Chapter 4

Electronic structure of the atom

I. Production of atomic emission spectra

II. Electromagnetic radiation

III. Photon theory: emission spectrum of the hydrogen atom and the empirical Balmer-Rydberg relation

IV. Classical models of the atom: Rutherford's planetary model and Bohr's model

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I. Production des spectres d’émission atomique

En excitant suffisamment (électriquement ou thermiquement) des éléments ou leurs sels (composés ioniques), ils émettent de la lumière (visible ou non) qui seront analysée par un spectroscope, d’où il nous donne toujours un spectre de raies monochromatiques discrètes (et en plus, éventuellement, un spectre continu). Les raies sont caractéristiques des atomes ou ions monoatomiques. En réalité, ce spectre continu est constitué de raies fines très serrées que les spectroscopes modernes arrivent à séparer grâce à leur meilleure résolution.

I. Production of atomic emission spectra

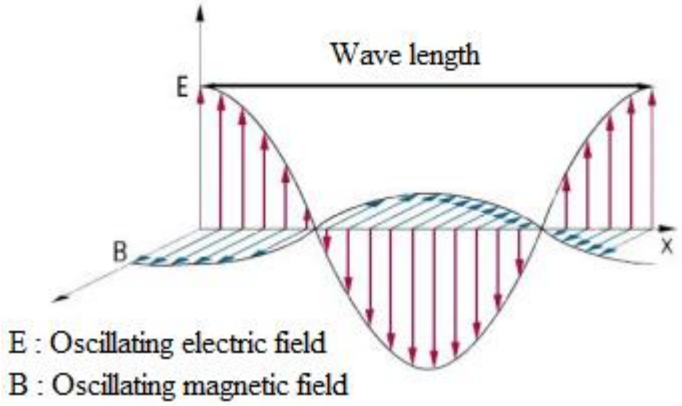
When elements or their salts (ionic compounds) are sufficiently excited (electrically or thermally), they emit light (visible or otherwise) which is analyzed by a spectroscope, always giving us a spectrum of discrete monochromatic lines (and possibly a continuous spectrum as well). The lines are characteristic of monoatomic atoms or ions. In reality, this continuous spectrum is made up of tightly-packed fine lines, which modern spectroscopes are able to separate thanks to their higher resolution.

II. Electromagnetic radiation

II.1 Electromagnetic waves

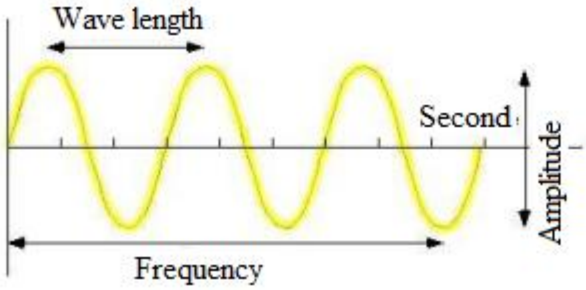
The shape and movement of electromagnetic radiation are analogous to those of a wave formed by the impact of a pebble on the surface of a lake: waves (crests and troughs), originating at the point of impact, form and move across the surface in concentric circles. According to the electromagnetic theory of light developed by **James Clerck Maxwell**, an electromagnetic wave is characterized by the simultaneous displacement of oscillating, perpendicular electric $(\overrightarrow{E})$ and magnetic $(\overrightarrow{B})$ fields.

Light is therefore undulatory in nature, known as a light wave or electromagnetic wave. It propagates in all directions rather than in a single plane, as is the case at the surface of a lake.



Four parameters determine a wave's properties:

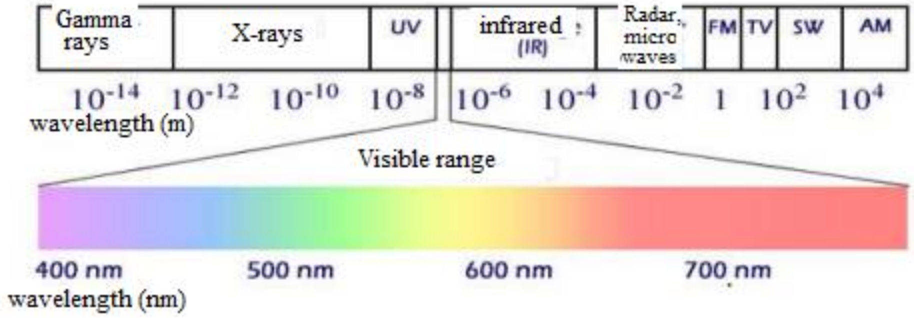
- Wavelength, λ (lambda): represents the distance between two consecutive peaks (or troughs); it is expressed in meters (m) and its most common submultiples, i.e. micrometers (µm) and nanometers (nm);
- Frequency,υ (nu): corresponds to the number of wavelengths passing a reference point each second; the unit of frequency is the hertz (Hz), which is equal to one wavelength per second (s^{-1});
- Amplitude: represents the intensity of the radiation;
- The wave period, T: is the time corresponding to the travel of a wavelength λ, expressed in seconds (s) ;
- The speed of propagation in a vacuum, C: a wave travels at the speed of light, or 3×10^8 m· s^{-1} .



The frequency and wavelength of an electromagnetic wave are related to its speed of travel by the following expression :

$$\lambda = c.T = \frac{c}{\nu}$$

Electromagnetic radiation occupies a very broad field, known as the electromagnetic spectrum. This spectrum ranges from very short, highly penetrating wavelengths, such as the γ-rays produced by nuclear decay, to wavelengths of up to 1 km, such as radio waves.



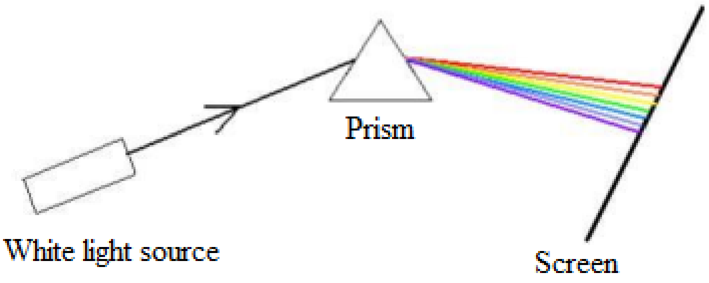
The visible range extends from violet (4.0.10^{-7} m) to red (7.0.10^{-7} m) and covers only a very small portion of the entire spectrum.

II.2 Light spectrum

A simple method for analyzing a radiation source is to pass it through a transparent prism, which separates the radiation source into its characteristic wavelengths, forming a spectrum.

II.2.1. Continuous spectrum

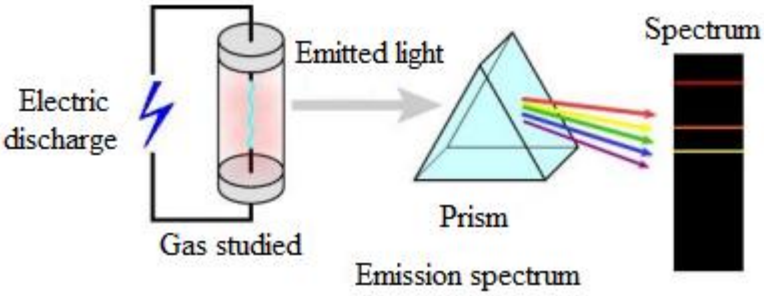
When the source of radiation is white light, such as sunlight or light from incandescent solids (tungsten bulbs), the dispersion by the prism forms a continuous spectrum, comprising all frequencies or wavelengths.



White light is polychromatic light, i.e. made up of several radiations of different frequencies. The color of light is related to the value of the frequency ν (or wavelength λ).

II.2.2. Discontinuous spectrum

When a source emits radiation with only certain frequencies, it is said to have a discontinuous spectrum, also known as a line spectrum.



When a spectrum has only one line, the light analyzed is called monochromatic light, and cannot be broken down by a prism.

II.3. Light appearance

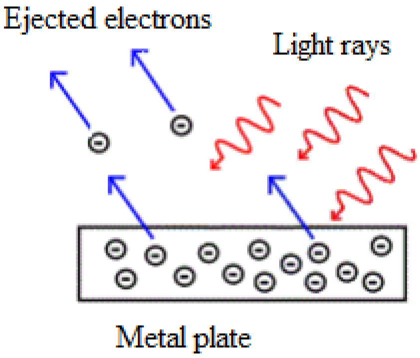
Light or electromagnetic radiation has two aspects :

- A wave aspect: resulting from the propagation of a wave of wavelength λ .
- A corpuscular aspect : corresponds to a flow of particles called photons. Each photon is a carrier of a grain of energy or quantum of energy: $E = h.\nu$ which is considered to be the smallest energy carried by a radiation; E: energy of light radiation and h: Planck's constant $6.626.10^{-34}$ J.s

II.4 Photoelectric effect or photoemission

In 1886, German physicist Heinrich Rudolf Hertz realized experimentally that a metallic material exposed to light could emit negatively charged particles (electrons). This discovery became known as the photoelectric effect.

When a metal plate is illuminated and the light swept in frequency, electrons are emitted from a threshold frequency ν_0, which is characteristic of the metal used. Albert Einstein explained Hertz's experiment in this way.



To extract electrons from a metal surface subjected to electromagnetic radiation, an energy E0 must be supplied, called the extraction energy or photoelectric threshold energy: $E0 = h.\ \nu0$

For the photoelectric effect to occur, $E > E_0$

$\Rightarrow h.\nu > h.\nu_0 \Rightarrow \nu > \nu_0 \Rightarrow c/\lambda > c/\lambda_0 \Rightarrow \lambda < \lambda_0$

Note:

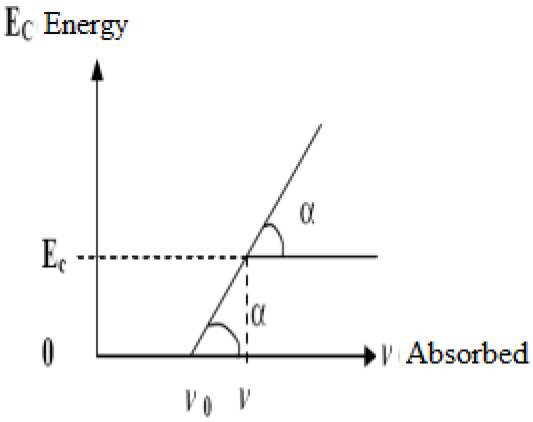
According to the mass-energy equivalence relation, the energy transported by a photon equals $m.C^2$ where m represents the fictitious mass of the photon (whose rest mass is zero), we have

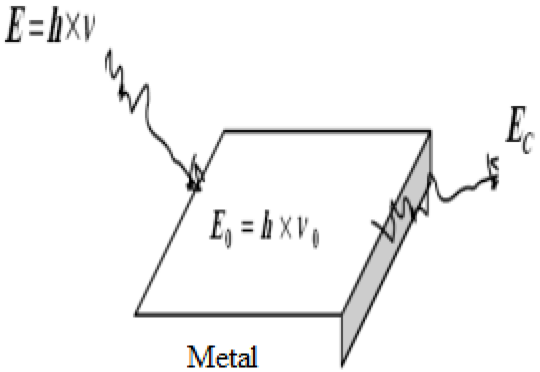
$$E = h.\nu = m.C^2 = h.\frac{C}{\lambda} \quad \Rightarrow \quad \lambda = \frac{h}{m.C}$$

Experience

If a metal plate is illuminated with light of frequency ν higher than the threshold frequency ν_0 the extra energy compared to the characteristic energy of the metal $E_0 = h.\nu_0$ is dissipated in the form of kinetic energy taken up by the electrons:

$$E_c = E - E_0 = h.\nu - h.\nu_0 = h(\nu - \nu_0)$$





- Seule la lumière de fréquence $\nu > \nu_0$ détermine une photoémission,
- Le surcroît d'énergie par apport à l'énergie caractéristique du métal $E_0 = h.\nu_0$ est dissipé sous forme d'énergie cinétique prise par les électrons
- Only light with a frequency $\nu > \nu0$ causes photoemission,
- The extra energy compared to the metal's characteristic energy $E_0 = h.\nu_0$ is dissipated in the form of kinetic energy taken up by the electrons.

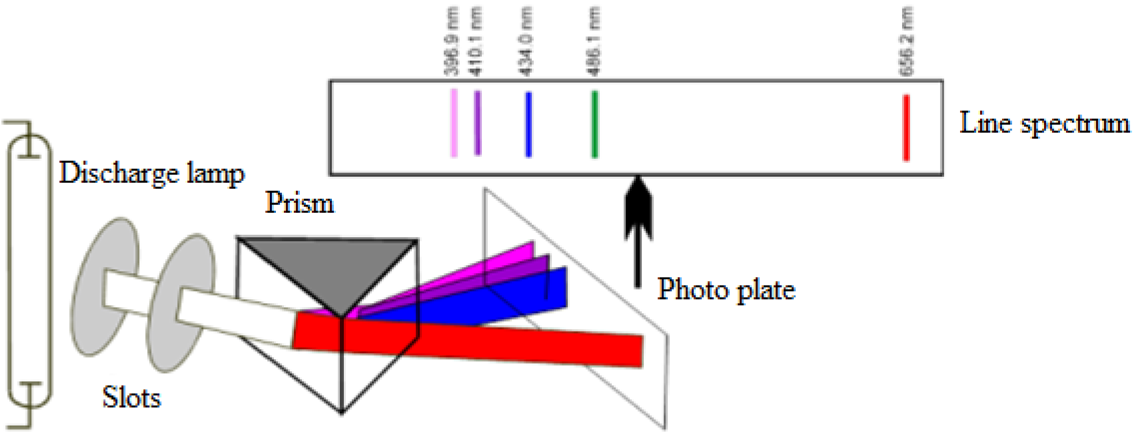
$$E_c = \frac{1}{2}.m.V^2 = h(\nu - \nu_0)$$

This equation shows that the curve representing energy versus frequency is a straight line with slope h: $Tg\,\alpha = \frac{E_c - 0}{\nu - \nu_0}$;by analogy with the previous equation, we find : tg α = h (Plank's constant)

III. Photon theory

III.1 Hydrogen atom emission spectrum and empirical Balmer-Rydberg relationship

Principle of the experiment: The hydrogen emission spectrum is obtained by applying an electric discharge (dop) to the hydrogen gas in a cathode ray tube, which excites the hydrogen atoms. The return of these atoms from the excited state to the ground state emits electromagnetic radiation.



C’est le spectre d’émission le plus simple. Chaque élément ou atome a son propre spectre spécifique, cela constitue une véritable empreinte digitale de cet atome. Il est obtenu par décharge électrique dans un tube contenant de l’hydrogène sous faible pression (1mm Hg). Les atomes d’hydrogène ainsi excité émettent une lumière rosée. A l’aide d’un prisme, cette lumière est décomposée en quatre bandes de lumière ou quatre raies lumineuses dans le domaine du visible :

This is the simplest emission spectrum. Each element or atom has its own specific spectrum, which constitutes a veritable fingerprint of that atom. It is obtained by electrical discharge in a tube containing hydrogen under low pressure (1mm Hg). Hydrogen atoms excited in this way emit a pinkish light. Using a prism, this light is decomposed into four bands of light, or light lines, in the visible range:

$$\begin{cases} \text{Violet : } \lambda = 410 \text{ mm} \\ \text{Indigo : } \lambda = 434 \text{ mm} \\ \text{Turquoise (blue-green) : } \lambda = 486 \text{ mm} \\ \text{Red : } \lambda = 656 \text{ mm} \end{cases}$$

These four visible lines in the hydrogen spectrum were first observed by Balmer in 1855. Rydberg (1889) found a simple relationship between the wavelengthλ of the lines in the hydrogen spectrum:

$$\wp = \bar{\upsilon} = \frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$\wp$, $\bar{\upsilon}$, $1/\lambda$: wave numbers (cm^{-1}); λ: wavelength; n: principal quantum number (n: an integer).

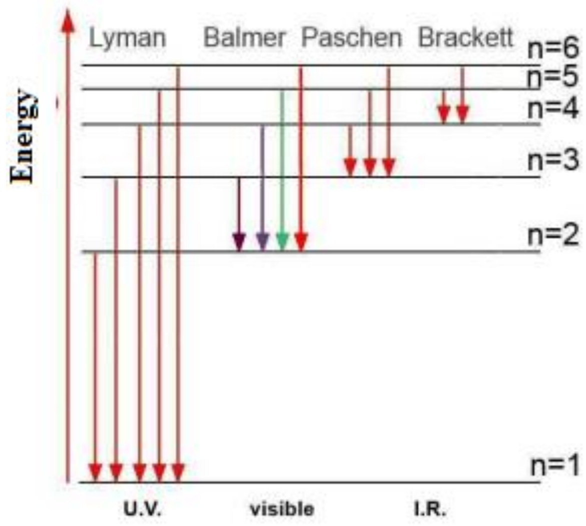
R_H : Rydberg constant, $R_H = 109677$ cm^{-1}

Hydrogen also emits UV (ultraviolet) and IR (infrared) radiation. These spectral lines were discovered by Lyman (UV), Pashen (IR), Brackett (IR) and Pfund (IR). To find the position of all the lines in the hydrogen spectrum, the Balmer-Rydberg formula was generalized:

$$\wp = \bar{\upsilon} = \frac{1}{\lambda} = R_H\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

n and m being integers with n < m. they represent energy levels.

Serie	**n**	**m**	**Domain**
Lyman	1	2, 3, 4, 5, 6,…….∞	UV ($\lambda < 400$ nm)
Balmer	2	3, 4, 5, 6, 7,…….∞	Visible ($400\text{nm} \leq \lambda \leq 780\text{nm}$)
Pashen	3	4, 5, 6, 7, 8,…….∞	IR ($\lambda > 780$ nm)
Bracket	4	5, 6, 7, 8,……….∞	
Pfund	5	6, 7, 8,………….∞	



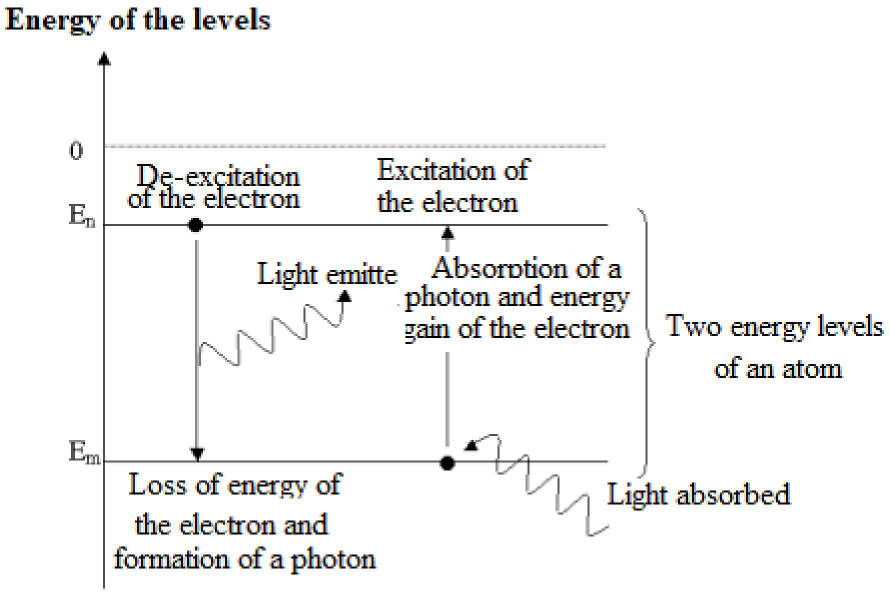
➢ Interpretation of the hydrogen emission spectrum

Based on the Rutherford atomic model (the electron of the hydrogen atom forms a circular orbit around the nucleus), Bohr (Danish physicist, 1913) explained the hydrogen spectrum as follows:

→ When the atom is not excited, the electron is in a low-energy orbit, in the ground state (at rest);

→ When this atom is excited, i.e. when it absorbs energy resulting in an electronic transition from the fundamental level to a higher-energy permitted level, the electron moves to a more distant orbit;

→ The electron of the excited atom doesn't stay in this orbit for long, as it finds itself in an unstable state, returning to its lower energy level (ground state) and releasing the energy it has received. This energy, emitted in the form of photons (light), corresponds to the energy difference between the two orbits.



→ Only certain levels of the atom are allowed: the energy levels are quantized,

→ The light energy of a line of frequency υ corresponds to the emission of a quantum of energy :

$$\Delta E = h\upsilon = h\frac{c}{\lambda} = h.c.R_H\left(\frac{1}{n^2}-\frac{1}{m^2}\right)$$

Note: λ_{max} and λ_{min}

$$\bar{\nu} = \frac{1}{\lambda_{n,m}} = R_H\left(\frac{1}{n^2}-\frac{1}{m^2}\right) \Rightarrow \lambda_{n,m} = \frac{1}{R_H}\left(\frac{1}{\frac{1}{n^2}}-\frac{1}{\frac{1}{m^2}}\right)$$

λ_{max} : corresponds to the maximum line: n=n and m = n+1

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

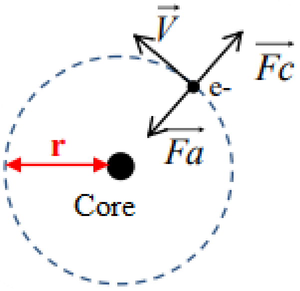
λ_{min}: corresponds to the limit line: n = n and $m \rightarrow \infty$

$$\lambda_{min} = \frac{1}{R_H}\left(\frac{1}{\frac{1}{n^2}-\frac{1}{m^2}}\right) \Rightarrow \lambda_{min} = \frac{n^2}{R_H}$$

IV. Classical models of the atom

IV.1 Rutherford's planetary model

According to Rutherford, the atom is made up of a set of electrons numbering Z and a nucleus at the center. These electrons revolve around the nucleus, describing circular orbits of radius r and uniform velocity v. At each instant, these electrons are subjected to two forces, F_a and F_c.



- $\vec{F_a}$: Electrostatic force of attraction between two charges (+e) and (-e).

$$Fa = -Z^2 k \frac{e^2}{r^2} \begin{cases} k = \dfrac{1}{4\pi\varepsilon_0} = 9.10^9 & \text{in the international system} \\ \varepsilon_0 = 8{,}85.10^{-12} & \text{is the permittivity of vacuum} \end{cases}$$

  In the case of the hydrogen atom Z = 1 : $Fa = -k\frac{e^2}{r^2}$

- $\vec{F_c}$: Centrifugal force pulling the electron outwards.

  According to Newton's second law, if a particle of mass m, with velocity v, rotates around the nucleus, we have :

$$Fc = m\gamma = m\frac{v^2}{r}$$

For the electron to be stable in a circular orbit, must be : $\vec{Fa} = -\vec{Fc}$:

We get : $k\frac{e^2}{r^2} = m\frac{v^2}{r} \Rightarrow v^2 = \frac{k.e^2}{m.r}$

On the other hand, the electron's mechanical energy in a given orbit can be calculated as the sum of the kinetic energy Ec and the potential energy Ep, i.e. E = Ec + Ep.

Or $Ec = \frac{1}{2}mv^2$ et $Ep = \int_r^\infty Fa.dr = -\int_r^\infty k\frac{e^2}{r^2}dr = k\frac{e^2}{r}\Big|_r^\infty$

$\Rightarrow Ep = -k\frac{e^2}{r}$ (Ep = 0 when r tends to ∞)

$$E = Ec + Ep = \frac{1}{2}mv^2 - k\frac{e^2}{r}$$

So :

Replacing the expression for v^2 in the latter, we get :

$$E = \frac{1}{2} m \frac{k.e^2}{m.r} - k\frac{e^2}{r} = \frac{1}{2} k\frac{e^2}{r} - k\frac{e^2}{r} = -\frac{1}{2} k\frac{e^2}{r}$$

Remarks :

- The electron's total energy is a continuous function of r, since the radius r varies continuously, which contradicts experimental observations (the spectrum of the hydrogen atom is a spectrum of discontinuous lines).
- When E increases, the absolute value $|E|$ increases, so r decreases, the electron would end up crashing into the nucleus; which is not the case.

Rutherford's model is not compatible with reality, which led Bohr to propose another model.

IV.2 Bohr model

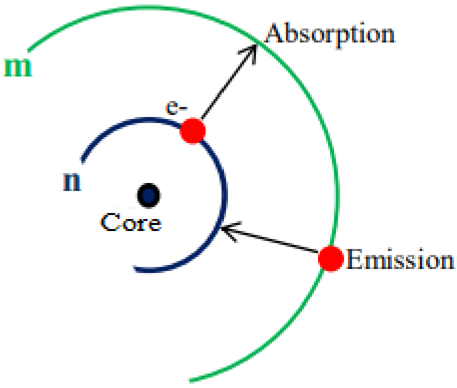
Bohr's model is based on the principles of classical mechanics and is an improvement on Rutherford's model. It is based on three postulates derived from quantum theory

IV.2.1. Bohr's assumptions

- **First postulate**: the electron's energy is quantized, i.e. it can only take on certain values, also known as energy levels. Each energy value corresponds to a stable circular trajectory.
- **Second postulate**: Bohr accepted that the electron's orbit is circular and that the electron's angular momentum (m_e.v.r) was quantized: $m_e.v.r = n\frac{h}{2\pi}$

  n: natural integer greater than zero.

- Third postulate: an atom emits or absorbs light radiation only when the electron jumps from one orbit to another. The frequency υ of the radiation is given by the relationship: $\Delta E = h.\upsilon = E_m - E_n$ i.e. $n < m$



- → When the electron passes from the n level to the m level, this is an absorption and the energy: $\Delta E = h.\upsilon = E_m - E_n$
- → When the electron passes from the m level to the n level, it emits energy: $\Delta E = h.\upsilon = E_n - E_m$

Based on these assumptions, Bohr was able to find all the lines in the spectrum of the hydrogen atom.

IV.2.2. Calculation of some quantities of the hydrogen atom

- **Calculating the radius of the Bohr atom**

According to Bohr's first two postulates, only orbits whose radii are defined by $m_e.v.r = n\frac{h}{2\pi}$ allow the electron to gravitate without emitting radiation around the proton.

Possible speeds are given by : $v = \frac{n.h}{2\pi m_e.r} \Rightarrow v^2 = \frac{n^2.h^2}{4\pi^2 m_e^2.r^2}$

Furthermore, we have $\left|\overrightarrow{Fa}\right| = \left|\overrightarrow{Fc}\right| \Rightarrow \frac{k.e^2}{r^2} = \frac{m.v^2}{r} \Rightarrow v^2 = \frac{k.e^2}{m.r}$

$$v^2 = \frac{n^2.h^2}{4\pi^2 m_e^2.r^2} = \frac{k.e^2}{m.r} \Rightarrow r = \frac{n^2.h^2}{4\pi^2.k.m_e.e^2}$$

So :

For n = 1, which corresponds to the ground state, we have : $r = \frac{h^2}{4\pi^2.k.m_e.e^2} = a_0 \approx 0{,}53\ A^0$;

(called the Bohr radius)

For n > 1, we have: $r = a_0.n^2 = 0{,}53.n^2$ Å ; the radius depends on n and is quantized.

- **Energy calculation**

In the case of the hydrogen atom, and using the Rutherford energy expression :

$$E_n = -k\frac{e^2}{2r}$$

By replacing the expression for r in the energy, we get : $E_n = -k\frac{e^2}{2}.\frac{4k.\pi^2.e^2.m_e}{h^2n^2} = \frac{-2m_e.k^2.\pi^2.e^4}{h^2}.\frac{1}{n^2}$

$E_n = \frac{E_1}{n^2}$ with : $E_1 = \frac{-2m_e.k^2.\pi^2.e^4}{h^2}$

$E_1 = -21{,}74.10^{-19}$ J $\Rightarrow E_1 = -13{,}6$ eV : is the lowest energy corresponding to the ground state.

For n > 1 :

Total energy is quantized and depends on n $E_n = \frac{-13{,}6}{n^2}(eV)$. The latter is the first quantum number, called the principal quantum number.

→ **In the case of hydrogenoids**

A hydrogenoid is an atom that has lost all but one of its electrons, such as $_2He^+$ and $_3Li^{2+}$

The energy expression is given by : $E_n = E_1\frac{Z^2}{n^2}(eV)$

And that of the radius is given by: $r_n = a_0.\frac{n^2}{Z}(A^0)$

- **Electronic transition from level n_i (initial) to level n_f (final)**

According to the principle of conservation of energy, in absolute terms, the variation in energy between the initial and final atomic states is equal to the energy of the photon emitted or absorbed. $E = |\Delta E_{ni \to nf}| = |E_{nf} - E_{ni}| = |E_1| . \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = h\upsilon$

Hence : n_i and n_f : natural numbers greater than zero.

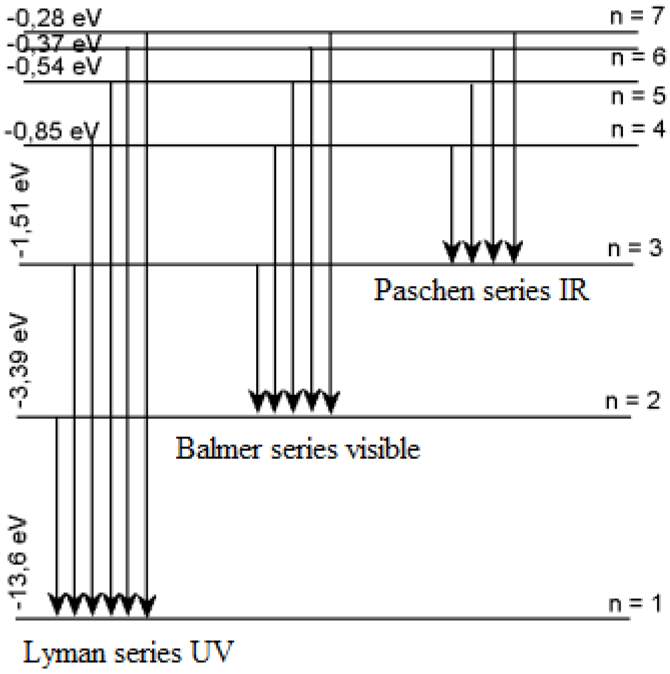
$$\Rightarrow \frac{-2m_e.k^2.\pi^2.e^4}{h^2} . \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = h\upsilon = h\frac{c}{\lambda}$$

$$\Rightarrow \frac{1}{\lambda} = \frac{2m_e.k^2.\pi^2.e^4}{h^3.c} . \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = R_H \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

With $R_H = 1{,}097.10^7$ m^{-1} close to the experimental value.

Bohr's theory provides a satisfactory explanation of the quantum spectrum of the hydrogen atom, and allows us to calculate R_H.

- **Energy diagram of the hydrogen atom**



For each series of lines, there is a limiting line that corresponds to the electronic transition from the n→∞ level to the n1 level of each series. The energy difference that accompanies this transition is : $\Delta E_{n1\to\infty} = E_{\infty} - E_{n1} = h\upsilon_{limit}$

υlimit: is the frequency of the limit line and $E_{\infty} = 0$ by convention

In the case of the Lyman series : $\Delta E = 0 - E_{n1} = +13{,}6eV$

This is the energy required to move the electron from the $n_1 = 1$ level to the $n = \infty$ level. In other words, it's the energy needed to pull the electron out of the hydrogen atom. This energy is called the **ionization energy Ei** of the hydrogen atom.

$$H \xrightarrow{E_i} H^+ + 1e^- \quad ; E_i = +13{,}6$$

Bohr's model provides a simple way of recovering experimental results for the hydrogen atom. The application of this model to poly-electronic atoms revealed problems, as it was unable to successfully describe their spectra. So efforts were made to improve it. Sommerfield proposed to complicate the model by using elliptical orbits instead of Bohr's simple circular orbits. This modification introduced two more quantum numbers (l and m), but also failed to describe large atoms adequately. This model was finally abandoned and replaced by the quantum or wave model.

V. Quantum or wave models of the atom

V.1 Wave-corpuscle duality, De Broglie hypothesis

He postulated that matter, like light, has a dual aspect : wave and particle. Any particle in motion with velocity v (notably electrons) of mass m, can be associated with a wave whose wavelength λ is related to the momentum by the following relationship: $\lambda = \dfrac{h}{mv}$ where h is Planck's constant.

According to De Broglie, even large (macroscopic) objects have wave properties, but it is impossible to observe the waves associated with them because their wavelengths λ are so small.

Wavelength has no physical meaning unless applied to the microscopic scale.

Example : Consider a tennis ball (macroscopic scale) of mass 114g traveling at a speed v of 175 km/h.

The wavelength associated with this ball is: $\lambda = \dfrac{6{,}626.10^{-34}}{(114.10^{-3}).(175.10^{3}/3600)} = 1{,}2.10^{-34}m$ it's so small that it can't be measured by any existing instrument.

In the case of an electron (atomic or microscopic scale) moving at a speed v of $2{,}2.10^{6}$ m/s, the wavelength is : $\lambda = \dfrac{6{,}626.10^{-34}}{(9{,}11.10^{-31}).(2{,}2.10^{6})} = 3{,}31.10^{-10}m$

V.2 Heisenberg's Uncertainty Principle (1927)

Heisenberg's principle states that it is impossible to simultaneously and accurately measure the position x and momentum (m.v) of a corpuscle. It translates into the following inequality :

$$\Delta x.\Delta p \geq \frac{h}{2\pi}$$

P is the momentum: m.v $\Rightarrow \Delta p = m.\Delta v$

This gives : $\Delta x.\Delta v \geq \dfrac{h}{2\pi.m}$ $\begin{cases} \Delta x \text{ is the uncertainty or error in position} \\ \Delta v \text{ is the speed uncertainty or error} \end{cases}$

Example: Apply Heisenberg's principle to the following two systems to calculate Δv: An electron moving in a straight line (Δx = 1Å), A ball of mass 10g moving in a straight line (Δx = 1µm).

Macroscopic scale	Microscopic scale
A ball	An electron
Mass : 10g = 10^{-2} Kg	Weight : 9,11.10^{-31} Kg
Δx = 1µm = 10^{-6} m	Δx = 1Å = 10^{-10} m
$\Delta v \geq \frac{6{,}626.10^{-34}}{2(3{,}14)(10^{-2})(10^{-6})} = 1{,}05.10^{-26} ms^{-1}$	$\Delta v \geq \frac{6{,}626.10^{-34}}{2(3{,}14)(9{,}11.10^{-31})(10^{-10})} = 1{,}16.10^{6} ms^{-1}$

At the atomic scale, the uncertainty in velocity (Δv) is very large. Thus, the position of an electron, with a well-defined momentum, will only be defined with a certain degree of uncertainty. Its presence will therefore be described in terms of its probability of presence, rather than its position on an orbit.

VI. Schrödinger model and probability of presence

VI.1 Principle of wave mechanics, wave-corpuscle duality

Like light, particles have both corpuscular (photon, electron, etc.) and wave (λ, ν) characteristics. Light (photon) is electromagnetic radiation with both these characteristics.

Corpuscular character	Wave character
$E_{photon} = h\nu = \frac{hc}{\lambda}$ Responsible for photoelectric phenomena	$\lambda = \frac{c}{\nu}$ Responsible for diffraction and reflection phenomena

Since the photon's energy is $E = m.c^2$, we deduce that $\lambda_{photon} = \frac{hc}{E} = \frac{hc}{mc^2} = \frac{h}{mc}$

By analogy, for the electron moving around the hydrogen nucleus (proton), we associate a wave such as $\lambda = \frac{h}{mv}$ (mv is the momentum)

VI.2. Wave function

For an electron in an atom, it is impossible to know its position and velocity simultaneously (Heisenberg). All we can know about the electron's state of motion is a mathematical function $\psi(x,y,z)$, where x, y and z are the electron's Cartesian coordinates in a reference frame linked to the nucleus at a point M(x,y,z).

ψ is called a wave function, or atomic orbital in everyday language. It has no physical meaning; its only significance is mathematical.

On the other hand, the square of the function $|\psi|^2$ at a point in space, determines the probability of finding the electron described by $\psi(x, y, z)$ in the volume defined by (x + dx), (y + dy) and (z + dz). In a volume dV we have: $dP = |\psi|^2\, dxdydz = |\psi|^2\, dV$, dP being the probability of the electron's presence in volume dV, around the point of coordinates x, y, z. Simplistically, we speak of electron density, or electron cloud.

For all space : $p=\int_{-\infty}^{+\infty}|\Psi|^2\,dv=1$ we are certain to find the electron, the ψ function is then normalized.

We will never be able to define a trajectory or orbit for the electron, as Bohr's model proposed. All we can provide is a probability distribution of the electron's presence around the nucleus, or the electron density. The electron is "somewhere" in an orbital.

VI.3. Equation de Schrödinger

The wave function ψ(x,y,z) is neither observable nor measurable. It is obtained by solving a differential equation known as the Schrödinger equation (the wave function is the solution to this equation), which in the case of the hydrogen atom can be written as :

$$-\frac{h^2}{8\pi^2 m_e}\left[\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right]+E_p\psi=E\ \psi$$

This is a partial differential equation where me is the mass of the electron and its potential energy. This equation expresses the conservation of total energy E. $E_p=-Z\frac{Ke^2}{r}$

If we note: $H=-\frac{h^2}{8\pi^2 m_e}\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right]+E_p$ where H ≡ Hamiltonian operato

Schrödinger's equation can be written in a more condensed form: Hψ = Eψ

With : $H=-\frac{h^2}{8\pi^2 m_e}\Delta+E_p=-\frac{\overline{h^2}}{2m_e}\Delta+E_p$ and : $\bar{h}=\frac{h}{2\pi}$ et $E_p=-Z\frac{Ke^2}{r}$

Schrödinger's equation synthesizes the corpuscular and wave aspects of the microscopic particle.

- **Wave aspect**: We start with a standing wave whose amplitude is independent of time for a one-dimensional system: $\psi(x)=\psi_0\cos\frac{2\pi\ x}{\lambda}$
- **Corpuscular aspect**: According to De Broglie : $mv=p=\frac{h}{\lambda}$

- **Conservation of energy**: $E = E_c + E_p(x)$

The combination of these three relations leads to Schrödinger's equation. Let's consider the simple case of a particle moving along an x-axis in a time-independent E potentialp (x).

$$\psi(x)=\psi_0 \cos\frac{2\pi\ x}{\lambda} \Rightarrow -\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2}+E_p(x)\ \psi(x)=E\ \psi(x)$$ (Schrödinger equation).

In this equation, the unknowns are E and ψ(x). The wave function ψ satisfies the Schrödinger equation must be :

1. It is necessary for $\psi(x, y, z)$ to be defined at any point in space ;

2. It is necessary for $\psi(x, y, z)$ to be continuous at any point in space ;

3. When $(x, y, z) \rightarrow \infty \Rightarrow \psi(x, y, z) \rightarrow 0$.

Demonstration:

$$E_c = \frac{1}{2}.mV^2 \Rightarrow 2E_c = m.V^2 \ ; \quad E = E_c + E_p(x) \Rightarrow E_c = E - E_p(x)$$

Where : $2\left(E - E_p(x)\right) = m.V^2$

$$\psi(x)=\psi_0 \cos\frac{2\pi\ x}{\lambda}$$

The first derivative: $\frac{d\psi}{dx} = -\frac{2\pi}{\lambda}\psi_0 \sin\frac{2\pi\ x}{\lambda}$

The second derivative : $\frac{d^2\psi}{dx^2} = -\frac{2\pi}{\lambda}\psi_0.\frac{2\pi}{\lambda}\cos\frac{2\pi\ x}{\lambda}$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{\lambda^2}\psi_0.\cos\frac{2\pi\ x}{\lambda} = -\frac{4\pi^2}{h^2}m^2.V^2.\psi_0 \cos\frac{2\pi\ x}{\lambda}$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{h^2}m.m.V^2.\psi_0 \cos\frac{2\pi\ x}{\lambda} = -\frac{4\pi^2}{h^2}m.2.E_c.\psi_0 \cos\frac{2\pi\ x}{\lambda}$$

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi^2}{h^2}m.2.\left(E - E_p(x)\right).\psi_0 \cos\frac{2\pi\ x}{\lambda} = -\frac{8\pi^2}{h^2}m.\left(E - E_p(x)\right).\psi(x)$$

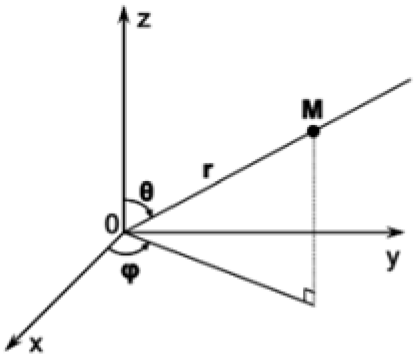
$$\frac{d^2\psi}{dx^2}+\frac{8\pi^2}{h^2}m.\,E\psi(x)-\frac{8\pi^2}{h^2}\,m.\,E_p(x).\,\psi(x)=0$$

$$-\frac{h^2}{8\pi^2m}.\frac{d^2\psi}{dx^2}+E_p(x).\,\psi(x)=E\psi(x)$$

VI.4. Results of solving the Schrödinger equation

- **Hydrogen atom in quantum mechanics**

In the hydrogen atom, there is spherical symmetry, so spherical coordinates are used to solve the Schrödinger equation. Any point in space can be located using the 3 coordinates r, θ and φ:



$\mathbf{r}$ = 0M ($0 \le \mathbf{r} \le +\infty$)

$\boldsymbol{\theta}$ = $\overrightarrow{OM}$ nail with Z axis ($0 \le \boldsymbol{\theta} \le \pi$)

$\boldsymbol{\varphi}$ = projection nail of $\overrightarrow{OM}$ on the XY plane with the x axis ($0 \le \boldsymbol{\varphi} \le 2\pi$).

We have the relations :

$$\begin{cases} x = r\sin\theta\cos\varphi\,; \\ y = r\sin\theta\sin\varphi\,; \\ z = r\cos\theta\,; \end{cases} \qquad r^2 = x^2 + y^2 + z^2\,; \quad dV = r^2\sin\theta\,dr\,d\theta\,d\varphi$$

If expressed as a product of the variables r, θ and φ, the probability of finding the electron in a volume is expressed as the product of a radial function R(r) and an angular function A(θ,φ):

$$\left|\psi(r,\theta,\varphi)\right|^2 dV = \left|R^2(r)A^2(\theta,\varphi)\right| dV$$

Solving H.ψ = E.ψ will only lead to physically acceptable solutions for certain energy values. For the hydrogen atom, the eigenvalues of the energy are given by the relation: $E_n = \frac{-m_e e^4}{8\varepsilon_0 n^2 h^2}$

with: m_e the mass of the electron and e its charge. ε_0 is the permittivity of vacuum and h is Planck's constant, n is a number that can take on the values 1, 2, 3, 4, etc. This number therefore already identifies the main quantum, which is the electron. This number is thus identified with the principal quantum number, already present in Bohr's model. Moreover, for n=1, we find exactly the energy value of the fundamental level of hydrogen: E_1 = -13.6 eV. In the case of the hydrogen atom, the SCHRÖDINGER equation can be solved to give :

$$E_n = -\frac{13,6}{n^2}$$

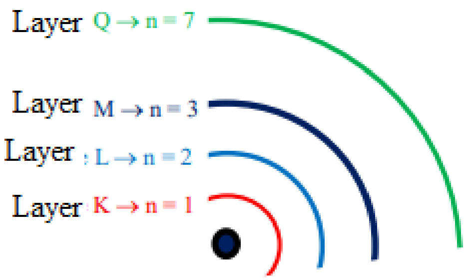
The mathematical determination of wave functions also includes two other quantum numbers, l and m : $\psi(r,\theta,\varphi) = R_n(r).\mathrm{A}_{l,m}(\theta,\varphi)$

VII. Quantum numbers

The state of an electron in an atom (its energy, its movements around the nucleus, the shape of its orbit) is defined by four parameters called quantum numbers.

A simple model consists in considering the electron pattern of poly-electron atoms as being made up of concentric layers, each characterized by a principal quantum number n (identical to that of Bohr's model); this is known as the concentric-layer model. Each layer is even made up of several sub-layers characterized by a second quantum number l. Finally, each sublayer is made up of several quantum cells, each characterized by a third quantum number m and a fourth spine quantum number (S).

VII.1 Main quantum number: n



This first quantum number comes directly from Bohr's model, and is a non-zero integer (n≥ 1). It characterizes the level occupied by the electron, or energy level. It defines an electron layer. This number also determines the size of the orbital, which increases with n.

The electronic layer is sometimes indicated by a capital letter instead of the numerical value of n :

Value of n	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Layer symbol	K	L	M	N	O	P	Q

VII.2 Secondary or azimuthal quantum number: l

Each layer is subdivided into one or more sublayers, whose shape is characterized by the secondary quantum number l. The latter is an integer such that: $0 \leq l \leq n-1$

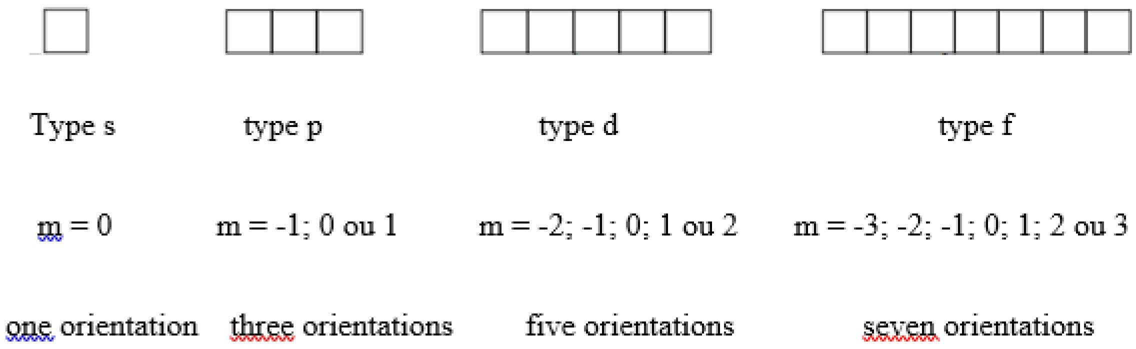
- l = 0 : type s underlay ;
- l = 1 : type p underlay ;;
- l = 2 : type d underlay ;;
- l = 3 : type f underlay ;.

- Example : Let the layer n = 3 be: l = 0 or l = 1 or l = 2. The n = 3 layer is therefore made up of three sub-layers (3s), (3p) and (3d).

VII.3 Magnetic quantum number: m

This number defines the number of orientations in space the electron can take when subjected to the action of a magnetic field. It characterizes the quantum bin occupied by the electron. The magnetic quantum number m is an integer such that: -l ≤ m ≤ +l; $soit\ 2l + 1$ different values.

Each orbital can be assigned a quantum square, represented by squares:



Type s	type p	type d	type f
m = 0	m = -1; 0 ou 1	m = -2; -1; 0; 1 ou 2	m = -3; -2; -1; 0; 1; 2 ou 3
one orientation	three orientations	five orientations	seven orientations

These three quantum numbers define a quantum bin, which contains two electrons. To distinguish between the two electrons, we introduce a fourth spin quantum number (S).

VII.4. Spin quantum number: m_s or s

The electron has its own magnetism. It rotates on itself. This motion is called the spin, noted ms or S. It has only two values: +1/2 and -1/2.

To symbolize this spin quantum number graphically, we use: an upward arrow (↑) for S = +1/2 and the electron is placed to the left in the quantum bin; or a downward arrow (↓) for S=-1/2 and the electron is placed to the right in the quantum bin:

:

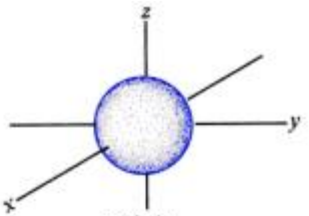
Example: The hydrogen atom1 H, n = 1, l = 0 and ms = +1/2 $\boxed{\uparrow}$

The permitted values of l, m, and the maximum number of electrons that a layer can contain are given in the following table for the first 4 layers:

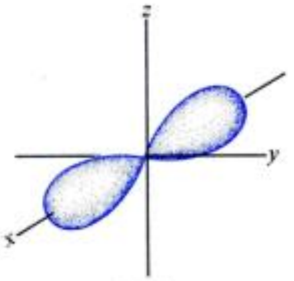
n	*l*	*m*	**Maximum number of electrons on the layer**
1	0	0	2
2	0	0	8
	1	-1, 0, +1	
3	0	0	18
	1	-1, 0, +1	
	2	-2, -1, 0, +1, +2	
4	0	0	32
	1	-1, 0, +1	
	2	-2, -1, 0, +1, +2	
	3	-3, -2, -1, 0, +1, +2,+3	

- **Geometric shape of the different atomic orbitals**

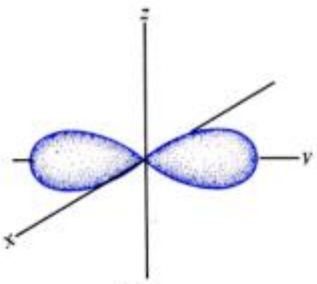
Atomic orbitals are represented by three-dimensional geometric shapes indicating the region of space where the probability of finding the electron is 95%, where the density of the electron cloud is highest. For the s sublayers, the orbitals are spherical in shape, their diameter increasing with the value of the principal quantum number n. For the 3 p sublayers, the orbitals have the shape of alters oriented along the 3 axes of coordinates x, y and z as a function of the magnetic quantum number m. The geometric shape of the 5 d orbitals is much more complex.



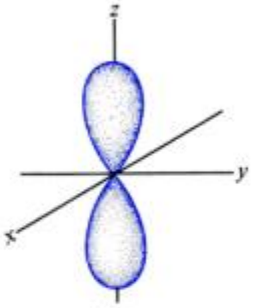
orbital s



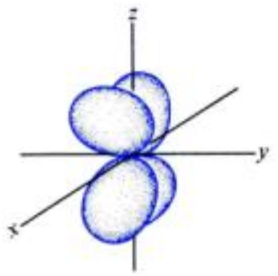
orbital p_x



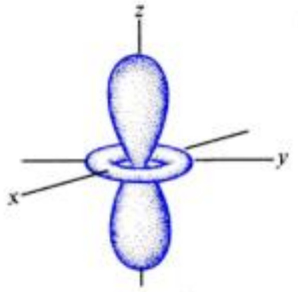
orbital p_y



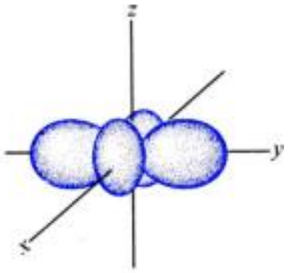
orbital p_z



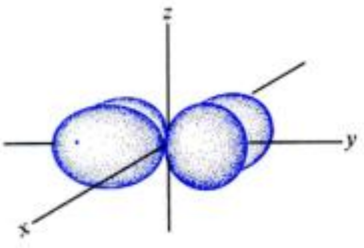
orbital d_{xz}



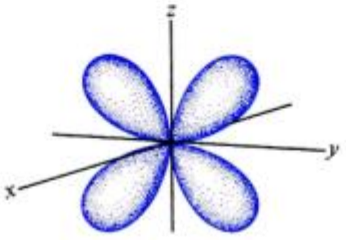
orbital d_{z^2}



orbital $d_{x^2-y^2}$



orbital d_{xy}



orbital d_{yz}

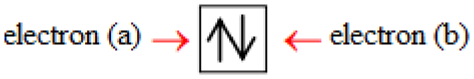
VIII. Electronic configuration of atoms and ions

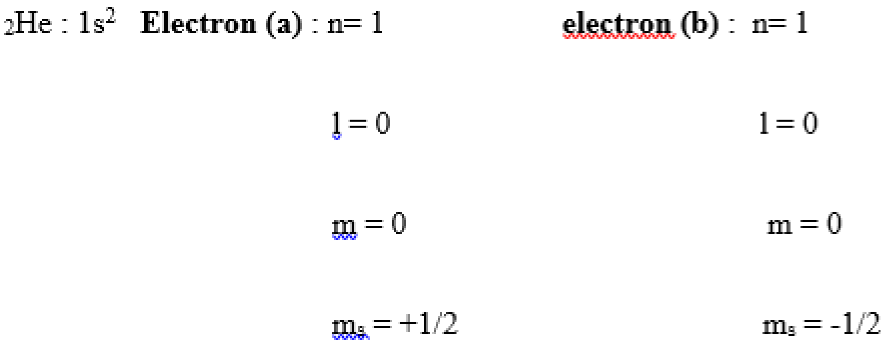
Establishing an electronic configuration means indicating the distribution of the atom's or ion's electrons within the various possible orbitals (1s, 2s, 2p. . .). The number of electrons occupying an orbital is indicated by a superscript: thus, the $1s^2$ configuration means that two electrons occupy a 1s orbital (they are described by an atomic orbital characterized by the quantum numbers n = 1 and l = 0). The order in which electrons fill atomic orbitals obeys three rules: Pauli's exclusion principle, the stability principle and Hund's rule.

VIII.1 Pauli's exclusion principle

In an atom, two electrons cannot have their four quantum numbers (n, l, m and ms) identical.

Example for the helium atom: it contains two electrons:



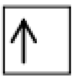
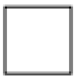


$_2$He : 1s^2 **Electron (a)** : n= 1 **electron (b)** : n= 1

l = 0	l = 0
m = 0	m = 0
m_s = +1/2	m_s = -1/2

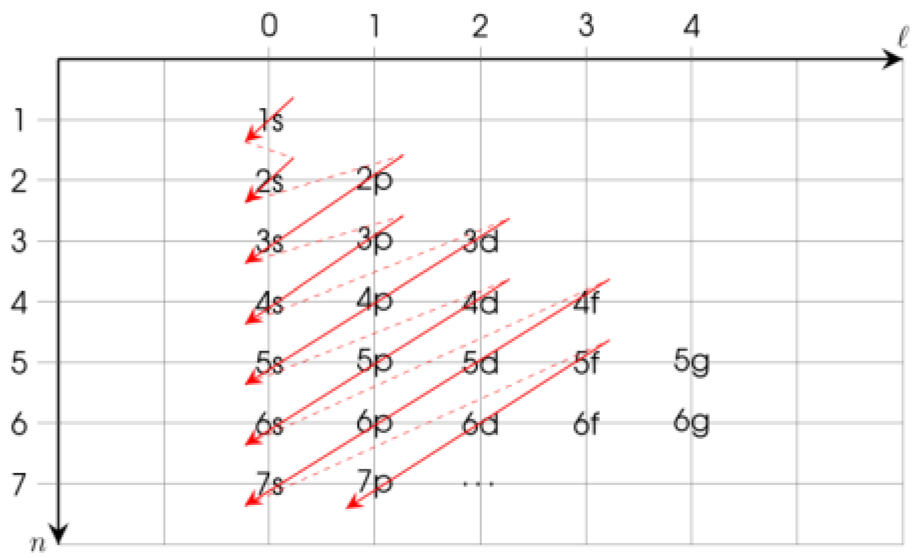
Remarque: une orbitale atomique ne peut contenir au maximum que deux électrons qui auront des spins opposés, ils sont appelés antiparallèles ou appariés

Note: an atomic orbital can only contain a maximum of two electrons with opposite spins. these are called antiparallel or paired electrons. 

- If the orbital contains only one electron, it is said to be unpaired or single. 
- An empty orbital is an electron gap 

VIII.2 Stability principle or Kelechkowski rule

Orbitals are filled according to increasing n + l values. In the case of equality, the orbitals of the lowest n value are filled first. Thus: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, ...



To quickly describe the electronic configuration of any element without having to write down all the inner layers and sublayers, the electronic configuration will be written in condensed form: [rare gas configuration] + outer layers.

A noble gas is one whose atomic number is as close as possible to the atomic number of the element in question, while remaining lower. The table below summarizes some rare gases.

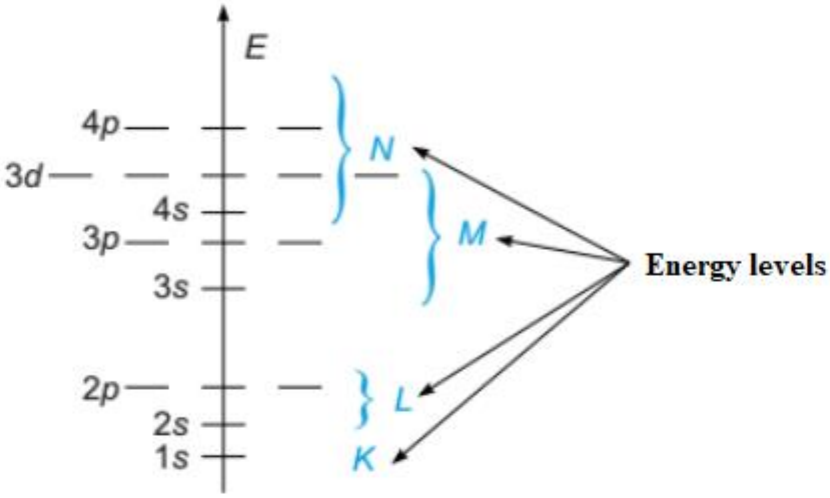
Noble gas	Symbol	Number of electrons	
Helium	He	2	$2 < Z < 10$
Neon	Ne	10	$10 < Z < 18$
Argon	Ar	18	$18 < Z < 36$
Krypton	Kr	36	$36 < Z < 54$
Xénon	Xe	54	$54 < Z < 86$
Radon	Rn	86	$Z > 86$

Exemple :

- For Z = 26   26Fe: $1S^2\ 2S^2\ 2p^6\ 3S^2\ 3p^6\ 4s^2\ 3d^6$, so the rare gas will be $_{18}[Ar]$ because Z < 26 $_{26}Fe$: $_{18}[Ar]\ 4s^2\ 3d^6$
- For : Z = 53 : $1S^2\ 2S^2\ 2p^6\ 3S^2\ 3p^6\ 4S^2\ 3d^{10}\ 4p^6\ 5S^2\ 4d^{10}\ 5p^5$ simply write : $_{36}[Kr]\ 5S^2\ 4d^{10}\ 5p^5$

- **Orbital energy classification**

The energy levels of atomic orbitals (or quantum bins) are arranged differently depending on whether the nucleus is surrounded by one or more electrons. Bohr had already established that the energy of the electron in a hydrogen atom or in chemical species with only one electron, such as the He^+ ion, depended solely on the value of n. Quantum theory did not alter this. Quantum theory has not altered this postulate. Consequently, the 2s and 2p orbitals of a hydrogen atom have the same energy. The same applies to the electron occupying one of the 3s, 3p or 3d orbitals, which are all at the same level.



The situation is quite different for polyelectronic atoms. In this case, the interactions are not limited to those between the nucleus and the electrons, but also include those between the electrons themselves. This is why the energies of electrons in polyelectronic atoms depend not only on the principal quantum number n, but also on the secondary quantum number l. As a result, the order of the quantum bins is determined by the sum of n and l; the lower the sum, the lower the energy associated with the orbital.

- **Ground state** : an atom is said to be in its ground state when it is in its most stable energy state, corresponding to its lowest energy.

Example : Establishing the electronic configuration in the ground state.

${}_{6}\mathrm{C}$: $1S^2\ \underline{2S^2\ 2p^2}$; ${}_{2}[\mathrm{He}]\ 2S^2\ 2p^2$

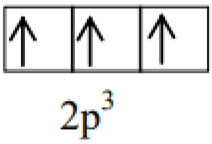
${}_{17}\mathrm{Cl}$: $1S^2\ 2S^2\ 2p^6\ \underline{3S^2\ 3p^5}$; ${}_{10}[\mathrm{Ne}]\ \underline{3S^2\ 3p^5}$

${}_{25}\mathrm{Mn}$: $1S^2\ 2S^2\ 2p^6\ 3S^2\ 3p^6\ \underline{4S^2\ 3d^5}$; ${}_{18}[\mathrm{Ar}]\ \underline{4S^2\ 3d^5}$

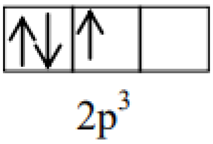
The electrons belonging to the last layer (the highest value of n) are called valence electrons and the layer : valence layer (in blue and underlined on the electronic configuration) (it's this layer that gives the elements their chemical properties). Core electrons are those in the layers closest to the nucleus (in red on the electronic configuration). They do not participate in the creation of chemical bonds.

VIII.3 Hund's rule (maximum spin rule)

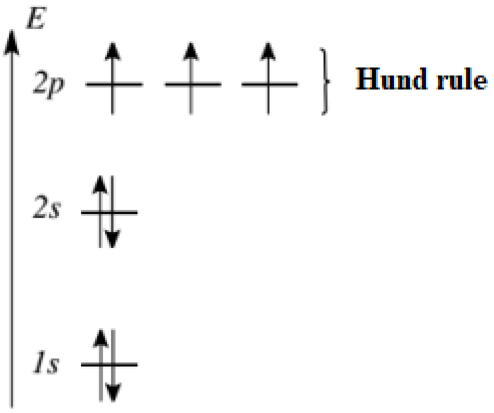
Friedrich Hund's rule states that electrons with parallel spins successively occupy orbitals of equivalent energy, i.e. differing only in orientation. Spins of the same direction are parallel. The three 2p orbitals, since they differ only in the orientation of their axes, x, y and z, are energetically equivalent. Consequently, when three electrons occupy these orbitals, they are placed in the three 2p orbitals, with their spins parallel (in the same sub-layer, electrons occupy the maximum number of quantum cells) :



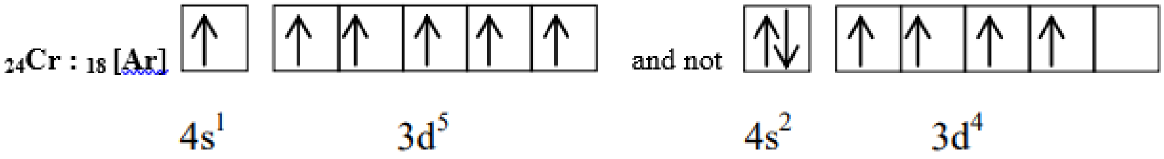
and not

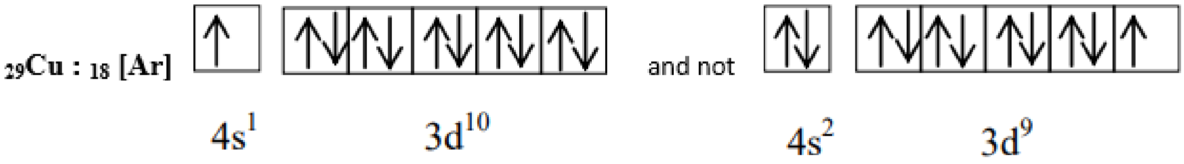


Such a representation corresponds to the ground state, as the electrons are not confined in the same space and therefore exert less repulsion on each other.



- **Exceptions to Klechkowski's rule for filling the d and f orbitals :** After filling the 3p orbitals, the 4s, 3d and 4p levels follow (see Kelechkowski's rule). The successive filling of the five d orbitals corresponds to the 10 transition elements of each period. With these elements, certain anomalies begin to appear in terms of orbital filling. For example, the electronic configuration of chromium (Z = 24) is $_{18}$ [Ar] $4S^1$ $3d^5$ rather than $_{18}$[Ar] $4S^2$ $3d^4$. Similarly, that of copper (Z = 29) is $_{18}$[Ar] $4S^1$ $3d^{10}$ rather than $_{18}$[Ar] $4S^2$ $3d^9$.



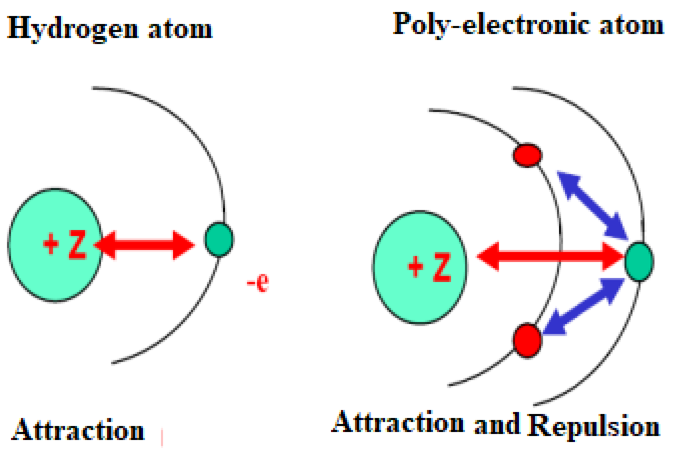


These exceptions apply to elements with an incomplete d or f sublayer, since a completely filled or 1/2-filled sublayer confers greater stability on the atoms. This principle particularly applies to configurations of the type d^9 S^2 (Cu, Ag and Au) and d^4 S^2 (Cr, Mo), which will transform into d^{10} S^1 and d^5 S^1 respectively. One electron from the S sublayer can be assumed to jump to the d sublayer, completing it with 5 or 10 electrons. The resulting configuration is then more stable than the initial one. The same rule applies to palladium, whose actual configuration is d^{10} (instead of d^8 S^2).

IX. Slater's method for polyelectronic atoms

In the case of a polyelectronic atom, solving Schrödinger's equation is impossible. A method for studying a polyelectronic atom was developed by J.S. Slater in 1930.

This method consists in calculating the atom's effective charge by considering that the numerous electrostatic interactions (attractions-repulsions) can be reduced to a small number of interactions that are simple to quantify.



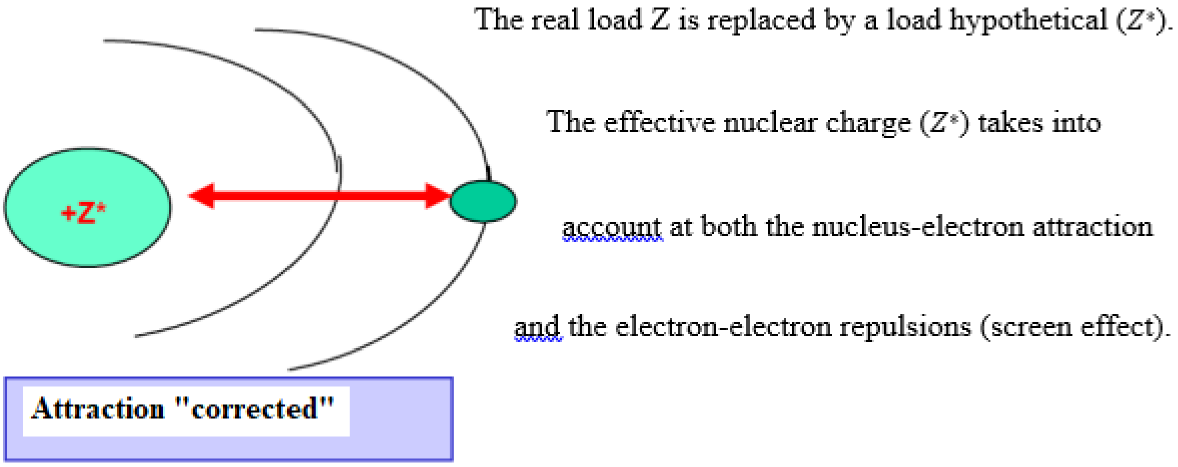
The other electrons form a screen between the nucleus and the electron

- **Effective load calculation method**

  Let's consider the attraction between the Z protons in the nucleus of an atom and any electron i under study. The attraction is disturbed by the electrons located between the nucleus and electron i, and these electrons are said to form a screen. The charge Z of the atom's nucleus then becomes an effective charge Z* relative to the electron i :

  $Z^* = Z - \Sigma\sigma$

  Where $\Sigma\sigma$: screen constant (of all other electrons). The effective charge of the nucleus Z* depends on the electron E chosen, and the total shielding coefficient $\Sigma\sigma$ is that of all other electrons.



The real load Z is replaced by a load hypothetical (Z^*).

The effective nuclear charge (Z^*) takes into account at both the nucleus-electron attraction and the electron-electron repulsions (screen effect).

Screen coefficient σ: According to Slater's proposal, screen coefficients σ are determined as follows:

- ✓ Atomic orbitals are separated into several groups: │1S│2S2p│3S3p│3d│4S4p│4d│4f│5S5p│5d│5f│…
- ✓ The σi screen coefficient for electron i is equal to the sum of the σij coefficients for all electrons other than i.

The calculation is based on the following rules: for an occupying electron:

The 1S atomic orbital : the screen coefficient of the other 1S electron is 0.31

The S or p atomic orbital : the screening coefficient due to an electron in an atomic orbital of principal quantum number n' is :

$$\sigma_{ij} = 1 \text{ if } n' < n-1$$

$$\sigma_{ij} = 0{,}85 \text{ if } n' = n-1$$

$$\sigma_{ij} = 0{,}35 \text{ if } n' = n$$

$$\sigma_{ij} = 0 \text{ if } n' > n$$

The d or f atomic orbital : the screen coefficient is 0.35 for one electron of the same group and 1 for all the others.

The values of σij are summarized in the following table :

	State of the shielding electron j						
Electron studied i	**1s**	**2s2p**	**3s3p**	**3d**	**4s4p**	**4d**	**4f**
1s	**0.31**	**0**	**0**	**0**	**0**	**0**	**0**
2s2p	**0.85**	**0.35**	**0**	**0**	**0**	**0**	**0**
3s3p	**1**	**0.85**	**0.35**	**0**	**0**	**0**	**0**
3d	**1**	**1**	**1**	**0.35**	**0**	**0**	**0**
4s4p	**1**	**1**	**0.85**	**0.85**	**0.35**	**0**	**0**
4d	**1**	**1**	**1**	**1**	**1**	**0.35**	**0**
4f	**1**	**1**	**1**	**1**	**1**	**1**	**0.35**

In 1960 Slater introduced an apparent quantum number n* to reduce the differences between experimental and calculated values. It is necessary to introduce n* from the 4ème period onwards.

n	**1**	**2**	**3**	**4**	**5**	**6**
n*	**1**	**2**	**3**	**3.7**	**4**	**4.2**

The energy of an electron i in a given atom is given by : $E_i = \frac{-13,6}{n_i^{*2}} Z_{eff}^{*2} (eV)$

The total energy of the atom is the sum of the contribution of each electron : $E_t = \sum_i E_i$

The radius of the atomic orbit is given by the formula :

$$E_i = \frac{n^{*2}}{Z_{eff}^{*}} a_0 \text{ avec } a_0 = 0.53 \text{ A°}$$

Adding one or more electrons increases the shielding effect and decreases $(Z*)$ the radius. Anions are therefore always larger than their original neutral atoms. Conversely, if electrons are removed, the shielding effect decreases and $(Z*)$ increases, causing the radius to decrease. Cations are therefore always smaller than their original atoms.

$$\text{Additio of electrons} \longrightarrow \text{Screen effect} \uparrow \Rightarrow Z^* \downarrow \Rightarrow r \uparrow$$

$$Retrait \text{ of electrons} \longrightarrow \text{Screen effect} \downarrow \Rightarrow Z^* \uparrow \Rightarrow r \downarrow$$

Example : consider the sulfur atom $_{16}S$: $1s^2 \,|\, 2s^2\, 2p^6 \,|\, 3s^2\, 3p^4$, 3 Slater groups

Group $[1s^2]$: each 1s electron receives the shielding effect of the second electron. Its effective charge is $Z_{1s}^* = 16 - \sigma_{1s} = 16 - 0,31 = 15,69$ and has an energy of

$$E_1 = \frac{-13,6}{n_1^{*2}} Z_{1s}^{*2} = \frac{-13,6}{1} \times (15,69)^2 = -3347,995 \text{ eV}$$

Group $[2s^2\, 2p^6]$: there are 8 electrons on the second layer, and each electron is shielded by 7 other electrons in addition to the shielding effect of the two electrons on the 1s layer. The effective charge of an electron is then : $Z_{2s,2p}^* = 16 - (7 \times \sigma_{2s,2p} + 2 \times \sigma_{1s}) = 16 - (7 \times 0,35 + 2 \times 0,85) = 11,85$

And its energy is : $$E_2 = \frac{-13,6}{2^2} \times (11,85)^2 = -1909,746 \text{ eV}$$

Group $[3s^2\, 3p^4]$: there are 6 electrons on layer 3, and each electron is shielded by 5 other electrons in addition to: the shielding effect of the 2 electrons on layer 1s and the 8 electrons on layer $2s^2\, 2p^6$. The effective charge of an electron on layer 3 is then :

$Z_{3s,3p}^* = 16 - (5\times0,35 + 8\times0,85 + 2\times1) = 5,45$

and its energy is : $$E_3 = \frac{-13,6}{3^2} \times (5,45)^2 = -44,8838 \text{ eV}$$

IX.1. Ionization energy

$$A - -\longrightarrow A^{+} + 1\ e-$$

$$E_{I1} = E_{A+} + E_{e-} - E_{A}$$

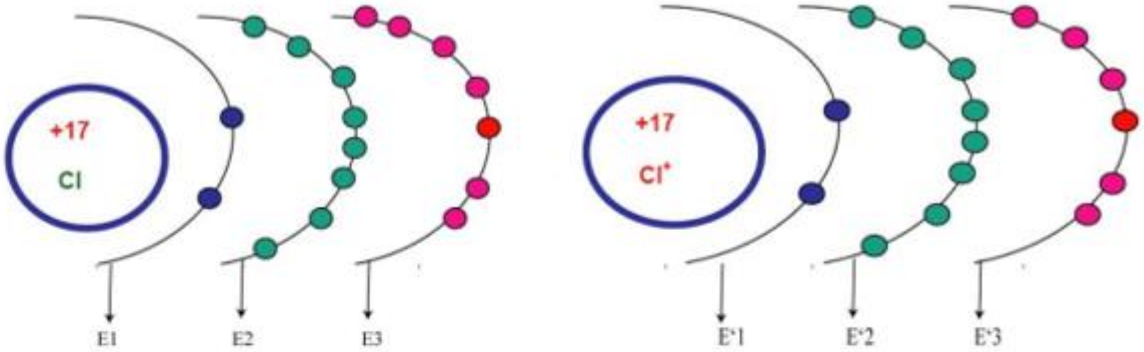
The electron's energy is zero, since ionization has taken place and the electron is at infinity and no longer interacts with the nucleus $Ee- = 0$ (no interaction with the nucleus).

$$\mathbf{E_{I1} = E_{A+} - E_{A}}$$

By evaluating the energy of (A) and (A^+), we can evaluate the ionization energy by the difference between the two. The total energy of the atom will be evaluated by the sum of the individual electron energies.

The energy of the atom = sum of the orbital energies of all the electrons.

Example : chlorine



: $[1\ s^2]$:$[2\ s^2, 2\ p^6]$: $[3\ s^2, 3\ p5]$

$E_{Cl} = 2\ E_1 + 8\ E_2 + 7\ E_3$

Bohr : $E_n = -13{,}6\frac{Z^2}{n^2}$

$[1\ s2]$:$[2\ s2, 2\ p6]$: $[3\ s2, 3\ p4]$

$E_{Cl+} = 2\ E'_1 + 8\ E'_2 + 6\ E'_3$

Slater: $E_{n.l} = -13{,}6\ \frac{Z^{*2}}{n^{*2}}$

The orbital energy of an electron depends only on Z* et de n, if these two quantities are identical, the energy will be the same. This is the case for the inner layers, which are not affected by ionization. We therefore have : $E_1 = E'_1$; $E_2 = E'_2$

$E_{I1} = E_{Cl+} - E_{Cl} = 2\,E'_1 + 8\,E'_2 + 6E'_3 - 2E_1 - 8E_2 - 7E_3 = 6E'_3 - 7E_3$

$Z_{E3^*} = 17 - (6.0{,}35) - (8.0{,}85) - (2\,.1) = 6{,}1$

$E_3 = -13{,}6\,.\frac{(6{,}1)^2}{(3)^2} = \text{-}56{,}23\ \text{eV}$

$Z_{E3'^*} = 17 - (5.\ 0{,}35) - (8.\ 0{,}85) - (2\,.1) = 6{,}45$

$$E'_3 = -13{,}6\,.\frac{(6{,}45)^2}{(3)^2} = -62{,}866\ eV$$

$E_{I1} = E_{Cl+} - E_{Cl} = 6E'_3 - 7E_3 = 16{,}39\ e\text{V}$

Successive ionization energies

These are the energies associated with the following reactions :

$A --\longrightarrow A^+ + 1\ e-$ $\quad 1^{\text{ère}}$ ionisation EI1

$A^+ --\longrightarrow A^{2+} + 1\ e-$ $\quad 2^{\text{ème}}$ ionisation EI2

....

$A^{(z-1)} --\longrightarrow A^{z+} + 1\ e-$ $\quad Z^{\text{ème}}$ ionisation EIz