$$\frac{\partial^2\Psi(x,y,z)}{\partial x^2}+\frac{\partial^2\Psi(x,y,z)}{\partial y^2}+\frac{\partial^2\Psi(x,y,z)}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-E_P)\Psi(x,y,z)=0$$

$$\Delta\Psi+\frac{8\pi^2 m}{h^2}(E-E_P)\Psi=0 \qquad / \Delta=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$$

Δ: Laplace operator

With:
E: total energy of the electron
$E_p$: potential energy (latent energy) of the electron
m: mass of the electron
h: Planck's constant

## d/ Solution of the Schrödinger equation

The solution of the Schrödinger equation will allow us to know the wave function Ψ(x,y,z), which is a function of three quantum numbers Ψ(n,l,m) to which an energy value will be assigned (E).

## e/ Quantum numbers

- **Principal quantum number « n »**

It defines the electronic shell. It is a positive integer (n ϵ N*). The shells are designated by symbols as represented in the table below:

| Values of « n » | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| shell or orbit | K | L | M | N | O | P | Q |

The maximum number of electrons that a shell can contain is : $2n^2$.

- **Azimuthal quantum number « l » (Orbital Angular Momentum Quantum Number)**

It defines the sub-shell occupied by the electron and characterize the geometry of the atomic orbital. **$0 \leq l \leq n-l$**. “l” is an integer as shown in the following table:

| Values of « l » | 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| sub-shell | s | p | d | f |

The maximum number of electrons that a sub-shell can contain is: 2(2l + 1).

- **Magnetic quantum number « m »**

It determines the number of atomic orbitals (quantum boxes) of each sub-shell. We symbolize the quantum box by a rectangle. There are as many rectangles as there are possible values of "m".

**$-l \leq m \leq +l$** ; i.e. $2l+1$: different values of « m » (quantum boxes).

| Sub-shell | s | p | d | f |
|---|---|---|---|---|
| Values of « m » | 0 | -1, 0, +1 | -2, -1, 0, +1, +2 | -3, -2, -1, 0, +1, +2, +3 |
| Number of quantum boxes | 1 | 3 | 5 | 7 |
| Representation of quantum boxes | ☐ | ☐☐☐ | ☐☐☐☐☐ | ☐☐☐☐☐☐☐ |

**Note:** The quantum box contains a maximum of two electrons.

- **Electron spin quantum number "s" :**

Electron spin can be seen as a rotation of the electron around its axis in two opposite directions. We represent this spin number symbolically by:

An upward arrow (↑): electron in the spin state: $s = +1/2$.

A downward arrow (↓): electron in the spin state: $s = -1/2$.

By convention, the electron with spin + ½ (↑) is placed on the left and the electron with spin - ½ (↓) is placed on the right in the quantum box.

Examples :

| **n** | **l** | **m** | **$\Psi_{nlm}$** | **$E_{nlm}$** |
|---|---|---|---|---|
| 1 | 0 | 0 | $\Psi_{100}$ | $E_1 = -13,6$ eV |
| 2 | 0 | 0 | $\Psi_{200}$ | $E_2 = -3,4$ eV |
| 2 | 1 | -1 | $\Psi_{21-1}$ | $E_2 = -3,4$ eV |
| 2 | 1 | 0 | $\Psi_{210}$ | $E_2 = -3,4$ eV |
| 2 | 1 | +1 | $\Psi_{21+1}$ | $E_2 = -3,4$ eV |

- **Notion of atomic orbital**

An atomic orbital is the region of space where the probability of finding the electron is very high (> 90%).

## 4.6. Polyelectronic atoms in wave mechanics

### a/ Electronic configuration of the elements

The electronic configuration of an atom or an ion is the distribution of Z electrons in the different atomic orbitals (1s 2s 2p, etc.) by writing the number of electrons as an exponent.

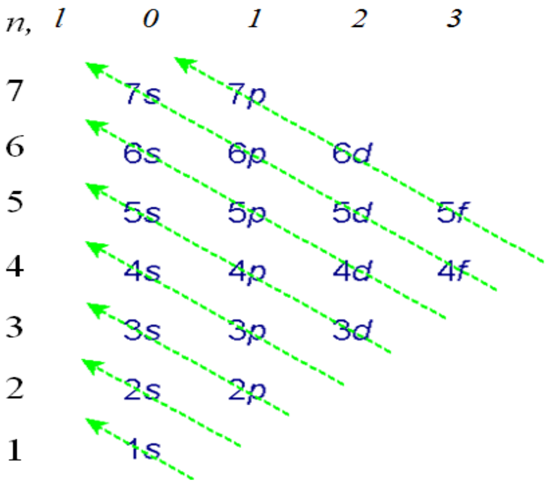
**Example:** $1s^2$ means that two electrons are described by the 1s orbital.

***Principle of stability:** Filling must be done according to the increasing order of the energy of the atomic orbitals (A.O).

***Klechkowsky's rule:**

It translates the order of filling of the shells and sub-shells by the electrons which is carried out by increasing values of the couple (n+l). If two or more pairs (n+l) lead to the same value, they will be classified in order of increasing (n).

**Example:** *n + l for 4s : 4 + 0 = 4 and for 3d : 3 + 2 = 5*



The order of filling the sub-shells is then:

**1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p**

**Examples :**

Li (Z=3) : $1s^2 2s^1$

Br (Z=35) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

$Br^-$ (Z=35) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$

## b/ Exceptions to Klechkowsky's rule

Exceptions to Klechkowsky's rule particularly apply to configurations like:

**$ns^2$ $(n-1)d^9$** which transform into: **$ns^1$ $(n-1)d^{10}$**

**$ns^2$ $(n-1)d^4$** which transform into: **$ns^1$ $(n-1)d^5$**

An electron from the "s" subshell transits to the "d" subshell to complete it with 5 or 10 electrons: the configuration obtained will be more stable than the initial configuration.

***The sub-shell "d" is more stable if it is totally or half filled.***

**Examples :**

$_{24}\text{Cr}\begin{cases} 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4 \\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5 \ \textbf{(more stable)} \end{cases}$

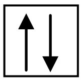
$_{29}\text{Cu}\begin{cases} 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9 \\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10} \ \textbf{(more stable)} \end{cases}$

## c/ Rules for filling atomic orbitals

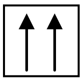
### c.1. Pauli exclusion principle

***"Two electrons from the same atom cannot have their four identical quantum numbers: n, l, m and s; they differ at least by one"***

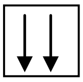
**Example :** $_2He$ : $1s^2$



(Yes)



(No)

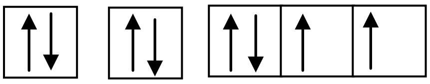


(No)

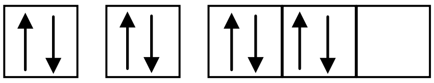
### c. 2. Hund's Rule:

***"In the same sub-shell, electrons tend to fill as many quantum boxes as possible with parallel spins"***

Example : $_8O$ : $1s^22s^22p^4$



(yes)



(No)

### d/ Slater approximation: Screening effect

We consider the electron "i". The electron "i" is subjected to:

- A field of attraction with the nucleus (+Ze).
- A repulsion field due to the presence of other electrons which represent a screen (mask) for the electron "i" considered.

This electron "i" is in contact with the nucleus of effective charge (Z*), such that:

$$\mathbf{Z^* = Z - \sum \delta_{ij}}$$

With:

δij: screening constant for each electron "j" which exerts a screening effect on an electron "i".

The energy of the electron "i" which is on a level (n) is written in the form:

$$\mathbf{E_n = \frac{-13.6}{n^2} Z^{*2}}$$

The following table gives the values of the coefficients δij exerted on the electron "i" by an electron "j".

| | | $e_j$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1s | 2s, 2p | 3s, 3p | 3d | 4s, 4p | 4d | 4f | 5s, 5p |
| $e_i$ | 1s | 0,31 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 2s, 2p | 0,85 | 0,35 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 3s, 3p | 1 | 0,85 | 0,35 | 0 | 0 | 0 | 0 | 0 |
| | 3d | 1 | 1 | 1 | 0,35 | 0 | 0 | 0 | 0 |
| | 4s, 4p | 1 | 1 | 0,85 | 0,85 | 0,35 | 0 | 0 | 0 |
| | 4d | 1 | 1 | 1 | 1 | 1 | 0,35 | 0 | 0 |
| | 4f | 1 | 1 | 1 | 1 | 1 | 1 | 0,35 | 0 |
| | 5s, 5p | 1 | 1 | 1 | 1 | 0,85 | 0,85 | 0,85 | 0,35 |

**Example 1**: Consider the sodium atom (Na (Z=11) : $1s^2 2s^2 2p^6 3s^1$)

$Z_{3s}{}^* = 11 - \sum \delta ij$

$\sum \delta_{ij} = 2*1 + 2*0{,}85 + 6*0{,}85 = 8{,}8$

So : $Z_{3s}{}^* = 11 - 8{,}8 = 2{,}2$

The energy of this electron will then be:

$E_{3s} = \frac{(-13{,}6)}{n^2} Z_{3s}{}^{*2} = \frac{(-13{,}6)}{3^2} (2{,}2)^2 = 7.313\ eV$

**Example 2 :** Be (Z=4) : $1s^2 2s^2$

${}_4$Be has 4 electrons; 2 e- on the K shell (1s), and 2 e- on the L shell (2s2p); we calculate Z* for each shell.

**Shell K (1s) :**

$Z_{1s}* = Z - \delta_{1s\text{-}1s} = 4 - 0.31 = 3.69$

**Shell L (2s2p) :**

$Z_{2s2p}* = Z - (\delta_{2s2p\text{-}2s2p} + 2\ \delta_{2s2p\text{-}1s}) = 4 - (0.35 + 0.85*2) = 1.95$

The calculation of the total energy of the Be atom is then obtained as follows:

$\mathbf{E_n = \frac{-13.6}{n^2} Z^{*2}}$

$E_{(1s)} = \frac{-13.6}{1^2} (3{,}69)^2 = -185{,}179\ \text{eV}$

$E_{(2s2p)} = \frac{-13.6}{2^2} (1{,}95)^2 = -12{,}928\ \text{eV}$

So : $E_t = 2.E_{1s} + 2.E_{2s2p} = -396{,}214$ eV