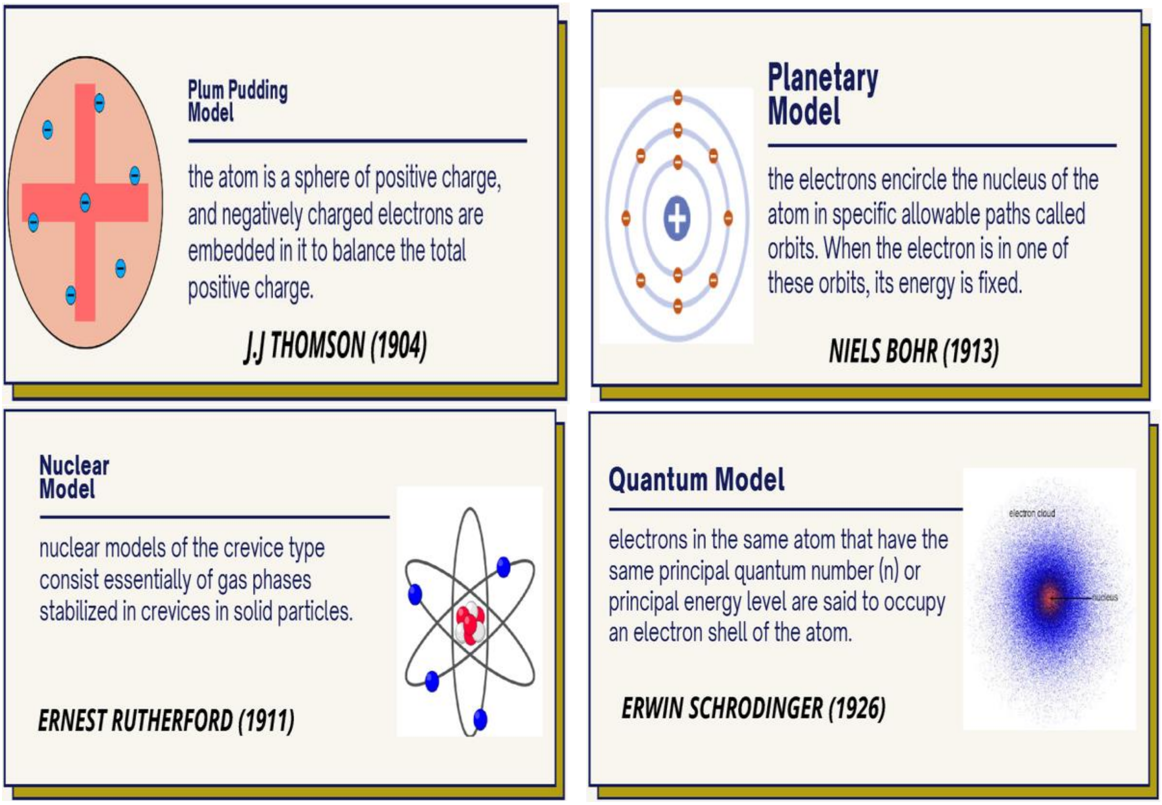
Chapter II: Energy quantification Part 1

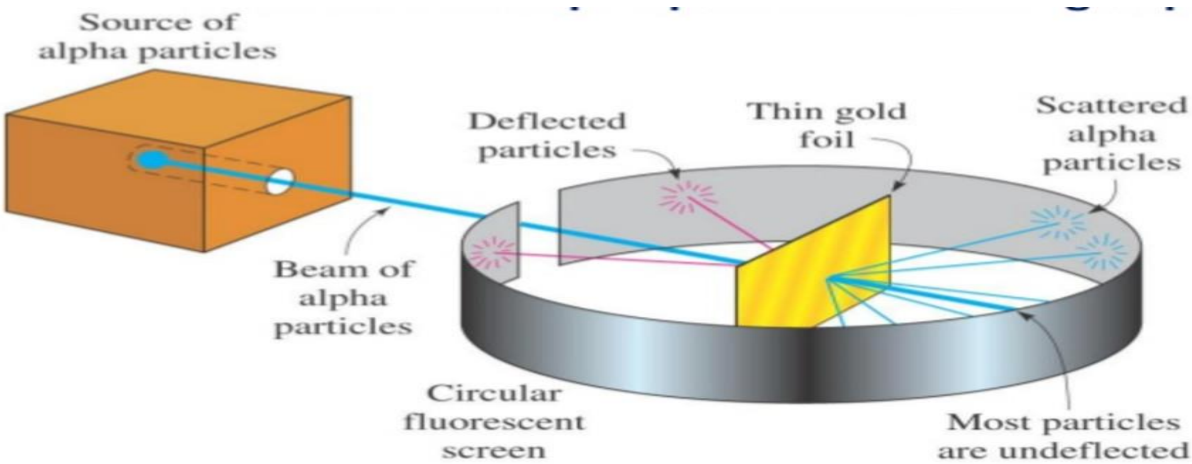
I-Classical model of the atom



I-1 Rutherford's model

- Rutherford experiment:

A sheet of gold, about 0.6mm thick, is bombarded with α particles.

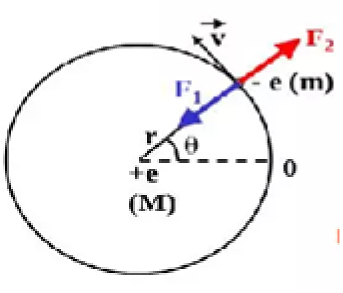


Most particles pass through the gold foil without deflection or absorption. However, some particles are slightly deflected, and others are even thrown back. According to Rutherford, if the α particles did not deviate, it was because there were no obstacles in their path. They therefore passed through the vacuum at the level of the gold foil.

Observations:

- The great mass of the atom is made up of its nucleus, which explains its lacunar structure; or the e-'s revolve around it like planets around the sun.

- The mechanical stability of the atom is ensured by the compensation of electrostatic attraction forces Fa =F1 due to the difference in nucleus-electron charges by centrifugal forces Fc= F2 due to the rotation of the electron around the nucleus on circular trajectories called orbits.



Advantages: this model uses only the laws of classical mechanics

Disadvantages:

- Electromagnetic theory requires the electron to radiate electromagnetic waves, so it will lose energy and eventually fall onto the nucleus.

Emitted light energy varies continuously. These two conclusions contradict experimental results (discontinuous spectrum).

I-2- Bohr's model 1913

I-2-1 Description (hydrogen atom)

To remedy the above contradictions, Bohr proposes four hypotheses:

- In the atom, the nucleus is immobile, while the electron of mass m moves around the nucleus in a circular orbit of radius r.

- The electron moves along privileged circular orbits without emitting energy; these are known as "stationary orbits" and are located at well-defined distances from the nucleus.

- When an electron moves from one level to another :

energy is absorbed (hν photons) if the electrons move away from the nucleus;

energy is emitted (hν photons) if the electrons move closer to the nucleus.

$$\Delta E = h\nu$$

- The electron's angular momentum can only take on integer values (quantization of angular momentum):

$$mvr = n.h/2\pi$$

h: Planck's constant ($6.626.10^{-34}$J.s) and n: natural number.

I-2-2 Quantitative aspect of the Bohr atom

The system is stable under the two forces $\overrightarrow{F_a}$ and $\overrightarrow{F_c}$:

• *Force of attraction*: $\overrightarrow{\mathbf{F_a}} = -\frac{\mathbf{K\,e^2}}{\mathbf{r^2}} = -\frac{\mathbf{e^2}}{\mathbf{4\pi\varepsilon_0 r^2}}$ (**K** $= \frac{1}{4\pi\varepsilon_0} = 9.10^9$ SI ; $\boldsymbol{\varepsilon_0}$ = 8.854187 SI : vacuum permittivity)

• *Centrifugal force:* $\overrightarrow{\mathbf{F_c}} = \frac{\mathbf{mv^2}}{\mathbf{r}}$

The system is in equilibrium if: $\overrightarrow{|\mathbf{F_a}|} = |\overrightarrow{\mathbf{F_c}}|$

$$\mathbf{mv^2 = \frac{Ke^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r}} \text{ ……………..(1)}$$

I-2-3 Total system energy

$$\mathbf{E_T = E_c + E_p}$$

E_c : kinetic energy

E_p : : potential energy, due to the attraction of the nucleus; we have :

$$\mathbf{E_c} = \frac{1}{2}\boldsymbol{mv^2} \quad \text{d'après } \mathbf{(1)} : \quad \mathbf{E_c = \frac{1}{2}\frac{Ke^2}{r}}$$

E_p (linked to the electron's position), the electron passing from an orbit of radius r to another of radius r' performs work of dw = Fdr = dE_p

Here F = $|Fa|$ = $\frac{\mathbf{Ke^2}}{\mathbf{r^2}}$ alors $E_p = \int \frac{\mathbf{Ke^2}}{\mathbf{r^2}}\,\mathbf{dr} = \mathbf{Ke^2}\int_{\infty}^{r}\frac{\mathbf{dr}}{\mathbf{r^2}} = -\frac{\mathbf{Ke^2}}{\mathbf{r}}$

The sign (-) to express that Ep decreases from r to ∞ we have E_p= 0

$$\mathbf{E_T = E = \frac{1}{2}\frac{Ke^2}{r} + \left(-\frac{Ke^2}{r}\right) = -\frac{1}{2}\frac{Ke^2}{r}}$$

$$\mathbf{E_T = -\frac{1}{2}\frac{Ke^2}{r} = -\frac{e^2}{8\pi\varepsilon_0 r} = f\left(\frac{1}{r}\right)} \text{ …………..}\mathbf{(2)} \text{ Energy of } e^- \text{ in steady state.}$$

I-2-4 Orbit radius :

We know that**: mvr = n.h/2π** where n is a positive integer**.**

Therefore: $\boldsymbol{V = \frac{nh}{2\pi mr}}$ **…………..(3)**

We replace (3) in (1)**:** $\mathbf{m\left(\frac{nh}{2\pi mr}\right)^2 = \frac{Ke^2}{r}}$

$$\mathbf{\frac{n^2h^2}{4\pi^2 mr} = Ke^2 \Longrightarrow \boldsymbol{r} = \frac{n^2h^2}{4\pi^2 Kme^2} \Longrightarrow \boldsymbol{r} = \frac{n^2h^2\varepsilon_0}{\pi me^2}} \text{ …………..}\mathbf{(4)}$$

This is the radius of the orbit in which the electron circulates; it is quantized.

If we replace (4) in (2), we obtain :

$$E_T = = -\frac{me^4}{8\varepsilon_0{}^2h^2n^2} \ldots\ldots\ldots\ldots\text{(5)}$$

The total energy of an electron is therefore quantized.

- For n=1 (ground state: the electron occupies the orbit of radius r_1 and energy E_1)

r_1= 0,529 Å (1Å = 10^{-10}m) ; E_1= -21,78.10^{-19} j = -13,6 eV (1eV = 1,6.10^{-19} j)

It is called r1 "Bohr radius", expression (4) is written :$\mathbf{r_n = n^2 .r_1}$

E1 is the energy of a hydrogen atom in which the electron is on the K layer, so relationship (5) can be written more simply:

$$\mathbf{E_n = E_1/n^2}$$

- For n = 2 (First excited state) : r_2= $4r_1$= 2,116 Å et E_2= E_1/4= -3,4 eV

- For n = 3 (Second excited state) : r_3= $9r_1$= 4,761 Å et E_2= 1,51 eV

Bohr's model is also known as the "layer model".

n = 1 layer K ; n = 2 layer L ; n = 3 layer M ; n = 4 layer N ; etc.

Note:

When n=1, the electron is said to be in the ground state (the most stable state);

For n>1, the electron is said to be in an excited state;

If n= ∞ the e- has left the atom, the atom is said to be ionized.

I-2-5 Energy absorption and emission

Each permissible orbital corresponds to a specific energy level. Electronic transitions from one orbit to another take place in jumps, accompanied by the emission or absorption of an energy photon:

$$\Delta\mathbf{E} = \left|\boldsymbol{E_f} - \boldsymbol{E_i}\right| = \left|\frac{\boldsymbol{E_1}}{\boldsymbol{n_f^2}} - \frac{\boldsymbol{E_1}}{\boldsymbol{n_i^2}}\right| = \mathbf{E_1}\left|\frac{\mathbf{1}}{\boldsymbol{n_f^2}} - \frac{\mathbf{1}}{\boldsymbol{n_i^2}}\right| = \mathbf{h\nu} = \boldsymbol{h}\frac{\boldsymbol{c}}{\lambda}$$

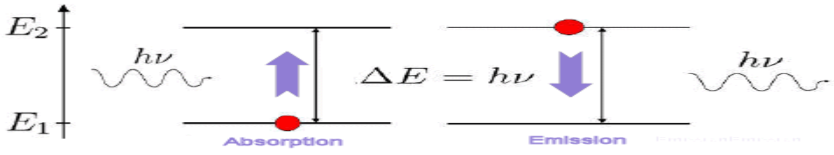
E_f : final state; **E_i** : initial state ; **h=6,626.10^{-34} j.s** (Planck's constant) ; **$\nu = \frac{c}{\lambda}$** (radiation frequency).

I-2-5-a Absorption:

When an electron moves from a level n (orbit of radius r_n) to a higher level p (p>n) (orbit of radius r_p), it absorbs radiation of frequency $\nu_{n\text{-}p}$.

I-2-5-b Emission:

When an electron passes from a level p to a level n (p > n), it emits radiation of frequency $\nu_{p\text{-}n}$.

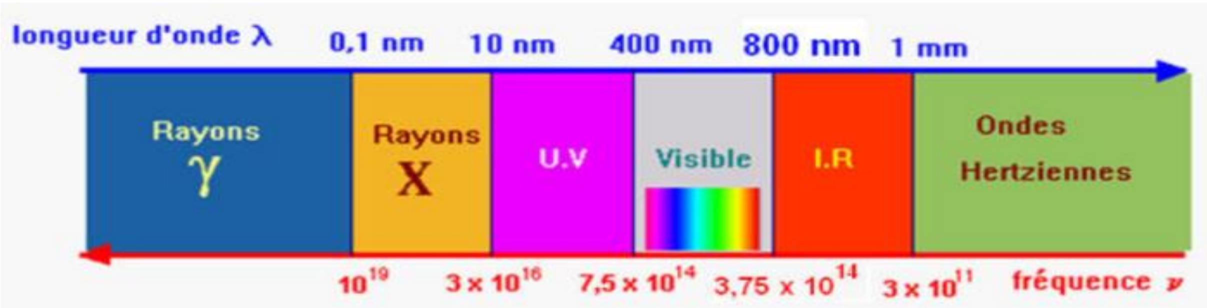


I-2-6 Rayonnement électromagnétique

Light rays are characterized by the propagation of an electromagnetic wave at the speed of light ($c = 3.10^8$ m/s). This wave is characterized by its wavelength λ or wave number $\bar{\nu}$ **:**

$$\boldsymbol{\lambda = \frac{1}{\bar{\nu}} = \frac{c}{\nu} \implies \bar{\nu} = \frac{\nu}{c}} \qquad \nu\text{: the frequency.}$$

The spectrum of all radiation can be presented as follows:



I-2-6 Emission or absorption spectrum of the hydrogen atom

Quantifying energy:

The energy emitted or absorbed by an electron is :

$$\boldsymbol{\Delta E = |E_p - E_n| = h\nu \qquad p>n}$$

$\boldsymbol{\Delta E = (1/n^2 - 1/p^2)\, me^4 / 8\varepsilon_0{}^2 h^2}$ Or $\boldsymbol{h\nu = h.c/\lambda}$

that is to say $\boldsymbol{1/\lambda = \bar{\nu} = (1/n^2 - 1/p^2)\, me^4 / 8\varepsilon_0{}^2 h^3 c}$

$$\boldsymbol{1/\lambda = R_H(1/n^2 - 1/p^2)}$$

With : $\boldsymbol{R_H = me^4 / 8\varepsilon_0{}^2 h^3 c = 1{,}09\,737\ m^{-1}}$, called constant of Rydberg

This relationship can be used to calculate the different wavelengths. In general, there are several series of spectra, depending on the state of the electron:

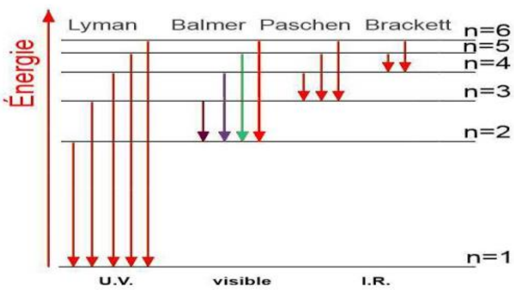
* **Lymann series** : n = 1 and p>1 (p = 2,3...,∞)

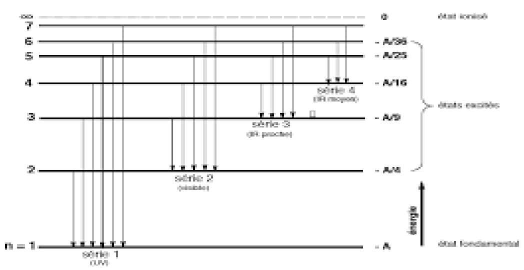
* **Balmer series** : n = 2 and p>2 (p = 3,4...,∞)

* **Paschen series**: n = 3 and p>3 (p = 4,5...,∞)

* **Brachett series**: n = 4 and p>4 (p = 5,6...,∞)

* **Pfund series** : n = 5 and p>5 (p = 6,7...,∞)





I-2-7 Generalization to hydrogenate ions

These are ions with a single electron.

Examples: **He** (Z=2) -------> **He^+** (1e- et 2p)

Li (Z=3) -------> **Li^{2+}** (1e- et 3p)

Be (Z=4) -------> **Be^{3+}** (1e- et 4p)

He^+, **Li^{2+}** and **Be^{3+}** are hydrogenoid ions.

With $|Fa| = \frac{ZKe^2}{r^2}$ then $E_p = -\frac{ZKe^2}{r}$

Their total energy is:

$$E_T = E_1 . \frac{Z^2}{n^2}$$

With: **$E_1 = -13,6$ eV**, the energy of the hydrogen atom in its ground state.

The radius of an n-rank orbit of a hydrogenoid ion is :$r = r_1 . \frac{n^2}{Z}$

with **$r_1 = 0,529$ Å** , being the radius of the hydrogen atom in its ground state.

$$\bar{\nu} = 1/\lambda = Z^2 . R_H(1/n^2 - 1/p^2).$$

I-2-8 Generalization to polyelectronic atoms

In the case of a multi-electron atom, we must take into account the effect of all electrons on the first electron we want to study, then the effect of all electrons on the second electron we want to study,..... And so on; we'll say that the electrons screen the one we're studying.Donc **:**

$|Fa| = \frac{Z_{eff}\, Ke^2}{r^2}$ with **$Z_{eff} = Z - \sigma$** : effective atomic number

σ : screen constant, which depends on the number of electrons between the electron in question and the nucleus.

Hence: $r_n = r_1 . \frac{n^2}{Z-\sigma}$ and $E_T = E_1 . \frac{(Z-\sigma)^2}{n^2}$

$$\bar{\nu} = 1/\lambda = Z_{eff}^2 . R_H(1/n^2 - 1/p^2).$$

I-2-9 Ionization energy

This is the energy required to bring the electron from its ground state to infinity.

$E_{ion} = E_\infty - E_1 = +13.6$ eV for the hydrogen atom; With **$E_\infty = 0$.**

I-2-10 Inadequacy of Bohr's model

Despite the importance of Bohr's model and its success in interpreting the spectrum of the hydrogen atom, it is not generalizable to the case of polyelectronic atoms, which is why this model has been abandoned and replaced by the quantum or wave model.