IV. Electronic structure of the atom

IV.1. Beginning of quantum theory

Classical physics (the body of physical theories validated up to the end of the 19th century) has shown a weakness when it comes to complicated scientific subjects.

- Rutherford's model takes into account the existence of different elements and isotopes, but provides no basis for interpreting the diversity of elemental properties (metals, non-metals, inert gases, etc.), nor their valence. What's more, it doesn't justify the characteristics of atomic emission spectra **.**

Other, more efficient models have been devised, including the quantum model or the Bohr model, in which the electron is considered as a particle in motion. It's not the most modern model of the atom, but its explanatory power is interesting**...**

- A black body is an idealized object that absorbs and emits all frequencies. We know, for example, that when the burner on an electric stove is heated, it first turns a dull red and then becomes progressively redder as the temperature rises. Classical physics was unable to explain and predict the variation in radiation intensity with temperature **.**

The first person to offer a successful explanation of blackbody radiation was German physicist Max Planck in 1900. He hypothesized that the radiation emitted by the black body was caused by the oscillations of electrons in the particles making up matter. He made the revolutionary assumption that the energies of the oscillators are discrete and must be proportional to an integer multiple of the frequency, or in the form of an equation, $E = nh\upsilon$,

where E is the energy of an oscillator, n is an integer h is a constant of proportionality (Planck's constant, $h = 6.626.10^{-34}$ J.s), υ is the frequency**.** The amount of energy that can be transferred is always an integer multiple of hu, $1h\upsilon$, $2h\upsilon$, $3h\upsilon$ ...etc. The energy is then said to be quantized,

- In 1905, Albert Einstein suggested that light energy is also quantized. It is made up of a stream of "particles", called photons, whose energy is:

$E = h\upsilon=hc/\lambda$

IV.1.1. Photoelectric effect

The photoelectric effect consists in the emission of electrons from a material subjected to light irradiation (Figure IV.1). The experiment was announced as follows: if a metal plate of energy E_0 is illuminated with monochromatic light of energy E greater than the energy of the metal ($E>E_0$), the excess energy over the characteristic energy of the metal is dissipated in the form of kinetic energy taken up by the electrons.

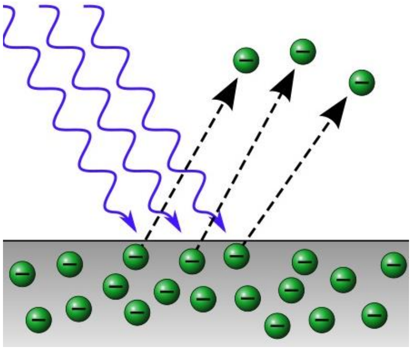

Figure IV.1 : Photoelectric effect experiment

According to Einstein: light, in addition to possessing wave-like properties, can be considered as composed of corpuscles called photons, which have no mass but possess energy E=hυ. If a photon is absorbed by a material, the electron ejected has a kinetic energy (Ec) equal to the difference between the two characteristic energies..

$$E_c=E_{photon} - E_{material} = \frac{1}{2}mv^2$$

Example:

Calculate the electron velocity extracted under the following conditions: λ = 430 nm, E_0 = 2.4 eV

IV.1.2. electromagnetic radiation

Electromagnetic radiation, of which Visible light is an example, is a form of energy. Electromagnetic radiation is an electromagnetic wave due to a perpendicular electric field $\vec{E}$ and magnetic field $\vec{B}$ oscillating in phase (Figure IV.2), can be difracted and interfered with (James Clark Maxwell 1860).

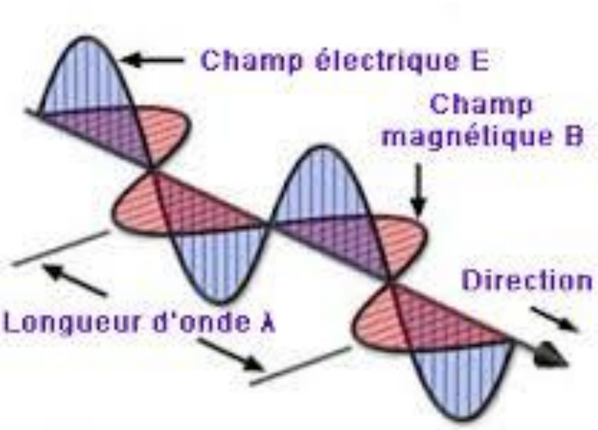

Figure IV.2 : Electromagnetic wave

Electromagnetic radiation is also characterized by a propagation speed c, which depends on the propagation medium, by a frequency υ (number of vibrations per second) and by a wavelength λ (distance covered per vibration). Since frequency is the number of wavelengths covered in one second, these three quantities are linked by the following relationship:

$$c = \lambda \times \nu = \frac{\nu}{\bar{\nu}}$$

c : 2,997925 . 10^8 m/s, λ : wavelength (nm), ν: frequency (Hz), $\bar{\nu}$: Wavenumber (cm^{-1})

$$\bar{\nu} = \frac{1}{\bar{\lambda}}$$

Frequency and wavelength can have various values, from which we distinguish particular domains of electromagnetic radiation, as shown in Figure IV.3.

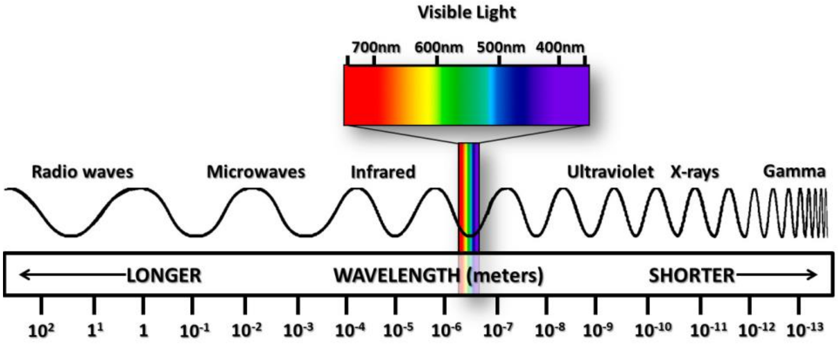

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Figure IV.3: Electromagnetic spectrum. Visible light (bottom enlargement) is only a small part of the spectrum.

Example:

The wavelength of sodium vapour is 5900 A°; the speed of light $C=3.10^8$ m/s; Plank's constant $h=6.62.10^{-34}$ J.s.

Calculate :

a) The associated wave number in cm^{-}.

b) The frequency and period of the wave.

c) The energy of the photons emitted.

IV.2 Wave-matter interaction

IV.2.1. Emission and absorption of radiation by matter

Energy can be exchanged between matter and radiation in two directions (Figure IV.4):

- Emission: These are phenomena of radiation emission due to a return to the stable state of one or more atoms.

Example: Light emitted by the sun and flame.

- Absorption: This is an absorption phenomenon due to a transition to the excited state of one or more atoms.

Example: X-rays are absorbed by a part of the human body.,

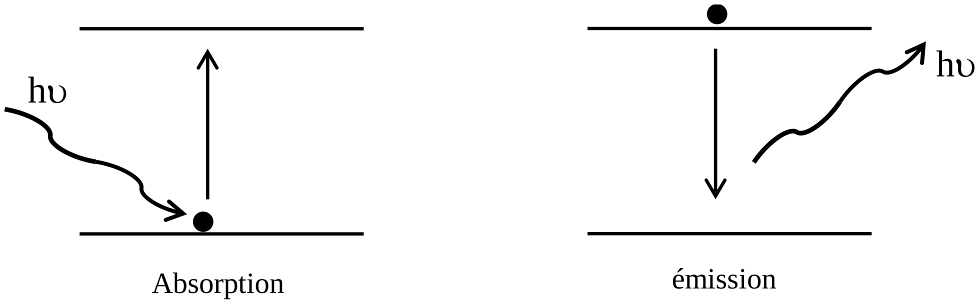

Figure IV.4 : Diagram of radiation absorption and emission phenomena

IV.2.2. Continuous and discontinuous spectra

A continuous spectrum shows continuity between the spectral lines. For example, the rainbow contains all the colors, with a continuous transition from ultraviolet to infrared; this is a continuous spectrum, because the wavelengths form an uninterrupted whole of colors (Figure IV.5.a).

A discontinuous spectrum does not present continuity between the spectral lines (Figure IV.5.b), for example, light emitted by an electric arc..

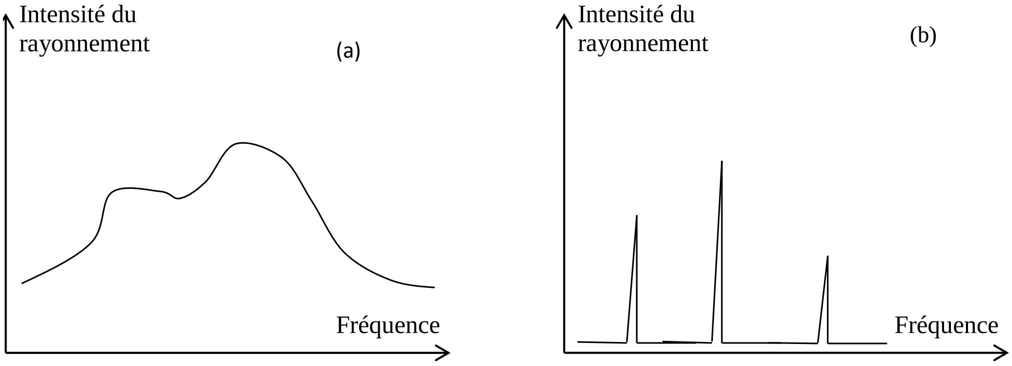

Figure IV.5: Variation of radiation intensity as a function of frequency. a) continuous spectrum, b) discontinuous spectrum

IV.2.3. Hydrogen spectrum

When a high voltage is applied to hydrogen atoms in a gaseous state under very low pressure, light is emitted. The resulting beam is decomposed by a prism to give lines corresponding to characteristic wavelengths in the IR, UV and Vis range, which can be detected using a photographic plate (Figure.IV.6).

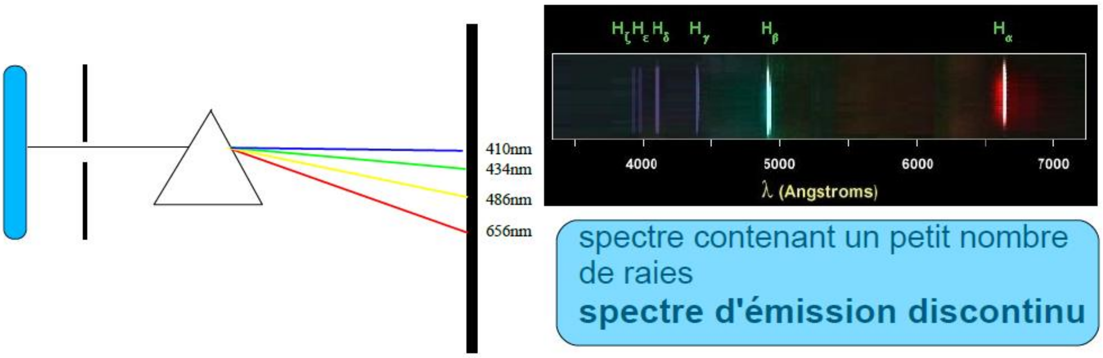

Figure.IV.6 : Hydrogen line spectrum

As atomic hydrogen gains energy, the atoms enter an unstable excited state. They then return to the ground state (lowest energy), emitting photons. Each line in the spectrum corresponds to a transition between 2 energy levels (Figure IV.7).

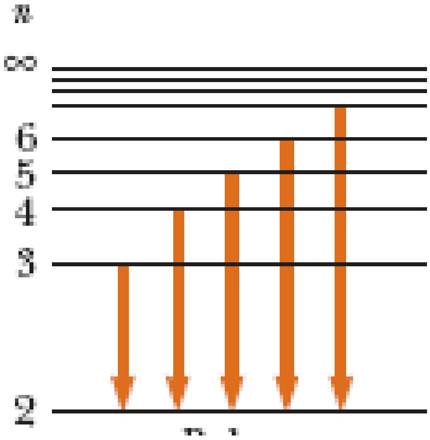

Figure IV.7 : Transitions to level n=2 (Balmer series)

In 1885, Johann Jacob Balmer published an empirical formula for calculating the wavelengths of the spectrum of the hydrogen atom. He found that the wavelengths of the red, green and blue lines emitted by hydrogen satisfied this equation.

$$\frac{1}{\lambda} = \mathrm{R_h} \times \left(\frac{1}{2^2} - \frac{1}{n^2}\right)$$

$\mathrm{R_h}$: constant of Rydberg=1.097373 10^7 $\mathrm{m^{-1}}$.

n : positive integer greater than 2

Example :

Calculate the hydrogen emission wavelength for a transition between level 2 and level 5.

Solution:

$$\frac{1}{\lambda} = 1{,}097373\ 107 \times \left(\frac{1}{2^2} - \frac{1}{5^2}\right) = 4{,}34\ 10^{-7} = 434\ 10^{-9} m = 434\ nm$$

The spectrum of hydrogen is a discontinuous spectrum, since it presents only a few lines in the visible and without continuity, known as the Balmer series lines. This series takes into account several values of n (n=3, 4, 5, 6 and 7) corresponding to the wavelengths 656.5, 486.1, 434, 410.1 and 397 nm respectively.

As we have shown in this short, the electromagnetic spectrum contains not only the visible range but other spectral regions such as the ultraviolet and infrared. Hydrogen has emission lines that did not satisfy the previous equation.

For this reason, in 1888 physicist Johannes Rydberg generalized Balmer's formula to satisfy all the emission lines of the hydrogen atom. The new formula is called the Rydberg equation..

$$\frac{1}{\lambda} = \mathrm{R_h} \times \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

n_f and n_i are integers such that $n_f<n_i$

The other transitions were discovered and each series was given the name of its owner. Table IV.1 shows the names of the series and the spectral ranges they occupy as a function of quantum number.

Table IV.1: Hydrogen atom spectral series

series	transition	spectral range
Lyman	$n_f =$ et $n_i > 1$	RX et UV
Balmer	$n_f = 2$ et $n_i > 2$	Visible
Paschen	$n_f = 3$ et $n_i > 3$	IR
Brackett	$n_f = 4$ et $n_i > 4$	IR
Pfund	$n_f = 5$ et $n_i > 5$	IR

IV.3. Bohr Model

IV.3.1. Quantum Theory

According to the classical model, the electron orbits the nucleus while emitting light, implying that the energy of this electron gradually decreases, and it should gradually approach the nucleus and eventually fall onto it. As a result, atoms become unstable, which contradicts reality. Niels Bohr proposed a model of the atom in 1913 that resolves these contradictions based on Planck's theory.

IV.3.2. Bohr's postulates

Niels Bohr was the first to establish a connection between the spectra and the quantum ideas of Planck and Einstein. He constructed a new model of the atom, with the following key features:

- In the atom, the nucleus is stationary while the electron, with mass 'm,' moves around the nucleus in a circular orbit of radius 'r.'
- The electron can only exist on privileged orbits without emitting energy; these are called "stationary orbits, and is subject to two forces
- When an electron transitions from one level to another, it emits or absorbs energy.

$$\Delta E = h\nu = \left|E_f - E_i\right|$$

Example

What is the wavelength of the radiation λ emitted during deexcitation from the E_4 level to the E_2 level? To which domain does this radiation belong?

Data: $h = 6.626 \,.\, 10^{-34}$ J.s;

$c = 3.00 \,.\, 10^{8}$ m.s-1 ; 1.00 eV = $1.60 \,.\, 10^{-19}$ J.

- Assuming that the electron is described by a wave and that an integer number of wavelengths must fit into the circumference of the electron's orbit, we have the following equation:

$\boxed{2\pi r = n\lambda}$ (n = 1, 2, 3...)

- Louis de Broglie : To every moving particle is associated a wavelength

$$\lambda = \frac{h}{mv}$$

- The angular momentum of the electron can only take on integer values (quantization of angular momentum :$\vec{L} = mvr = \frac{nh}{2\pi}$

We know that the vector product of two vectors yields a vector perpendicular to both.

$$\vec{L} = \vec{p} \wedge \vec{r}$$

p is the movement quantity equal to the mass multiplied by the velocity (p=m*v)

$$\vec{L} = m * \vec{v} \wedge \vec{r} \implies \vec{L} = m\vec{v} * \vec{r} sin 90 = mvr$$

Bohr evoked a relationship between the electron's angular momentum and the quantum number n: the variation of implies a variation in L. He translated this result into the following relationship

$$\vec{L} = \mathrm{mvr} = \frac{nh}{2\pi}$$

h: Planck's constant and n: natural number.

- The electron and nucleus are separated by a distance r, which is the radius of the orbital.

$r = \frac{h^2}{4k\pi^2 me^2} n^2 = 0.52 \, . \, 10^{-10}$ m

n: principal quantum number

r: distance between nucleus and electron

h: Planck's constant

m: electron mass

e: charge

The closest orbit to the proton is that corresponding to the n = 1 layer.

- The energy levels of the hydrogen atom have the following values in eV:

En = – 13.6 / n^2.

- For hydrogenoids: An hydrogenoid is a monoatomic entity having only one electron ($_1H$, $_2He^+$, $_3Li^{2+}$…). An hydrogenoid can be written in the following way $_ZX^{(Z-1)+}$, where X is the chemical element, and Z is the atomic number. An hydrogenoid leads to results similar to those of hydrogen. Indeed, for the considered energy level n, we have

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

$$r_n = a_0 \times \frac{n^2}{Z}$$

$$\nu = \mathrm{R_h} \times \mathrm{c} \times Z^2 \left(\frac{1}{\mathrm{n_f^2}} - \frac{1}{\mathrm{n_i^2}}\right)$$

Examples:

1. Calculate, in eV and joules, the energy of the first four levels of the Li^{2+} hydrogenoid ion

2. What energy must a Li^{2+} ion absorb, for the electron to pass from the ground state to the first excited state?

We give: Li (Z=3) 1eV= $1.6.10^{-19}$ Joules

h= $6.62.10^{-34}$ J.s c = 3.10^{8} m.s^{-1}

IV.4. Shortcomings of the Bohr Model

- The relation used to calculate the frequency of the transition between two energy levels is not valid for a polyatomic atom.
- This theory proves insufficient to explain the splitting of spectral lines observed when applying an intense magnetic field (Zeeman effect) or an intense electric field (Stark effect).
- The energy of electrons is quantized; it can only take certain values, and this idea is retained.
- The motion of electrons occurs in circular or elliptical trajectories; this idea is abandoned and replaced by the probability of presence.

IV.5. Quantum numbers

IV.5.1. The principal quantum number n:

The principal quantum number, n, describes the main energy level of an occupying electron. This number defines the size of the orbital, and as we've seen before, the system's energy is expressed in terms of the principal quantum number, n

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

The principal quantum number, n, is an integer: n = 1: K shell n = 2: L shell n = 3: M shell n = 4: N shell n = 5: O shell n = 6: P shell n = 7: Q shell"

IV.5.2. The secondary (or azimuthal) quantum number, l

The secondary quantum number describes the shape of the region in space that an electron occupies. This number (l) can take integer values from 0 up to and including (n - 1). It defines the electron subshells

"l = 0: s orbitals, l = 1: p orbitals, l = 2: d orbitals, l = 3: f orbitals

IV.5.3. The tertiary (or magnetic) quantum number, m_l

The magnetic number is an integer; it can take negative values ranging from –l to +l. Thus, when the secondary number l equals 3, the magnetic number ml can take the seven following values: -3, -2, -1, 0, +1, +2, +3. This number defines the orientation of the atomic orbital.

IV.6.4. The spin quantum number, s (or m_s)

The spin quantum number is related to the intrinsic magnetism of the electron. It can only take two values, equal and opposite: -1/2 and +1/2. This number defines the electron's rotation about its own axis

.

Table IV.2. Allowable values of quantum numbers at n = 3

n	**l**	**m_l**	**S(m_s)**	**Electron number in external shell $2n^2$**	**Electron number of subshell (4l+2)**
1	0	0	-1/2, +1/2	2	2
2	0 1	0 -1, 0, +1	-1/2, +1/2 ±1/2 for each value of m_l	8 8	2 6
3	0 1 2	0 -1, 0, +1 -2, -1, 0, +1, +2	-1/2, +1/2 ±1/2 for each value of m_l	18 18 18	2 6 10
4	0 1 2 3	0 -1, 0, +1 -2, -1, 0, +1, +2 -3, -2, -1, 0, +1, +2, +3	-1/2, +1/2 ±1/2 for each value of m_l	32 32 32 32	2 6 10 14

IV.7. Wave Model of the Atom

Bohr's quantum model incorporates two main ideas: the electron's energy is quantized, and its movement occurs in stable and circular trajectories. The latter has been replaced by the probability of presence in a new model of the atom called the wave model. This model was developed by the Austrian physicist Erwin Schrödinger, who studied the atom's structure by considering the electron as a wave.

IV.7.1. Louis De Broglie's Hypothesis

To explain the photoelectric effect, Einstein proposed the hypothesis that light, generally perceived as a wave, can be considered as a particle without mass. In 1924, Louis de Broglie suggested associating a free electron with mass (m) moving at a velocity (v) with a wavelength (λ) defined by the relationship:

$$\lambda = \frac{\mathrm{h}}{\mathrm{m} * \mathrm{v}} = \frac{\mathrm{h}}{\mathrm{p}}$$

Considering that (p) represents the momentum.

IV.7.2. Heisenberg's Uncertainty Principle

In our everyday lives, we can simultaneously determine the position and speed of a car, but this is not the case for microscopic particles. Heisenberg's uncertainty principle is stated as follows: All physical quantities in the macroscopic world cannot be observed simultaneously in the submicroscopic world.

For example: If a mass (m) is moving along a trajectory with a velocity (v) at time (t), we cannot precisely know both its position and its momentum (p) at the same time. If we denote Δx as the uncertainty in its position and Δp as the uncertainty in its momentum (p),

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

$$\Delta p = m * \Delta v$$

$$\Delta x * \Delta v \geq \frac{h}{2\pi * m}$$

In the case of an electron, we cannot ignore both terms Δx and Δp

IV.7.3. Wave Function and Schrödinger's Equation

The wave model takes the perspective of considering the electron as a wave rather than a particle (Figure IV.12). A moving particle is associated with a wave whose amplitude depends on the space and time coordinates of the particle, denoted as Ψ(x, y, z, t). Ψ (psi) is the wave function of the particle (electron).

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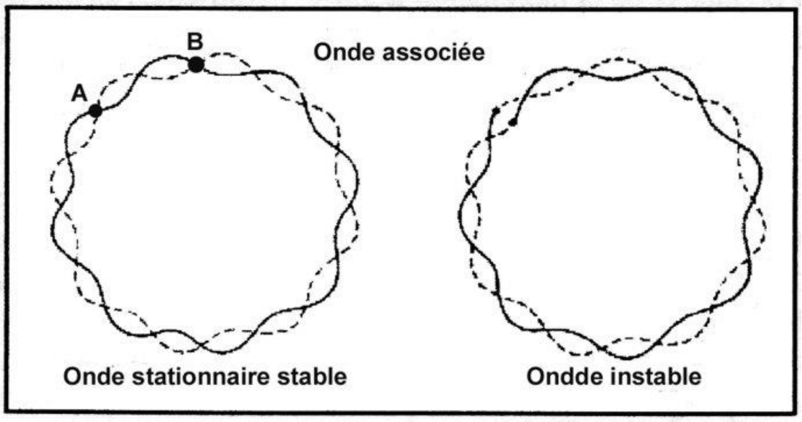

Figure IV.12 : Representation of the trajectory of an electron around the nucleus and its associated wave

IV.7.3.1. Schrödinger model

Generally, the Schrödinger model is summarized in the following points:

- The behavior of the electron in the atom is described using a stationary wave (a wave that has at least two nodes separated by a distance λ/2 (Figure IV.13)).

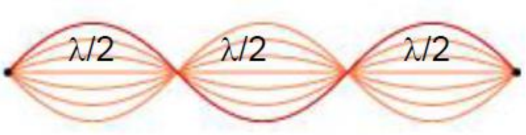

Figure IV.13 : Diagram of a standing wave.

- Each wave function (Ψ) corresponds to an energy En.
- As a consequence of the first two points, the energy of an electron is quantized, meaning the electron can only have certain values of energy.
- The square of the wave function (Ψ^2) is related to the probability of finding the electron, denoted as dP, in a given region of space. The probability of finding the electron in a volume dV at the point M(x, y, z) is expressed as:

$$dP = \Psi^2 \times dV$$

The ratio dP/dV = Ψ^2 is called the probability density of the electron's presence at the considered point, also referred to as "electron density”

For an infinite volume, we are certain to find it there, and thus the probability is equal to 1. This is the normalization condition.:

$$\int_{espace} \Psi^2 \times dV = 1$$

- Other boundary conditions:

- Ψ(x,y,z,t) must be continuous at every point,
- Ψ(x,y,z,t) must be finite at every point.,
- Ψ(x,y,z,t) →0 when x or y or z → ∞

Schrödinger's theory precisely defines the energy of the electron. According to the Heisenberg principle, it is impossible to pinpoint the electron's location accurately. The model provides a probability of finding the electron at a given point in space in a determined energy state. The region where it is most likely to be found is called an orbital. Different orbitals can be obtained based on the variation of Ψ^2.

- Solving the Schrödinger equation for an electron in three-dimensional space necessarily involves three integers, the quantum numbers n, l, and ml: Ψ_(n,l,m). These numbers follow specific rules.

IV.7.3.2. Wave Function

The Schrödinger equation can be derived from the particle's motion equation. The vibrational motion of the electron on a stationary orbital (same amplitude "a" and same λ) is considered (Figure IV.14).

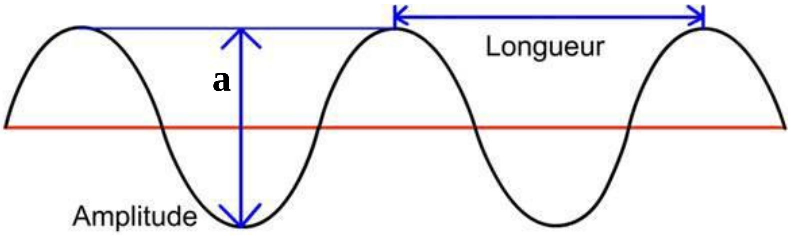

Figure IV.14 : Diagram of the propagation of a wave.

The expression for the standing wave is:

$$\psi(x) = A * sin\frac{2\pi}{\lambda}x$$

The first and second derivatives of this equation yield:

$$\frac{d\psi(x)}{dx} = A.\frac{2\pi}{\lambda}.cos\frac{2\pi}{\lambda}x$$

$$\frac{d^2\psi(x)}{dx^2} = -\frac{4\pi^2}{\lambda^2}A.sin\frac{2\pi}{\lambda}x = -\frac{4\pi^2}{\lambda^2}.\psi(x)$$

We obtain a second-order differential equa:

$$\frac{d^2\psi(x)}{dx^2} + \frac{4\pi^2}{\lambda^2}.\psi(x) = 0$$

Let E be the total energy of the particle, Ec its kinetic energy, and Ep its potential energy:

$$E = E_c + E_p \Rightarrow E - E_p = \frac{1}{2}mv^2 \Rightarrow 2m(E - E_p) = m^2v^2$$

$\frac{4\pi^2}{\lambda^2} = 4\pi^2\left(\frac{m^2v^2}{h^2}\right)$ d'où $\frac{4\pi^2}{\lambda^2} = 8\pi^2m\left(\frac{E-E_p}{h^2}\right)$

D'où $\frac{d^2\psi(x)}{dx^2} + \frac{8\pi^2m}{h^2}(E - E_p)\psi(x) = 0$ The one-dimensional Schrödinger equation can be expressed as follows:.

Generalizing to three spatial dimensions and introducing the Laplacian operator ∇^2, the Schrödinger equation becomes::

$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ avec $E_p = E_x + E_y + E_z$

$$\hat{H} = \frac{-h^2}{8\pi^2m}\Delta + E_p$$

$\Delta\psi + \frac{8\pi^2m}{h^2}(E - E_p)\psi = 0$ Schrödinger's equation in three dimensions is written in symbolic form as follows:

$\hat{H}\psi = E\psi$

$\hat{H}$: It represents an operator, called the Hamiltonian, which, when applied to the function ψ, transforms it into another function. Its expression depends on the system under consideration.

$E\psi$: It is a product of the function ψ and its associated energy E.

The solutions of the Schrödinger equation must satisfy a number of conditions: the wave function ψ must be unique, finite, and continuous with respect to x, y, and z. It must also satisfy the normalization condition, which is achievable only for certain values of the energy called eigenvalues. This leads to the quantization of the system's energy.

IV.8. Solution of the Schrödinger Equation for the Hydrogen Atom

The hydrogen atom consists of a proton and an interacting electron. Since the mass of the proton is approximately 2000 times that of the electron, we consider the proton as fixed (Born-Oppenheimer approximation). The reference frame with the nucleus as the origin is thus considered Galilean (Figure IV.15)..

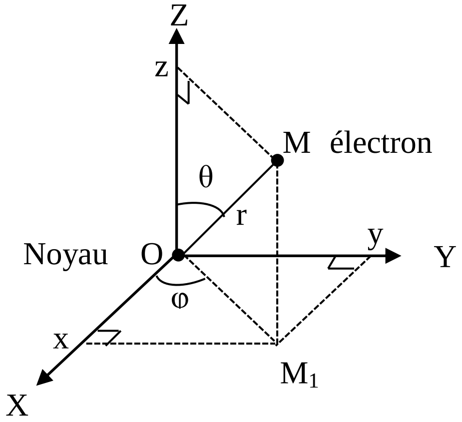

Figure IV.15 : : Presentation of the electron using spherical coordinates.

The forces applied to the electron include the electrostatic force $(\overrightarrow{f_{el}})$ exerted by the nucleus and the gravitational force, the latter being negligible compared to the electrostatic force.

$$\overrightarrow{f_{el}} = +\frac{(-e).(+e)}{4\pi\varepsilon_0}.\frac{\overrightarrow{u_r}}{r^2}$$

The space is referred to a trihedron (O, x, y, z) where the origin coincides with the nucleus position. For an isolated hydrogen atom, space is isotropic (does not depend on the direction), and the position of the axes is arbitrary. Furthermore, since the potential energy of the system originates from electrostatic forces and only involves the nucleus-to-electron distance, it is convenient to use spherical coordinates with the origin O..

Solving the Schrödinger equation for this system leads to wave functions ψψ dependent on the variables rr, θθ, and ϕϕ. The position of point M is represented in Cartesian coordinates by the triplet (x,y,z). We can also use the triplet (r,θ,ϕ), where θ and ϕ are angle measures, and r is a distance: θ=(Oz,OM) ; φ=(Ox,OM_1). To cover the entire space, it is sufficient for r to vary from 0 to +∞, θ to vary from 0 to π, and ϕ to vary from 0 to 2π.

The relationship between the Cartesian coordinates M and its spherical coordinates is expressed as follows::

$z= r . \cos \theta$

$x= r . \sin \theta . \cos \varphi$

$y= r . \sin \theta . \sin \varphi$

IV.8.1. Wave Functions of the Hydrogen Atom

The function $\psi(r,\theta,\varphi)$ It is the product of three functions:

$\psi(r,\theta,\varphi) = R(r) . \Theta(\theta) . \Phi(\varphi)$

R : The radial part of psi, as it only depends on the variable r..

Θ(θ) . Φ(φ) : The angular part of the wave function, as it only depends on the angular coordinates θ and φ, often referred to as Y(θ, φ).

The solutions of the Schrödinger equation for the hydrogen atom provide wave functions that describe the various states accessible to a single electron in hydrogen. Each of these potential states is described by four quantum numbers. These quantum numbers play a crucial role in describing the energy levels of electrons and the shapes of orbitals that depict the distributions of electrons in space.

The wave functions of the hydrogen atom, or atomic orbitals, are characterized by the quantum numbers n, l, and m_l:

$\psi_{n,l,m_l}(r,\theta,\varphi) = R_{n,l}(r) . \Theta_{l,|ml|}(\theta) . \Phi_{ml}(\varphi)$

As we can see, R(r) depends on the numbers n and l, Θ(θ) depends on the numbers l, |ml|, and $\Phi_{ml}(\varphi)$ depends on the quantum numbers m_l.

IV.8.2. Expressions of the Orbitals of the Hydrogen Atom

The mathematical expression of the radial and angular parts of the wave function is written as follows:

$$R_{n,l}(r) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n\,(n+l)!}}\, e^{-\left(\frac{r}{na_0}\right)} r^l L_{n-l-1}^{2l+1}(r)$$

$$Y_{l,m_l}(\theta,\phi) = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m_l)!}{(l+m_l)!}}\, P_l^{m_l}(\cos\theta) e^{i m_l \phi}$$

Table IV.3 provides the expressions of the radial and angular parts of some orbitals of the hydrogen atom.

n	ℓ	$R_{n,\ell}(\mathrm{r})$	m_ℓ	$Y(\theta, \varphi)$	orbitale
1	0	$R_{1,0} = \left(\frac{1}{a_0}\right)^{3/2} . 2\,\mathrm{e}^{-\frac{r}{a_0}}$	0	$\frac{1}{\sqrt{4\pi}}$	1 s
2	0	$R_{2,0} = \left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{2\sqrt{2}} \cdot \left(2 - \frac{r}{a_0}\right) . \mathrm{e}^{-\frac{r}{2a_0}}$	0	$\frac{1}{\sqrt{4\pi}}$	2 s
2	1	$R_{2,1} = \left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{2\sqrt{6}} \cdot \frac{r}{a_0} . \mathrm{e}^{-\frac{r}{2a_0}}$	0	$\sqrt{\frac{3}{4\pi}} . \cos\theta$	2 p_z
3	0	$R_{3,0} = \left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{9\sqrt{3}} \cdot \left(6 - \frac{4r}{a_0} + \frac{4r^2}{9a_0^2}\right) . \mathrm{e}^{-\frac{r}{3a_0}}$	0	$\frac{1}{\sqrt{4\pi}}$	3 s
3	1	$R_{3,1} = \left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{9\sqrt{6}} \cdot \frac{2r}{3a_0}\left(4 - \frac{2r}{3a_0}\right) . \mathrm{e}^{-\frac{r}{3a_0}}$	0	$\sqrt{\frac{3}{4\pi}} . \cos\theta$	3 p_z
3	2	$R_{3,2} = \left(\frac{1}{a_0}\right)^{3/2} \cdot \frac{1}{9\sqrt{30}} \cdot \frac{4r^2}{9a_0^2} . \mathrm{e}^{-\frac{r}{3a_0}}$	0	$\sqrt{\frac{5}{16\pi}} . (3\cos^2\theta - 1)$	3 d_{z^2}

IV.8.3. Graphical Representations of Atomic Orbitals

In the case of an ns orbital, the volume corresponding to maximum probability of presence is spherical. The wave function ψ_n00,l=0 depends neither on θ nor on φ, but it depends on r. Its value is the same in all directions. The probability of presence is also independent of the direction, so the orbitals will be spherical (Figure IV.16).

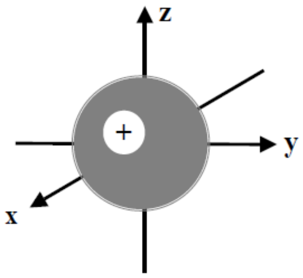

Figure IV.16 : Représentation graphique de l’O.A ns

The p orbitals (l = 1) can be represented by two approximately spherical lobes, attached, with axes of symmetry along the x, y, and z axes of the reference trihedron. They are called "n px," "n py," and "n pz" depending on the value of ml (n≥2) (Figure IV.17).

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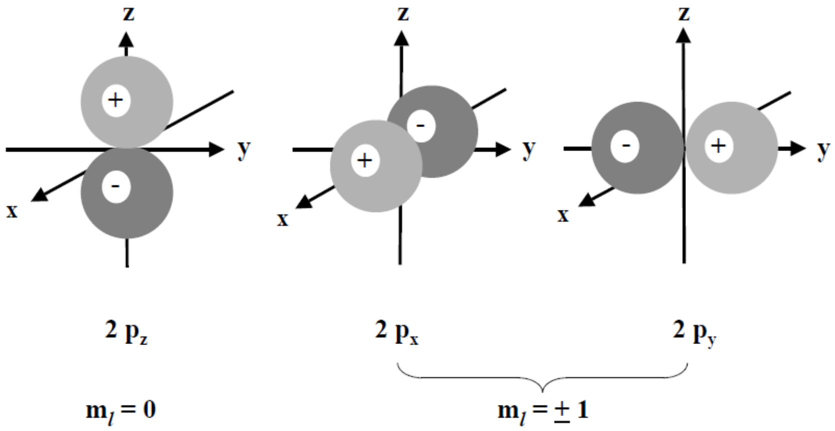


Figure IV.17 : Graphical representation of the np atomic orbital, the + and – signs indicate the sign of ψ.

In the case of nd orbitals, the wave function depends on the angular quantities Θ(θ), Φ(φ). The probability of presence takes different values depending on the direction. The symmetry of these orbitals is no longer spherical. To represent this geometric shape, the square of their angular part is used. This results in a lobe-shaped envelope. l = 2 ⇒ ml = -2, -1, 0, 1, 2 (n≥3) (Figure IV.18)..

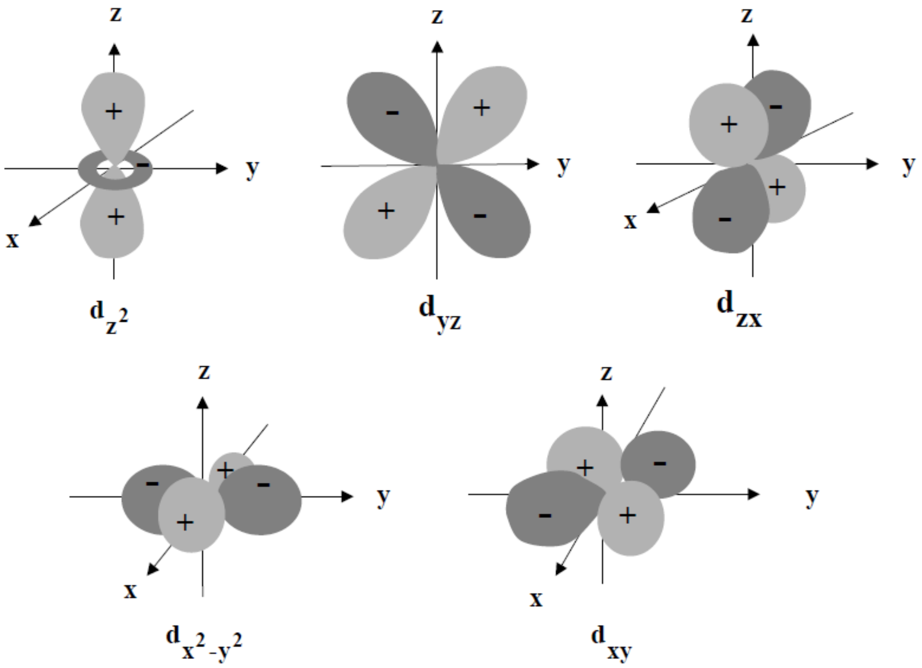


Figure IV.18 : Graphical representation of the nd atomic orbital, the + and – signs indicate the sign of ψ.

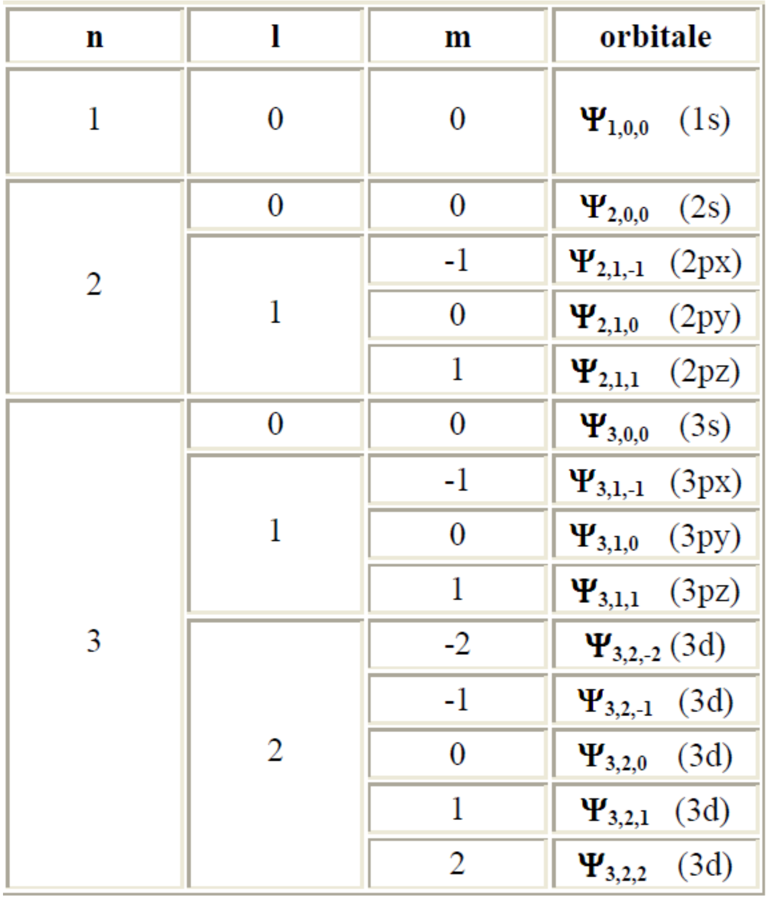
Exercises for practice

Exercise 1

1. Using the relationships between the three quantum numbers n, l, and m, determine the number of orbitals in the first three energy levels of the hydrogen atom.
2. Show that the maximum number of electrons that can be accommodated in a shell with quantum number n is equal to $2n^2$.
3. Give the usual designation of the following orbitals: $\Psi_{3,0,0}$; $\Psi_{3,2,0}$; $\Psi_{2,1,-1}$.

Solution:

1. Each orbital is designated by the term Ψnlm as indicated in the following table



n	l	m	orbitale
1	0	0	$\Psi_{1,0,0}$ (1s)
2	0	0	$\Psi_{2,0,0}$ (2s)
	1	-1	$\Psi_{2,1,-1}$ (2px)
		0	$\Psi_{2,1,0}$ (2py)
		1	$\Psi_{2,1,1}$ (2pz)
3	0	0	$\Psi_{3,0,0}$ (3s)
	1	-1	$\Psi_{3,1,-1}$ (3px)
		0	$\Psi_{3,1,0}$ (3py)
		1	$\Psi_{3,1,1}$ (3pz)
	2	-2	$\Psi_{3,2,-2}$ (3d)
		-1	$\Psi_{3,2,-1}$ (3d)
		0	$\Psi_{3,2,0}$ (3d)
		1	$\Psi_{3,2,1}$ (3d)
		2	$\Psi_{3,2,2}$ (3d)

2. The maximum number of electrons that can be accommodated in the shell with quantum number n: In the n = 1 shell, we have one atomic orbital (A.O) => $n^2 = 1$

In the n = 2 shell, we have four atomic orbitals => $n^2 = 4$

In the n = 3 shell, we have nine atomic orbitals => $n^2 = 9$

The number of A.O for each value of n (or level) is n^2.

In each orbital, we have a maximum of two electrons. Therefore, the maximum number of electrons that the shell with quantum number n can contain is equal to $2n^2$. (This is no longer valid for n > 4).

The wave function (or orbital) is determined by three quantum numbers n, l, and m.

$\Psi_{3,0,0}$ => $\Psi_{n,l,m}$ => n = 3, l = 0 (orbital s) et m = 0 => orbital 3s

$\Psi_{3,2,0}$ => $\Psi_{n,l,m}$ => n = 3, l = 2 (orbital d) et m = 0 => orbital 3d

$\Psi_{2,1,-1}$ => $\Psi_{n,l,m}$=> n = 2, l = 1 (orbital p) et m = -1 => orbital 2p

IV.9. Atomes polyélectroniques (Effet écran : Approximation de Slater)

Les atomes polyélectroniques tel que l'hélium (l'atome polyélectroniques le plus simple) possèdent dans leurs couches électroniques plusieurs électrons en interaction. Donc il est impossible de traiter chaque électron indépendamment, des autres. En effet le potentiel auquel est soumis un électron dépend des positions de tous les autres électrons. Il faut donc résoudre l'équation de Schrödinger pour tous les électrons en même temps. Pour un atome à k électrons l'expression de l'hamiltonien est ::

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\sum_{i=1}^{k}\nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0}\cdot\left(\sum_{i=1}^{k}\frac{-Z}{r_i} + \sum_{j=1}^{k}\sum_{i=1}^{k}\frac{1}{r_{ij}}\right)$$

ri represents the distance between the nucleus and the ith electron, rij represents the distance between the ith and jth electrons. The wave functions that are solutions of the Schrödinger equation are multi-electronic wave functions $\psi(r_1, r_2, r_3, r_k)$. This problem is complex and to solve it analytically, we need to make approximations. The usual approximation involves writing the multi-electronic wave function as a product of single-electron wave functions:

$$\psi(r_1, r_2, \dots, r_k) = \psi_1(r_1)\psi_2(r_2)\dots\psi_k(r_k)$$

We then have a system of k equations:

$$\widehat{H_i}\psi_i = E_i\psi_i$$

The total energy is the sum of E_i:

$$E = \sum_{i=1}^{k} E_i$$

The problem in solving this system is to determine the various Hamiltonians, that is, to determine the potential energy field for the different electrons.

En 1930, John Slater publia un modèle qui considérait chaque électron comme étant soumis uniquement à un potentiel central de la part du noyau. Les électrons des couches inférieures ont une influence sur le potentiel ressenti par l'électron, car ils font écran entre le noyau et l'électron considéré. Ainsi, celui-ci ne perçoit plus une charge Ze, mais une charge inférieure $Z_i^* e$.

Slater enunciated the following empirical rules:

1. First, establish the electron configuration by ordering the atomic orbitals (A.O.) by increasing values of n, then distribute the A.O. into several groups: (1s); (2s, 2p); (3s, 3p); (3d); (4s, 4p); (4d); (4f); (5s, 5p); (5d)...
2. The screening constant σi for the electron occupying the A.O. is obtained by adding the screening factors $\sigma_{j\rightarrow i}$ reflecting the screening effect exerted by the other electrons. The screening factors $\sigma_{j\rightarrow i}$ are calculated with the following conventions:

- For an electron occupying a 1s A.O., the screening created by another 1s electron corresponds to a screening factor $\sigma_{j\rightarrow i}$ equal to 0.30.
- For an electron occupying a ns or np A.O., the screening created by an electron in an A.O. with principal quantum number n' corresponds to a screening factor $\sigma_{j\rightarrow i}$ such that: $\sigma_{j\rightarrow i} = 1$ if n' < n – 1 (total screening) $\sigma_{j\rightarrow i} = 0.85$ if n' = n – 1 (strong screening) $\sigma_{j\rightarrow i} = 0.35$ if n' = n (weak screening)

$\sigma_{j\rightarrow i} = 0$ si n' > n (zero screening)

- For an electron occupying a nd or nf A.O., the screening created by an electron in the same group corresponds to a screening factor σj→i = 0.35, and a screening factor σj→i = 1 for all electrons in lower groups.

The table shows the values of the coefficients σij exerted on electron j by electron i.

In the Slater approximation, it is considered that the attraction between the Zth electron of the atom and the nucleus is subject to the action of a nucleus whose charge number is no longer that of Z protons. The charge of the atom's nucleus then becomes an effective charge Z*. This charge, which is weaker than the actual charge of the nucleus, is obtained by subtracting the screening effects of the other electrons from the real Z:

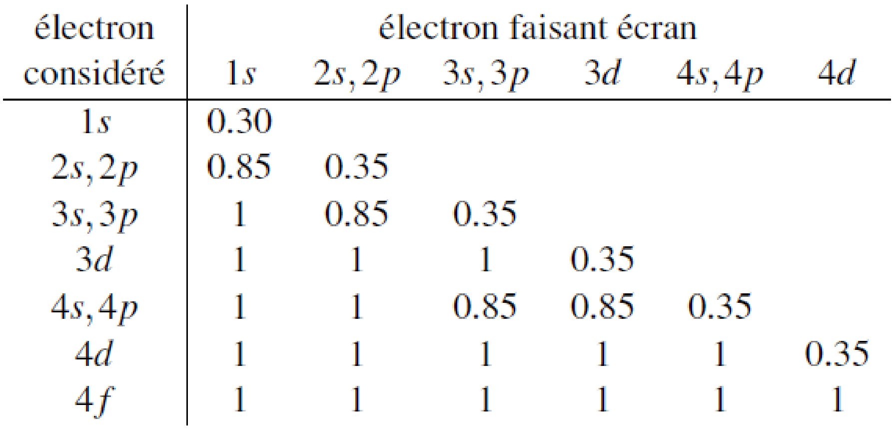
$$Z_j^* = Z - \sigma_j \; avec \; \sigma_j = \sum_i \sigma_{ij}$$

σij: screening constant for each electron i that has a screening effect on electron j (Table IV.4)

σj, screening constant

This formula is called Slater's single-electron attraction; it depends on the positions of the (Z-1)th electrons of the atom relative to the Zth electron j.

Table IV.4 : Values of the coefficients σij exerted on electron j by electron i.



électron	électron faisant écran					
considéré	$1s$	$2s,2p$	$3s,3p$	$3d$	$4s,4p$	$4d$
$1s$	0.30					
$2s,2p$	0.85	0.35				
$3s,3p$	1	0.85	0.35			
$3d$	1	1	1	0.35		
$4s,4p$	1	1	0.85	0.85	0.35	
$4d$	1	1	1	1	1	0.35
$4f$	1	1	1	1	1	1

The energy of the jth electron is calculated by the following relation: $E_j = \frac{-13{,}6 * Z^{*2}}{n^{*2}}$

The distance between the atom and this electron is equal to $r = \frac{0{,}53 * n^{*2}}{Z^*}$

n* = apparent quantum number introduced by Slater to reduce the differences between experimental and calculated values (Table IV.5).

Table IV.5 : values of the apparent quantum number for each value of the principal quantum number n.

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

In the Slater approximation, the energy E of an atom is equal to the sum of the energies of the electrons in different electron groups: $E = \sum n_j E_j$

Example:

Calculate the effective charge and energy of an outer electron of the chlorine atom Z=17.

Solution:

The effective nuclear charge can be calculated based on the figure below:

Z* = 17 - (2 x 1) - (8 x 0.85) - (6 x 0.35) = 6.1

Its energy

$$\mathrm{E}_3 = \frac{-13{,}6 * \mathrm{Z}^{*2}}{\mathrm{n}^{*2}} = \frac{-13{,}6 * 6{,}1^2}{3^2} = -56{,}22 \text{ eV}$$