

I-Wave Particle Duality

two concepts are distinguished: wave and corpuscle.

- Corpuscles are small (grains) of matter, located in space and with defined trajectories.

Throughout its trajectory position and velocity of corpuscle can be known.

- The waves for their part are not localized, they have a spatial extent and do not have a proper trajectory, they do not carry matter, but they can give us information, amount of movement and energy.

To study atoms scientists observe them indirectly through light, which atoms emit or absorb when stimulated by heat or electric shock.

The analysis of this light made it possible to propose a model of the electronic structure of atoms and to experimentally test their model.

To do this, we need to understand the nature of light which is a form of electromagnetic radiation.

I-1-Wave aspect of the light: electromagnetic or light wave and electromagnetic spectrum

Light or electromagnetic radiation is one of the forms of energy displacement in space, it is an association of electric and magnetic fields that propagate through space with a wave motion.

It is composed of an electric field (E) and magnetic field (M).

The magnetic field is oriented perpendicular to the electric field. The two fields move at the speed of light c (equal to 3×10^8 m/s). Each of these waves is characterized by its wavelength λ or its wave number $\bar{\nu} = 1/\lambda$.

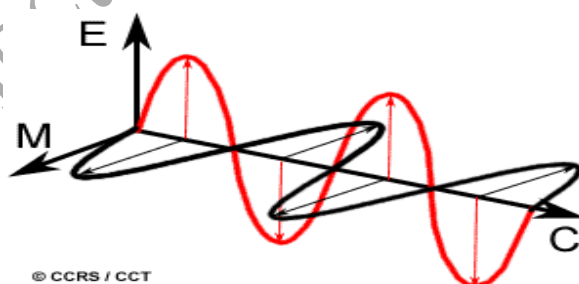
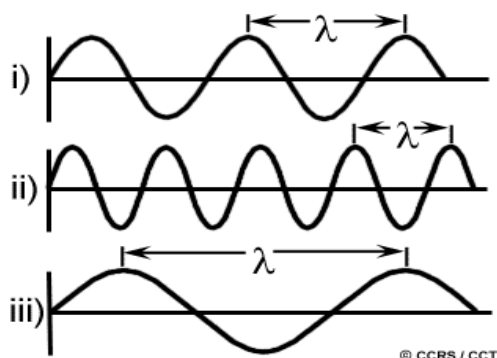


Figure II-1: Diagram of an electromagnetic or light wave

the wavelength λ (lambda) is the distance between two consecutive peaks, or two consecutive troughs. The unit is the meter (m).



The frequency ν (nu) is the number of wavelengths per second. The unit is s^{-1} or hertz (Hz).

The relationship between wavelength λ and frequency ν is:

$$\lambda \nu = c$$

c : speed of light c (equal to $3 \times 10^8 \text{ m/s}$).

λ : wavelength (m)

ν : frequency (s^{-1})

So Frequency and wavelength are therefore inversely proportional

I-2- Electromagnetic Spectrum

The electromagnetic spectrum consists of all electromagnetic radiation. In this set, the frequency can take all values continuously.

The visible spectrum is only a small portion of the complete electromagnetic radiation spectrum (Figure II-2). It represents the part of the full spectrum to which the human eye is sensitive. It extends from violet to red.

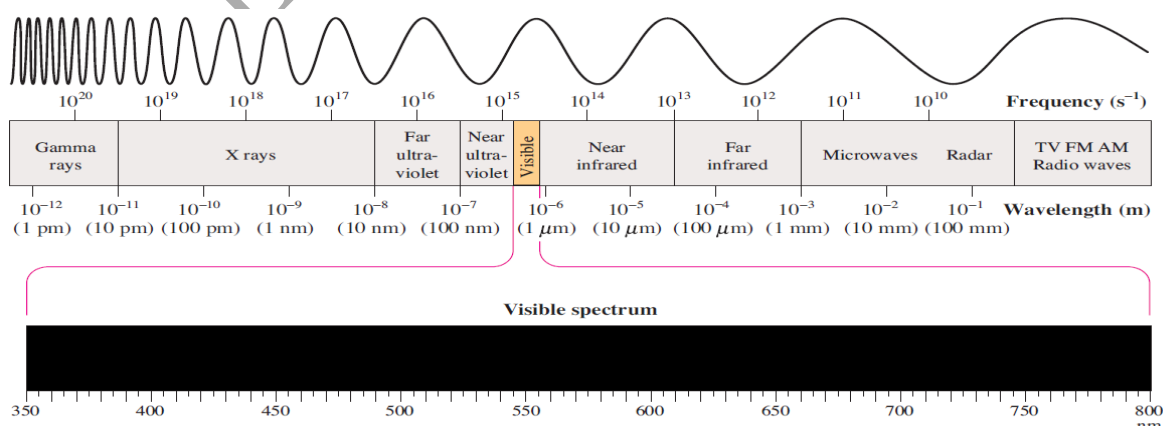


Figure II-2: Electromagnetic spectrum

I-3-Corpuscular nature of light

White light is a set of wavelengths emitted by the sun, it is composed of an infinity of colors: red, blue, violet, etc., and each color corresponds to an energy, a frequency and a wavelength.

Planck's studies the corpuscular aspect of a luminous radiation, he say that led can be considered as a set of particles each carrying a quantum (quanta) of energy called photons. Whose value is proportional to the frequency associated with it and carrying an energy ΔE :

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

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

E : Energy of the light carried by the radiation in Joule

ν : frequency of the radiation in s^{-1} (Hz)

c : speed of light in a vacuum in (m/s)

λ : wavelength in vacuum in (m)

I-3-1- Photoelectric effect

The photoelectric effect is the ejection of electrons from the surface of a metal or from another material when light shines on it. Electrons are ejected, however, only when the frequency of light exceeds a certain threshold ν_0 value characteristic of the particular metal.

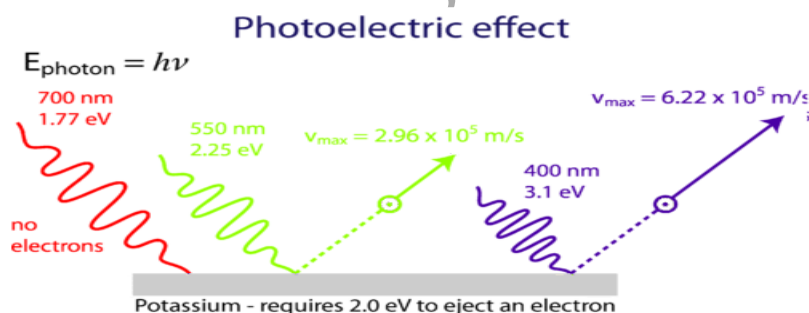


Figure II-3-1: Photoelectric effect

If ν_0 is the frequency threshold of the emitted light, the minimum energy required to eject an electron is $h\nu_0$, so the excess energy over $h\nu_0$ is given by:

$$E_c = E - E_0 = h\nu - h\nu_0$$

E_c represents the kinetic energy of the ejected electrons.

The photoelectric effect occurs only if the energy of the incident photon $E = h\nu$ is greater than the work of extraction $E_0 = h\nu_0$ of an electron from the metal, the energy of extraction depending only on the nature of the metal and the threshold frequency ($\nu_0 = c/\lambda_0$, λ_0 threshold wavelength).

$E < E_0 \Rightarrow \nu < \nu_0 \Rightarrow \lambda > \lambda_0 \Rightarrow$ the electron is not injected from the metal,

$E > E_0 \Rightarrow v > v_0 \Rightarrow \lambda < \lambda_0 \Rightarrow$ the electron leaves the metal with a Speed

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

If a photon with energy ($E = h\nu$) \geq ($E_0 = h\nu_0$) is absorbed, the emitted electron will reach a maximum kinetic energy:

$$E_c = \frac{1}{2} m v^2 = h (\nu - \nu_0) = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right)$$

Conclusion

Light not only has wave-like properties, it also has corpuscular characteristics. We therefore speak of the dual nature of light

II-The interaction between light and matter

When a source of energy strikes an object, it will send back radiation at a certain wavelength and will therefore appear in a specific color, depending on the mechanisms of emission, reflection, absorption and transmission.

II-1-Emission spectrum of the hydrogen atom

The emission spectrum of the hydrogen atom is the set of electromagnetic waves that can be emitted by an excited hydrogen atom that has received excess energy. This is obtained experimentally (figure III-1) in a discharge tube containing dihydrogen and fitted with two metal electrodes. The tube contains dihydrogen under low pressure, and a discharge is produced that partially ionises the dihydrogen H_2 .

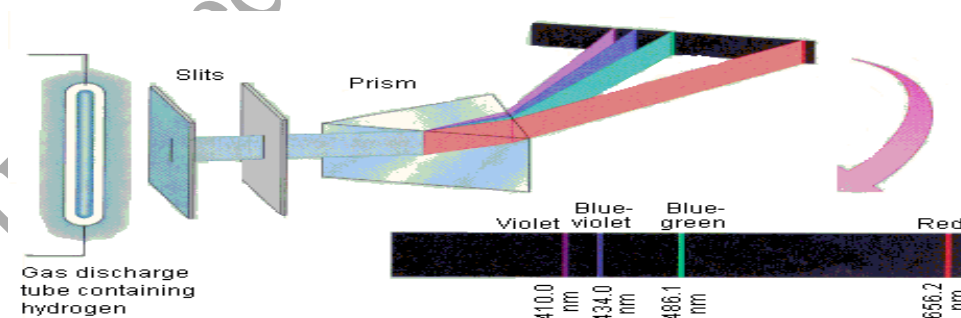


Figure III-1: Emission spectrum of the hydrogen atom

- Radiation appears in groups: the spectrum is made up of several series of lines. The first series was observed by BALMER (a series in the visible range). LYMAN discovered a series in the ultra-violet, then PASHEN located a new series in the infra-red range.

II-2-BALMER-RYDBERG empirical relationship

Balmer proposed an empirical formula in 1885 to calculate the wavelengths (λ) of the visible hydrogen lines (Balmer series).

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

λ : wavelength.

R_H : Rydberg constant for hydrogen, found experimentally ($1.09677 \times 10^7 \text{ m}^{-1}$)

n_1 and n_2 : integers taking the following values for each series:

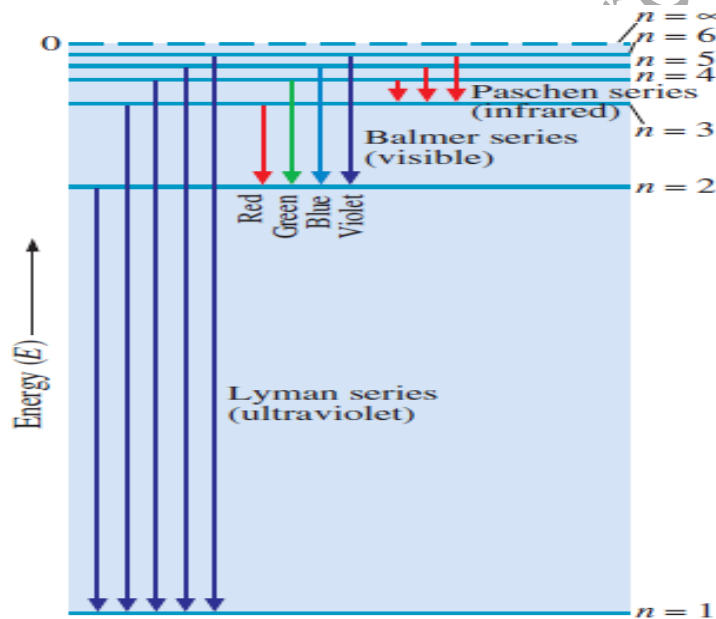


Figure III-1-2: Series of Lines in the Hydrogen Atom's Spectrum

the first series, known as the **Lyman** series, corresponds to the electron returning from an excited state to the ground state ($n_1=1$ and $n' > n$)

The hydrogen atom's emission spectrum is composed of monochromatic radiations with well-defined wavelengths.

Experimental observations have shown that the hydrogen atom's emission spectrum contains numerous lines in the ultraviolet, visible, and infrared regions. The first lines studied are found in the visible range and belong to the "**Balmer series**".

II-3- Interpretation of the Hydrogen Emission Spectrum

Due to the high voltage, the electron in H_2 is excited, absorbing energy and moving away from the nucleus, making it unstable. To regain stability, it prefers to return near the nucleus, emitting energy in the form of visible light radiation (photons with frequency ν).

Absorption of Light: When the hydrogen atom is not excited, the electron is in a low-energy orbit, which is called the ground state. When this atom is subjected to a potential, it absorbs energy, resulting in an electronic transition from the ground state to a higher energy level (excited state).

Emission of Light: The excited electron in the atom is in an unstable state and returns to its most stable energy level, the ground state, emitting radiation. The hydrogen emission spectrum shows that only certain energy levels are allowed.

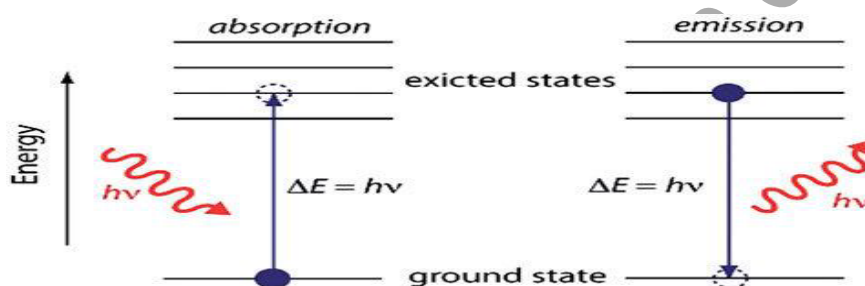


Figure IV.6: Diagram of an Electronic Transition

III-Bohr's atomic model

In 1913, Niels Bohr presented a new model of the atom based on the quantification of energy. This model explained the structure of the hydrogen atom and its spectrum; it also provided a theoretical basis for the Rydberg equation. The characteristics of this model are summarised in three postulates:

- 1st postulate/mechanical postulate:

The atom does not radiate when the electron is in motion on well-defined orbits or stationary orbits.

- 2nd postulate/postulate of kinetic moment:

the angular momentum of the electron, which is the product of the mass times the velocity times the radius of the orbit, is :

$$mvr = \frac{nh}{2\pi}$$

h: Planck's constant, n: quantum number

- 3rd postulate/optical postulate:

when the electron moves from one stationary orbit to another, the atom's energy undergoes a sudden change

$$\Delta E = E_{n2} - E_{n1} = h\nu = \frac{hc}{\lambda}$$

This relationship is known as the Bohr frequency condition

h : Planck's constant = $6.623 \cdot 10^{-34}$ j.s

ν : frequency of radiation

III-1- Absorption and Emission of Energy

An electron can only absorb or emit energy, radiate, when transitioning from one level (orbit) to another. The amount of energy absorbed or emitted is equal to the difference in energy between the two levels $\Delta E = E_2 - E_1$

Where:

E_2 : Energy of the final state.

E_1 : Energy of the initial state.

During an **emission** process, the electron jumps from the orbit of rank n_2 to the orbit of rank n_1 , such that the atom passes from an energy level E_{n2} to a lower level E_{n1} , then it will give up its excess energy in the form of light. The radiation emitted will be $E_1 - E_2 < 0$

During an **absorption** process, the electron jumps from an orbit of rank n_1 to an orbit of rank n_2 , such that the atom passes from an energy level E_{n1} to a higher level E_{n2} , so the radiation absorbed will be $E_2 - E_1 > 0$.

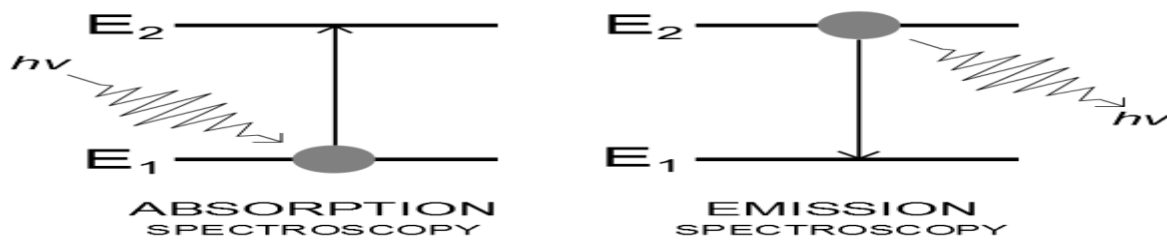


Figure IV-1: Photon absorption-emission process

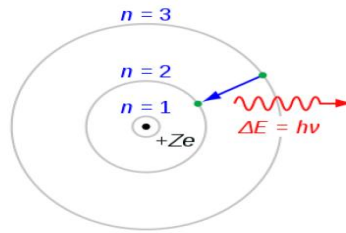


Figure IV-1: Illustration of a transition by a spectral line

The lowest energy stationary state ($n=1$) is called the **ground** state, and the higher energy permitted states are called **excited** states.

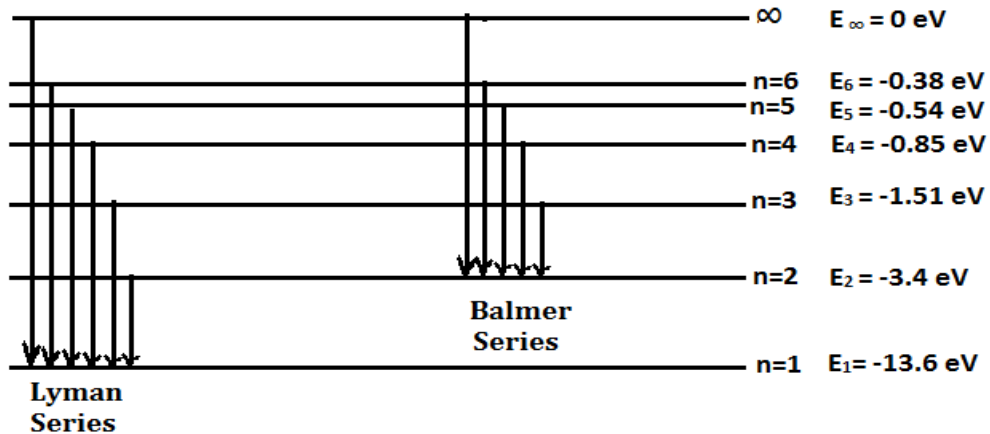


Figure VI-1: Energy diagram of the hydrogen atom

III-2-Ionisation energy

The ionisation energy E_i is the energy required to move the electron from the ground state to infinite distance. This phenomenon corresponds to the tearing of the electron from the atom, i.e. sending the electron to the energy level $E = 0$.

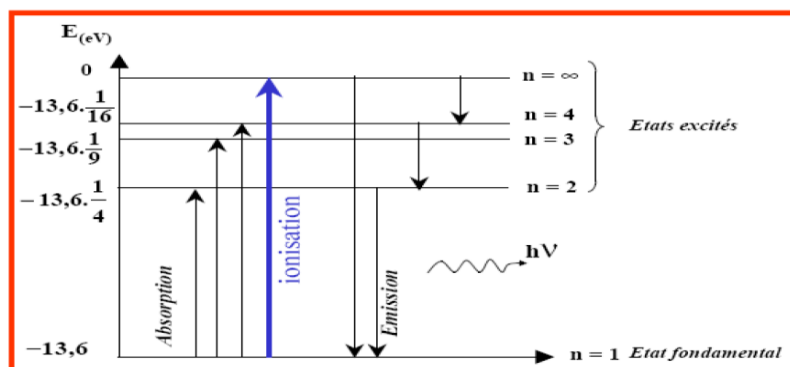


Figure IV-2: Ionisation energy E_i of the hydrogen atom

III-3- Application to Hydrogen-like Ions

These are atoms that have lost all their electrons except one, making them similar to hydrogen in terms of the number of electrons. Therefore, Bohr's theory can be applied to these hydrogen-like ions

Example: ${}_2\text{He}^+$; ${}_3\text{Li}^{+2}$; ${}_4\text{Be}^{+3}\dots$

Calculating the energy of the electron of a hydrogen-like ion in an orbit n gives the following expressions:

$$E_n = - 2,178. 10^{-18} \left(\frac{Z^2}{n^2} \right) \text{ J} = -13,6 \left(\frac{Z^2}{n^2} \right) \text{ eV}$$

These expressions can be found by replacing the charge on the nucleus (+e) with (+Ze) in the expressions for the hydrogen atom.

The wave numbers $1/\lambda$ (Rydberg formula) of the series observed in the spectrum of hydrogen ions are given by:

$$\frac{1}{\lambda} = R_H Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

With R_H : Rydberg constant

III-4-Insufficiency of The BOHR Model

Bohr's model is based on his ability to explain the experimental results for the hydrogen atom. This modelling revealed a number of inconsistencies and several shortcomings quickly became apparent in Bohr's model

The model is valid only for chemical species with a single electron, i.e. the hydrogen atom and the He^+ , Li^{2+} , Be^{3+} , ect.

He was unable to explain the presence of additional lines in more refined spectroscopes.

It was an important step towards quantum mechanics, which describes the behaviour of electrons more precisely.

IV-The Hydrogen Atom in Wave Mechanics

IV-1-Wave-Corpuscle Duality and The De BROGLIE Relation

In 1924 LOUIS DE BROGLIE put forward the hypothesis that wave-corpuscle duality is a general property of physics. He stated that any particle in motion is associated with an associated wave of wavelength λ :

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

λ : DE BROGLIE wavelength

h : PLANCK's constant (6.626×10^{-34} J.s)

p : Momentum

m : Particle mass

v : Particle velocity

BROGLIE's law can be used to find the quantification condition used by BOHR if we consider the electron as a wave, the electron can only move in orbits for which it has been designed.

$$mvr = nh/2\pi.$$

In fact, by isolating the number mv from this equation and the BROGLIE equation, we can demonstrate that $2\pi r$, which is the circumference of the orbit, corresponds to an integer wavelength λ .

$$mvr = \frac{nh}{2\pi} \Rightarrow mv = \frac{nh}{2\pi r} ; \quad \lambda = \frac{h}{mv} \Rightarrow mv = \frac{h}{\lambda} \text{ et } \frac{nh}{2\pi r} = \frac{h}{\lambda} \Rightarrow 2\pi r = n\lambda$$

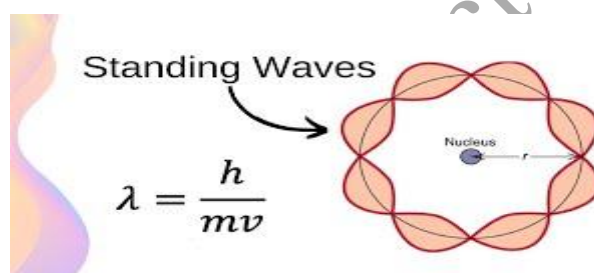


Figure V-1: Representation of the electron as a standing wave

IV-2-Heisenberg Uncertainty Principle

If we describe the electron using the wave model and the particle model "It is impossible to know the position and velocity of a moving particle precisely at the same time".

$$\Delta x \cdot \Delta(mv) \geq \frac{h}{4\pi}$$

Δx : uncertainty relative to the position of the electron

$\Delta(mv)$ or Δp : uncertainty relative to the quantity of movement (i.e. speed/velocity)

h : Planck's constant

According to this principle, we cannot therefore know the precise trajectory of the electron around the nucleus. Consequently, we cannot assume that the electron describes a well-defined orbit, as Bohr's model does.

IV-3- Concept of Probability of Presence

In classical mechanics (Bohr's conception), studying the motion of an electron involves precisely determining its trajectory. However, in quantum mechanics, we discuss the probability of finding the electron at a certain point in space.

This spatial distribution is described by a function of the electron's coordinates called the wave function Ψ .

IV-3-1-Schrödinger Equation

Schrödinger's method: replace the electron orbit (Bohr's model) with a mathematical function called the wave function Ψ (psi). the value of Ψ depends on the x,y,z coordinates of the point in the space.

This wave function must be a solution of the Schrödinger equation.

Atomic orbitals are the wave functions of atomic electrons. In 1926, Schrödinger demonstrated that the wave function and the energy E are solutions to a second-order partial differential equation. The Schrödinger equation is written as:

$$H\Psi = E\Psi$$

This is the fundamental principle of quantum mechanics. Where:

E : Total energy of the electron, called the eigenvalue

Ψ : Wave function, called the eigenfunction

H is called the Hamiltonian operator of the hydrogen atom, and it is expressed as:

$H = (-h^2 / 8\pi^2m) \Delta + V$; this is called the Hamiltonian operator of the hydrogen atom.

$\Delta = \partial^2 / \partial x^2 + \partial^2 / \partial y^2 + \partial^2 / \partial z^2$; this is the Laplacian operator.

m : mass of the electron

V : potential energy operator

This equation is the fundamental principle of quantum mechanics. Solving this equation leads to different values of E and Ψ :

$$E_n = -\frac{2mZ^2K^2\Pi^2e^4}{n^2h^2}$$

It is the same expression as that found by the Bohr model. With quantum mechanics, we can also explain the quantization of energy.

In other words, $\Psi^2 \cdot dV$ is the probability of finding the electron in a volume dV surrounding the point(x,y,z) \implies The position of the electron cannot be determined precisely, but we can give a probability that the electron is in a particular region of space.

The volume in which this probability of the electron's presence has a fixed value (99%, for example) is called an atomic orbital.


V-Quantum Numbers and The Concept of Atomic Orbitals

V-1- Quantum Numbers

Atomic orbitals depend on four numbers called quantum numbers: principal, azimuthal, magnetic and spin.

V-1-1- Principal Quantum Number (n)

It characterizes the energy level occupied by the electron or the shell it occupies. It is sometimes designated by an uppercase letter.

 $n = 1, 2, 3, \dots$ Each value of n corresponds to a layer (level)

Example: orbitals with $n = 1$ are the orbitals of the first layer.

This defines **the size** of the orbital and **the energy** associated with it.

$n=1$ layer K

$n=2$ layer L

$n=3$ layer M

$n=4$ layer N

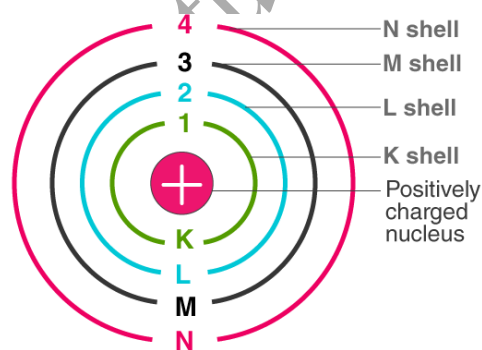



Figure VI-1-1: Representation of the Atom with the Principal Level (layer, shell)

V-1-2-Secondary Quantum Number (or Azimuthal) (l)

It defines **the shape** of the orbital; it characterizes the sublayer (subshell) occupied by the electron.

 The azimuthal number can take the values: $0 \leq l \leq n-1$ ($l = 0, 1, 2, \dots, n-1$)

$l=0$ Subshell s

$l=1$ Subshell p

$l=2$ Subshell d

$l=3$ Subshell f

- Orbitals are designated by first writing the value of n (1,2,3,...) followed by the letter indicating the value of l (s, p, d, f...)

Example: orbital 2p: $n = 2$ and $l = 1$

V-1-3- Magnetic Quantum Number (m)

It characterizes the quantum box occupied by the electron and determines its **orientation** in a magnetic field. Its value depends on the value of the secondary quantum number (l).

There are $2l+1$ different values for m .

Graphically, this number is represented by a rectangle, and as many rectangles are represented as there are possible values of (m).

- The magnetic number can take the values: $-l \leq m_l \leq +l$ or $m_l = -l, \dots, 0, \dots, +l$

A different orbital corresponds to each value of m_l , for given values of n and l

These three quantum numbers define a quantum box, and this box can contain two electrons.

To distinguish between the two electrons, a fourth quantum number, spin (s), is introduced.

V-1-4- Spin Quantum Number (s)

It characterizes the intrinsic angular momentum of the electron and can only take two different values: $\pm \frac{1}{2}$

By convention: $s = +\frac{1}{2} \uparrow$ and $s = -\frac{1}{2} \downarrow$

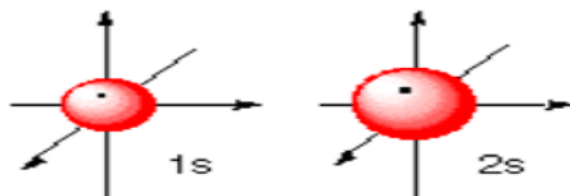
$$s = \pm 1/2$$



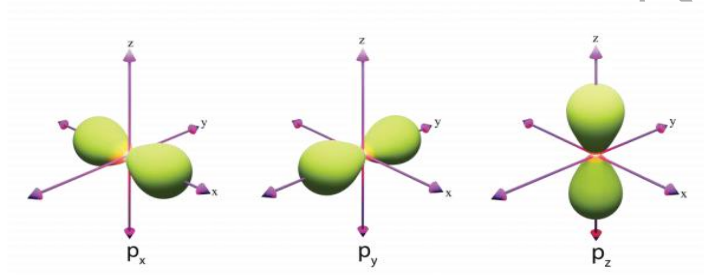
Figure VI-1-4: Motion of the electron on itself

VI-Atomic Orbitals

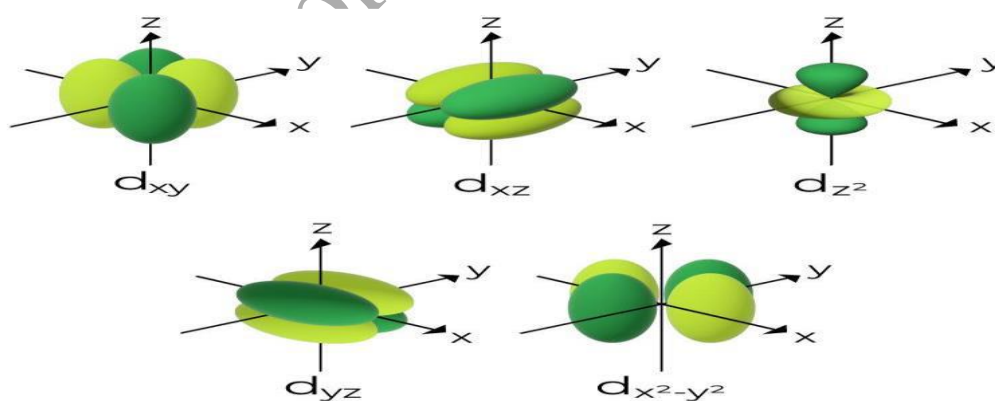
s orbitals: These are spheres whose volume increases with the value of n



p orbitals: these are made up of two lobes separated by a zone of zero probability called a node. They are identified according to the axis of the coordinate system (x, y, z) along which the orbital is oriented.

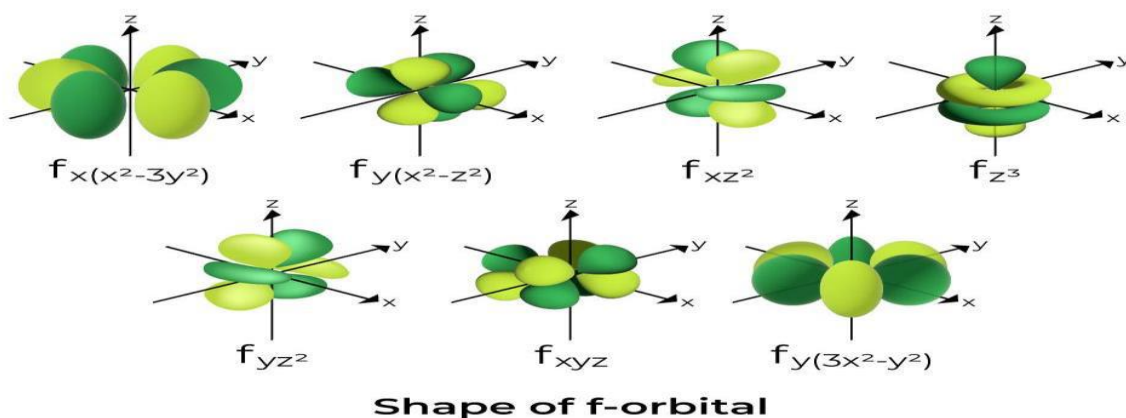


d orbitals: these orbitals are found from $n = 3$ ($l = 2$). There are 5 forms of 3d orbitals



Shape of d-orbital

f orbitals: If $l = 3$, m can take the values: $m = (-3, -2, -1, 0, +1, +2, +3)$, resulting in seven f orbitals.



VII-1- Energy of Atomic Orbitals

In the atom, the energy of a given orbital is a function of its n value (obtained by solving Schrödinger's equation)

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

This is the same energy expression as that obtained by Bohr.

Therefore, all orbitals with the same value of n have the same energy: they are said to be degenerate orbitals.

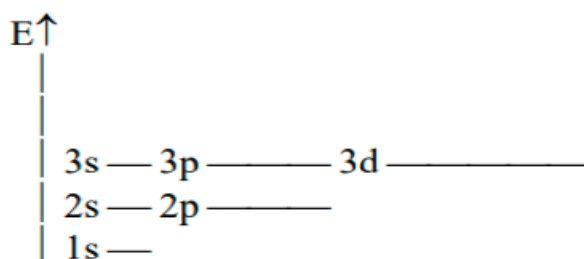


Figure VII-1: Degenerate Atomic Orbital energy levels

In polyelectronic atoms,

each electron is subject to the attraction of the nucleus but also, to repulsive forces from the other electrons in the atom. the electrons occupy orbitals similar to that of hydrogen. But the energies of these orbitals are not the same as those of hydrogen.

□ There are two opposing effects:

- electron-core attraction
- electron-electron repulsion

□ In polyelectronic atoms, because of inter-electronic repulsions, the energy of the orbitals varies according to the order :

$$E_{ns} < E_{np} < E_{nd} < E_{nf}$$

For example, for the $n = 3$ shell: $E_{3s} < E_{3p} < E_{3d}$

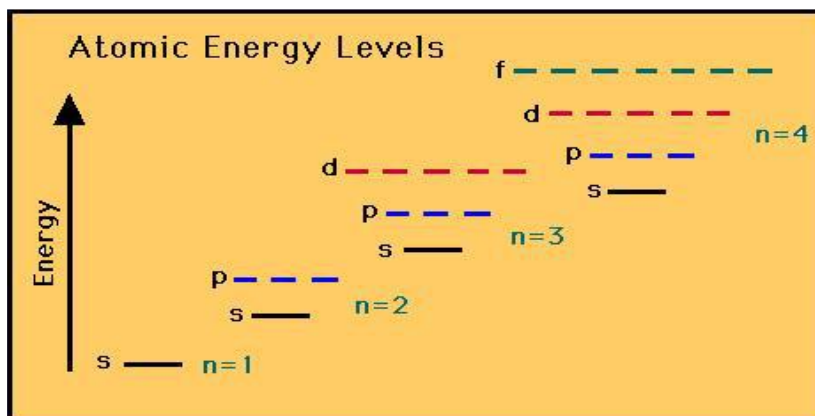


Figure VII-2: Energy Levels of Atomic Orbitals in a Poly-Electronic Atom

VIII- Electronic configuration of the atom

We try to place Z electrons (neutral atom) on the different levels, this is called: Writing the electronic configuration.

The electronic configuration of an atom is the distribution of Z electrons of the atom in a ground state over the atomic orbitals.

Step 1: place the electrons, one after the other, in the orbitals according to Klechkowski's rule. Never put more than two electrons in the same orbital (Pauli's principle).

Step 2: If there is more than one orbital in a sublayer, place the electrons, with parallel spins, in different orbitals instead of pairing two electrons in one of them (Hund's rule).

- The electrons in the outermost layer (the largest value of n) are called valence electrons (or peripheral electrons).
- In general, only valence electrons can be given up during chemical reactions, because the core electrons are too tightly bound.

The atomic orbitals are filled using the following three rules:

- ❖ KLECHKOWSKY rule.
- ❖ PAULI rule.

❖ HUND rule.

VIII-1-Klechkowski's rule (filling order)

"With a few exceptions, the energy of the electronic orbitals or layers follows the order of $(n + l)$ increasing."

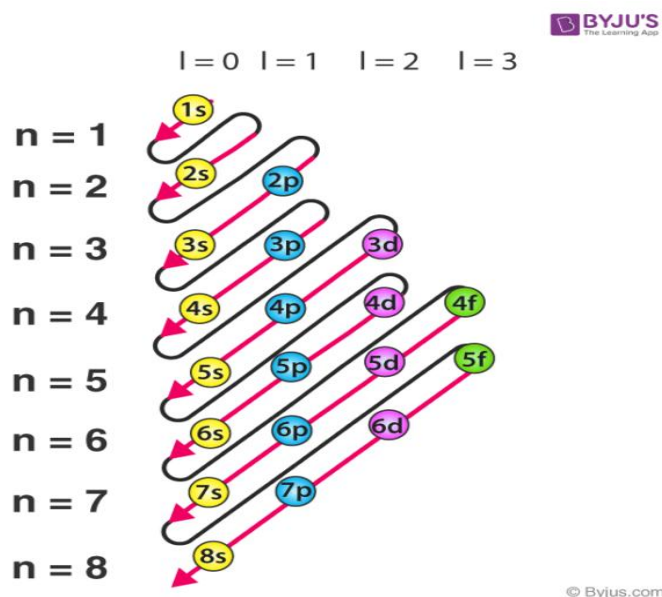


Figure VIII-1: Klechkowski's rule

VIII-1-1 Exceptions to Klechkowski's Rule

Starting from the $n = 4$ level, the filling of atomic orbitals does not strictly adhere to Klechkowski's rule.

Example:

Copper (^{29}Cu): The most stable configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

Chromium (^{24}Cr): The most stable configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

These exceptions correspond to half-filling and full-filling of the 3d sublayer.

They are explained by the small energy gap between the 4s and 3d orbitals.

VIII-2- Hund's Rule

When electrons fill the orbitals of a given energy level, they successively occupy the maximum number of orbitals with parallel spins. When a subshell is not complete, electrons occupy the maximum number of orbitals with the same spin.

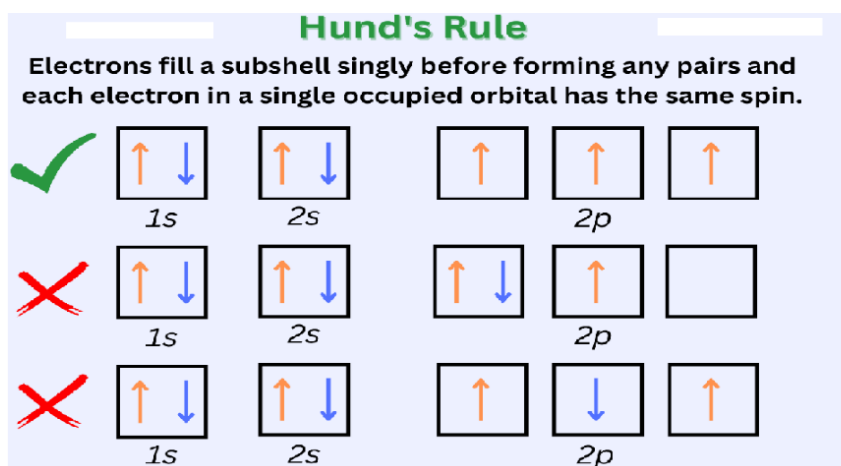


Figure VIII-2: Hund's rule

VIII-3-Pauli's exclusion principle

"Two electrons of the same atom cannot have their four quantum numbers n , l , m_l and m_s equal". If electrons in the same orbital have the same values of n , l and m_l , they must necessarily have different values of spin. However, we know that spin has only two values, so an orbital can have at most two electrons, which must be of opposite spin.



Figure VIII-3: Pauli's exclusion principle

VIII-4-Valence Shell

The electrons in the shell (layer) with the highest value of the principal quantum number (n) play a significant role in chemical reactions, especially in the formation of chemical bonds between atoms. This shell is called the outermost valence shell.