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وزارة التعليم العالي والبحث العلمي

Ministry of Higher Education and Scientific Research

National Polytechnic School of Oran Maurice Audin (ENPO)

Department of Preparatory Training in Science & Technology

Course handout

“Structure of matter”

(Chemistry 01)

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Foreword

This course document was primarily designed for students in technical sciences (ST) and material sciences (SM), especially those enrolled in their first year in the preparatory training department for science and technology. It is also intended for students from different specialties who are taking a general chemistry course. Researchers working in fundamental or applied research laboratories who are faced with questions about the structure of matter will also find this document useful.

The objective of this document is to help learners understand the structure of matter, which is an essential part of general chemistry. It is a general chemistry learning manual that aims to provide definitions, basic concepts, and general laws related to the structure of matter.

Entitled "Structure of Matter," this 140-page document is divided into four chapters and provides an in-depth understanding of the structure of matter, which is necessary in various disciplines related to chemical sciences or materials. It is accompanied by a series of reference books that cover all concepts and methods. This document is highly educational and consists of clear and concise text, as well as numerous instructional diagrams. The theoretical foundations are presented in a logical and progressive manner throughout the chapters, and solved exercises are included in each chapter. It is in line with the approved general chemistry curriculum by the ministry. The first chapter introduces general concepts such as states of matter, atoms, molecules, and solutions, summarized in a brief overview.

The second chapter focuses on the main constituents of matter, particularly the atom, as well as some of its physical properties such as mass and charge. This chapter also describes the experiments that led to the discovery of the electron, proton, and neutron, including the experiments of Crookes, J.J. Thomson, Millikan, and Goldstein. Finally, the structure of the atom, isotopes, their separation through techniques such as Bainbridge and Dempster spectroscopy, and their stability are discussed at the end of the chapter.

The third chapter of the document is divided into several parts. ***The first part*** examines the electronic structure of the atom and discusses the quantification of energy in the semi-atomic model. This section deals with the wave-particle duality of light, the optical spectrum of hydrogen, classical models of the atom, and the spectra of hydrogenoid.

The second part of this chapter prepares the transition to the quantum model of the atom by introducing a theory necessary for the rigorous description of the properties of the atom, wave mechanics. This section addresses Louis de Broglie's hypothesis, Heisenberg's uncertainty principle, Schrödinger's equation, and the electronic configurations summarized by Pauli's exclusion principle, the principle of energy stability and the Klechkowski's rule, Hund's rule, exceptions to filling rules, electronic structures of noble gases, core and valence electrons, dia and para-magnetic properties, as well as electronic structures of ions. Finally,

The third part of this chapter is devoted to the periodic classification of elements. This part describes the principle of classification and the arrangement of the modern periodic table into rows and groups, chemical families, the evolution and periodicity of physical and chemical properties of elements, such as atomic and ionic radius, ionization energy, electron affinity, and electronegativity, as well as electronegativity scales (Pauling scale, Mulliken scale, and Allred-Rochow scale).

The fourth chapter of this course deals with chemical bonding and covers various theories such as Lewis theory for covalent bonding, polar covalent bonding, dipole moment, molecular geometry according to Gillespie's or VSEPR theory, molecular orbital theory (LCAO method) for chemical bonding in the quantum model, formation and nature of bonds, as well as the energy diagram of molecules. The hybridization of atomic orbitals (sp, sp2, sp3) is also presented in a simple and clear manner for the study of polyatomic molecules. Each concept is illustrated with concrete examples.

This document is a summary of the author's experience as a teacher of a course on the structure of matter, given at the Department of Preparatory Training in Science and Technology at the National Polytechnic School of Oran. Although this part of the course has been done carefully, it may contain omissions or errors. If you have any remarks or comments on the manuscript, please contact the author at the following email addresses.

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Introduction

In prehistory, chemistry already held an important place in human life without constituting a separate science. It originated from two great and valuable sources: the philosophy of nature and alchemy. The former was based on observation, deduction, and attempts to interpret all natural phenomena, while the latter was more experimental. Chemistry has strongly influenced and also left its mark on many other scientific fields such as physics, biology, astronomy, materials science, etc. It encompasses all the works, laws, theories, inventions, and experiments that have dramatically changed our understanding of matter's composition and the interpretation of its interactions.

In This handout, we discuss the development of the electromagnetic theory of light and the hypothesis of its discontinuous nature. Knowledge about the electronic arrangement of atoms stems from the electromagnetic theory of light and the hypothesis of its discontinuous nature. The relationship between the electromagnetic radiation emitted by atoms and the energy levels of their constituent electrons led N. Bohr to propose the hypothesis of discontinuous energy levels, wherein electrons follow fixed orbits. It was possible to associate electromagnetic radiation with the energy levels of electrons, since their precise distance from the atomic nucleus could be calculated from their energy.

The Rutherford model, which posited that electrons have random orbits, was then abandoned. With de Broglie's hypothesis that material particles exhibit wave-like characteristics, the Bohr model led to the quantum theory of the atom. The wave-particle duality of the electron led to the Schrödinger equation, the equation of quantum theory. The concept of an orbital, which represents the regions of probability of finding the electron, emerged from this theory. Electron is no longer described solely as a particle, but also attributed with wave-like characteristics; it can be associated with an electron cloud of varying density. The solution of the Schrödinger equation also led to the quantum numbers that provide precise information about the state of an electron, referred to as the quantum state. The distribution of electrons in quantized energy levels, which depend on the values of the quantum numbers, can be described by a simple system. This leads to expressions of the electron configurations specific to each element, from which a large number of properties can be predicted. The electronic structure of a chemical species, developed from the atomic model, is clearly described in this handout.

The description of the various models of chemical bonding has been developed based on the modern atomic model. The theory of hybridization of atomic orbitals is explained in a simple, clear, and easy-to-understand manner in this document.

Since it is not possible to cover the entire history of chemistry in detail, we will mention some significant dates that mark major revolutions and the associated laws that enable us to understand the transition from classical mechanics to quantum mechanics.

Antoine de Lavoisier (1777-1789): Law of conservation of mass.

Joseph Proust (1802): Law of definite proportions which states that elements always combine in the same weight ratio to form a compound.

John Dalton (1804): Law of multiple proportions and first theory of the atom Dalton's law shows the discontinuous nature of matter: the ratio of reacting masses does not vary continuously and chemical species only react in extremely small but indestructible discrete quantities, referred to by Dalton as "atoms", which join together in well-defined proportions; consequently, a chemical compound or molecule is simply a combination of two or more atoms.

Louis Joseph Guy Lussac (1809): He discovered several chemical and physical properties of air and many other gases and was able to interpret Boyle's and Charles's laws experimentally.

Amedeo Avogadro (1811): developed several theories, but died in 1856 without seeing them recognised. He set out Avogadro's famous law, which states that "under the same conditions of temperature and pressure, the number of atoms or molecules in a given volume of gas is always the same, whatever the gas". This law led to the determination of Avogadro's number (N) in 1865 by Johann Josef Loshmidt, which corresponds to the number of atoms in 12 grams, or one mole of carbon.

The Karlsruhe conference was the first international congress of chemistry organised in 1860 by Friedrich August Kekulé, the aim of which was to bring together all chemists to agree on a common nomenclature. During this conference, Stanislao Cannizzaro demonstrated that Avogadro's atomic theory made it possible to establish unambiguous notations and was able to convince the entire international scientific community to adopt a nomenclature based on the concept of atoms.

Periodic classification 17 February 1869: Dimitri Mendeleïev proposed a classification of atoms in ascending order of atomic mass, after the appearance of a periodicity in their properties. He was able to classify the 63 elements known at the time and predicted the existence of other elements for which he left the space open.

Discovery of the electron: in 1897, Joseph John Thomson showed that, during an electrical discharge in a gas, there were negatively charged particles for which he determined the e/m ratio. A few years later Millikan (1910) determined the charge of the electron by studying the movements of electrified oil droplets between the plates of a horizontal condenser. This value is conventionally known as e, and is the smallest electrical charge that a particle can carry.

Ernest Rutherford (1911): Discovered that almost all the mass and all the positive charge of an atom are located at its centre, which he called the nucleus, around which the electrons gravitate in layers, hence the conception of the planetary model.

I-1-- States and macroscopic characteristics of states of matter.

In physics, a state of matter is one of the three ordinary forms that any substance can take in nature; classically, there are three states of matter: solid, liquid and gas. The state in which matter is found depends not only on the matter in question, but also on the temperature and pressure, for example ***[Water is found in three different states: solid (ice, snow), liquid and gaseous (water vapour), depending on the pressure and temperature of the environment in which it is found]***, in other words: matter is everything that has mass and occupies space. All objects - air, water, oil, etc. - are matter, they are bodies. These bodies can exist in different forms called physical states of matter. They can be solid, liquid or gaseous, depending on the degree of cohesion of the molecules that make them up.

These properties result in different "behaviours", described by the laws of physics: malleability, viscosity, the law of perfect gases………

***Note:* The behaviour of matter is not always uniform within the same state. For example, there are intermediate states (plasma) in which a solid behaves like a fluid (powdery or granular matter) or, on the other hand, a liquid has certain properties specific to solids.**

I-1-1 The states of Matter

The states of matter from the microscopic point of view correspond to a substance composed of atoms and possessing mass; the atom is the fundamental constituent and from the macroscopic point of view are: The solid state, the liquid state, the gaseous state and plasma, the fourth state of matter...

***Note:* The list of states of matter is actually a little longer. And it's getting longer all the time. In the category of solids, we find crystalline solids, amorphous solids and supersolids. Other examples include the plasma state, the superfluid state, the Bose-Einstein condensate,....**

I-1-1-a Solids: The solid state has a defined volume and shape. (The particles are very close to each other; there is a strong force of attraction between the particles).

Solids have a shape of their own because, when no action is exerted on them, they retain the same shape ***(Figure I-1)***:

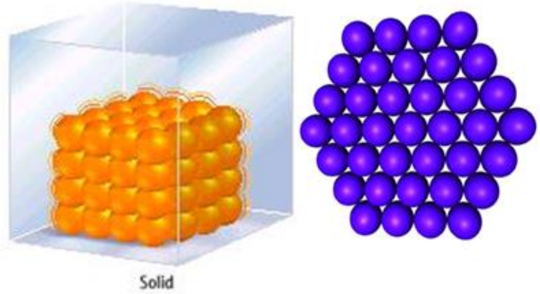


Figure I.1 : The solid state

I-1-1-b Liquids: have a defined volume but no precise shape; they take on the shape of their container. (The particles are close together but there is space between them; the force of attraction between the particles is less than in solids) ***(Figure I-2***):

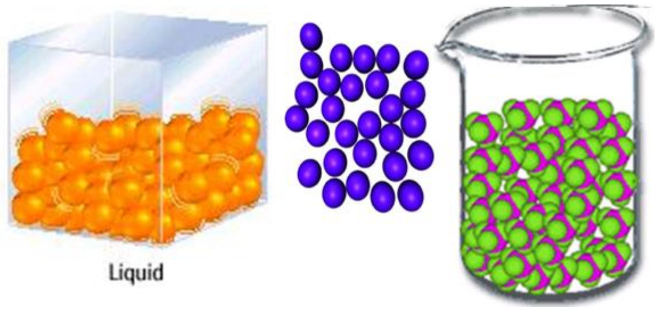


Figure I-2 : The liquid state

I-1-1-c Gases: Has no defined volume or shape; they take on the volume and shape of their container (the particles are very far apart; the force of attraction is very small, as is the force of gravity) ***(Figure I-3):***

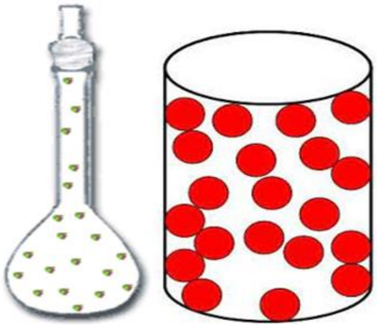


Figure I-3: The gas state

I-1-2 The characteristic quantities of matter and its states

A physical quantity, or simply a quantity, is any property of the science of nature that can be measured or calculated, and whose various possible values are expressed using any real number or a complex number, often accompanied by a unit of measurement. There are four characteristic quantities of matter and its states:

I-1-2-1 Volume and mass

Volume and mass are two characteristic quantities of a body. Mass is a quantity proportional to the amount of matter in a body. It is measured with a balance. Volume is a quantity that indicates the space occupied by a body. It is measured with a graduated cylinder, in other words; the mass and volume of a body indicate respectively the quantity of matter of which it is composed and the space that it occupies. These quantities can be expressed in several units, so you need to know how to convert them. What's more, they vary with each other, hence the concept of density, which is generally expressed in (Kg/l).

Property: the mass and volume of a body are proportional quantities.

I-1-2-1-a The volume:

All objects occupy a certain amount of space, and some more than their volume. The volume of a body is a physical quantity indicating the space that the body occupies. Its unit of measurement is the cubic metre, noted m^3.

Example: A body with a volume of 4 m^3 occupies twice as much space as a body with a volume of 2 m^3.

In everyday life, to express volumes, the litre (L) or its sub-multiples (dL, cL, mL, cm^3, dm^3.....) is most often used.

I-1-2-1-b The Mass:

All objects are composed of matter, the more so the greater their mass. The mass of a body is a physical quantity used to evaluate the amount of matter in that body. Its unit of measurement is the kilogram, noted Kg. We can also use multiples or sub-multiples of the gram to express the mass of a body.

(hg, gr, dg, cg, mg,.......).

Example: A body with a mass of 4 kg contains twice as much matter as a body weighing 2 kg

I-1-2-2 Pressure and temperature

For every variation in temperature, there is a corresponding variation in pressure, and vice versa.

Example: Gay-Lussac's law describes the relationship between the pressure and temperature of a gas. It states that at constant volume, the pressure of a certain quantity of gas is directly proportional to its absolute temperature (P ∝ T).

I-1-2-1-a The pressure:

Pressure (p) is the ratio of a force (F) acting on a given surface (S). For physicists, the term pressure refers to a force measured in Newtons (N) exerted on a given surface measured in square metres (m2). In the international system, the unit of measurement for pressure is the pascal (Pa). A pressure of 1 Pa corresponds to a force of 1 N exerted on a surface over a period of 1 min 2 s. The pascal is therefore a unit of measurement characteristic of low pressure. In fact, other more appropriate units of pressure measurement can be used. These include the bar (bar), which corresponds to 105 Pa. Or the atmosphere (atm), which is equivalent to 101.325 Pa. Or even the millimetre of mercury (mmHg), which is 133 Pa.

I-1-2-1-b The temperature:

Temperature is a physical quantity measured with a thermometer and studied in thermometry. Temperature is the sensation of heat or cold, objectively measured by a thermometer. In other words, temperature corresponds to the degree of agitation of molecules. The higher the temperature, the more agitated the molecules and the more they disperse, increasing molecular disorder. Ambient temperature is the temperature of the environment. Temperature symbol: (T). Unit: the kelvin, symbol (K) (International Metric System). Older scales: Celsius and Fahrenheit scales.

I-2-1 Change of state of matter

When matter passes from one state to another, it is said to undergo a change of state. Changes of state can be effected by influencing temperature or pressure, or both. Changes of state are significant physical changes that occur at temperatures that are characteristic of the substance. ***(Figure I-4):***

Examples : Solid-liquid transition - Liquid-gas transition - Solid-gas transition: - Gas-solid flow: - Gas-liquid transition............... ***(Figure I-4)***

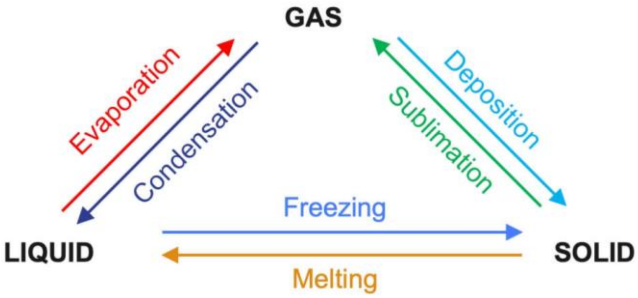


Figure I-4 : variations in the state of matter

I-2-2 The characteristics of changes of state

During a change of state of a body, mass is conserved but volume is not. During this change of state, the molecules are conserved; only their arrangement in relation to each other is modified. There are two physical and chemical changes of state.

I-2-2-a Physical change:

A physical change is a transformation that does not change the nature of a substance. simply involves a change in its physical state, form or dimensions.

I-2-2-b Chemical change:

A chemical change is a transformation that changes the nature of a substance by means of a chemical reaction.

Example: Corrosion: iron produces rust. Combustion: wood burns to produce ash and gases.

Melting temperature (Solid------liquid) of water: 0°C

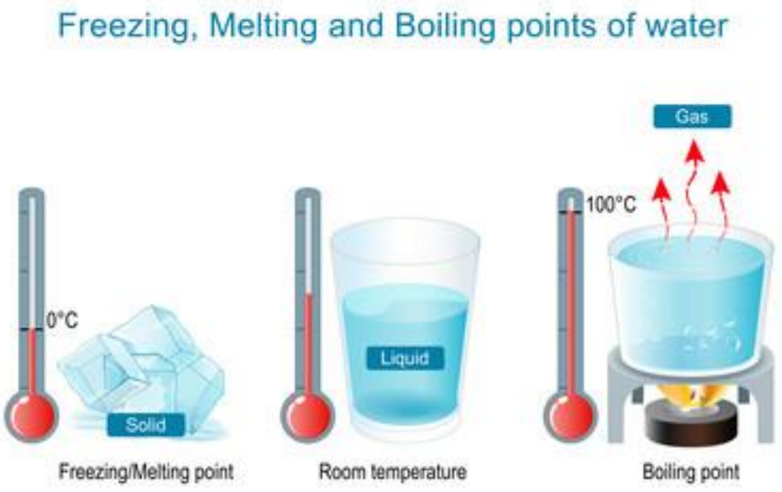


Figure I.4: variations in the state of matter

I-2-2-1 The Melting: is the transition from solid to liquid state.

Example: If the solid is a pure substance (e.g. ice), when it changes to a liquid state, it is called free fusion or, more simply, melting. The characteristic of fusion of a pure substance is that it occurs at a given temperature, which remains constant throughout the change of state.

I-2-2-2 The Freezing: is the transition from liquid to solid.

Example: This is what happens when you put water in the freezer of a fridge or in a freezer. But here again, when the water starts to solidify, the temperature of the water-ice mixture remains constant (very close to 0°) as long as there is still liquid water. The ice cube will reach (-18°C) if the freezer is at (-18°C). The temperature of change of state (here 0°) means that above this temperature, the water is in liquid form and below this temperature, it is in solid form.

I-2-2-3 The sublimation: is the transition from the solid to the gaseous state and vice versa.

Example: Some substances pass from the solid to the gaseous state without passing through the solid state. This is the case with naphthalene and camphor, which evaporate slowly at "ordinary" temperature and pass directly from the solid state to the gaseous state. Another example: after a few days of bitterly cold, dry weather, icy ground may become clear, meaning that the ice has been transformed into a gas.

I-2-2-4 The Condensation: is the transition from a gaseous state to a liquid state..

Example: water easily changes from a gaseous state to a liquid state, as we saw in the section on evaporation. Generally speaking, a gas can be liquefied by increasing the pressure, but there is a temperature - known as the critical temperature - above which it is impossible to liquefy it. To liquefy a gas, it must be brought to a temperature below this critical temperature and the pressure increased. For example, for nitrogen, the critical temperature is (-147°C), which means that liquid nitrogen can only be obtained at temperatures below -147°. In dermatology, liquid air is used to "remove" a wart.

I-2-2-5 The Evaporation: is a general phenomenon of the passage from the liquid state to the gaseous state.

Example: Evaporation is a surface phenomenon. Between the melting temperature and the boiling temperature, the pure substance is in equilibrium with its vapour (the same substance in a gaseous state), the quantity of vapour in relation to the quantity of liquid water being highly dependent on temperature. The boiling point of water is 100°C at sea level, 85°C at the top of Mont Blanc and 72°C at the top of Mount Everest. Above this boiling temperature, liquid water is in the form of a gas.

I-3- Concept of atom

Democritus first introduced the concept of the atom. He defined it as the smallest part of an element that can exist, invisible to the naked eye, and which is the basis of the constitution of matter. However, it was not until the 19th century, notably with J. Dalton and A. Avodagro, for the atom to move from a philosophical to a scientific concept. It was not until the beginning of the twentieth century that we had the technical means to probe matter on a subatomic scale. Atoms combine to form molecules, and a molecule is therefore a union of atoms.

I-3-a Structure of the atom

An atom is made up of a nucleus, which contains nucleons (positively charged protons and electrically neutral neutrons) - the nucleus is therefore positively charged overall - and negatively charged electrons, which gravitate around the nucleus.

I-3-b Characteristics of these particles

An atom consists of a nucleus made up of neutrons, protons and electrons.

- **Protons** have a positive electric charge of the order of (**$1,6 \times 10^{-19}$ Coulomb)**
- **Neutrons** have no electric charge.
- **Electrons** have a negative electric charge of the order of (**$-1,6 \times 10^{-19}$ Coulomb)**

Remarque :

It is not necessary to know the masses of the particles that make up the atom. It is important to remember that they are infinitely small and their order of magnitude, $\mathbf{10^{-27}}$.

particle	Mass (in kg)
proton	**$1,67 \times 10^{-27}$**
neutron	**$1,67 \times 10^{-27}$**
électrons	**$9,1 \times 10^{-31}$**

I-3-1 Molecules

Atoms come together to form molecules, and a molecule is therefore a union of atoms. In other words, a molecule is a set of atoms (at least two), which may or may not be identical, joined together by chemical bonds. These atoms cannot separate spontaneously: only a chemical transformation can change the composition of a molecule. A molecule is represented by a chemical formula that indicates the nature of the atoms and the number of index atoms present in the molecule.

Exemple :

- The water molecule contains 2 hydrogen atoms and one oxygen atom.

Its chemical formula is H_2O.

I-3-2 Mole

The mole is the unit for measuring the quantity of matter containing N identical entities (entities = molecules, atoms or ions). The mole is therefore a very practical unit in chemistry and physics. It allows objects as small as atoms and molecules to be described using "everyday" units. The unit of the mole is [mol].

- The symbol for the mole is (**mol).**

- The number of moles is represented by the letter **(n)**.

The mole is also defined as the number of carbon-12 atoms contained in 12 g of carbon 12.

1 mol= $\frac{12g}{1.9926*10-23}$ **=6.023 10** ^{23}**.**

- The mole number is the ratio between the mass of the compound and its molar Mass.:

$$n = \frac{m}{M}$$

n: number of moles**;** **m:** mass of compound in g**;** **M:** molar mass of compound in **g/mol**

Gaseous compounds: Avogadro-Ampère law

Under normal conditions of temperature and pressure, one mole of gas molecules always occupies the same volume. This volume is the molar volume **(Vm)** :

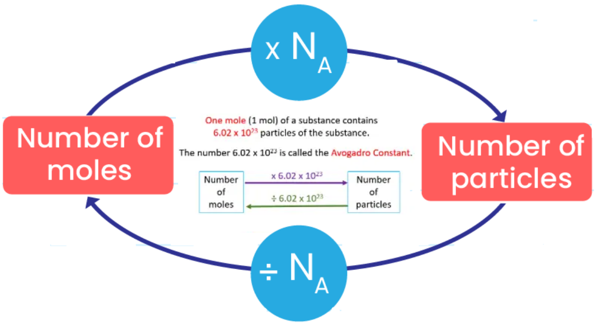
Vm= 22,4 l/mol (Under these conditions, the number of moles becomes:

$$n = \frac{V}{V_m} = \frac{V}{22,4}$$

I-3-3 Avogadro Number N_A

The number of atoms contained in one mole of carbon is called Avogadro's number and is given by N_A. One mole of an atom corresponds to **6.023** 10^{23} atoms,

Note: **6,02** 10^{23} converts the number of entities (molecules, atoms or ions) into the number of moles and vice versa ***(Figure I-5)***



One mole (1 mol) of a substance contains 6.02×10^{23} particles of the substance.

The number 6.02×10^{23} is called the Avogadro Constant.

Figure I-5 Relationship between Mole and Avogadro's Constant

I-4-Unité de masse atomique (uma)

The masses of particles (electron, proton, neutron, etc.) are not all on our scale, so we use a mass unit that is different from the kg but better suited to the quantities being measured: the **u.m a**. The atomic mass unit is 1/12 f the mass of a carbon 12 atom.

$$1\ \text{u.m.a} = \frac{1}{12}\ \text{MC} = \frac{1}{N_a} = 1,\ 66 \times 10\text{-}24\ \text{g} = 1,\ 66 \times 10^{-27}\ \text{Kg}4$$

MC: molecular mass of carbon.

I-4-1 Molar atomic mass

Atomic molar mass: is the mass of one mole of atoms of an element, because the masses of the atoms are all very small (between $\mathbf{10^{-24}}$ and $\mathbf{10^{-26}}$ kg)

Exemple :

- MC= 12,0 $g.mol^{-1}$ et MO = 16,0 $g.mol^{-1}$ MO: molecular mass of oxygen.
- Calculate the atomic mass of element (X), knowing that the mass of the atom of element (X), is (**m_X gr) ; M(X) = m (atom of element (X)) x N_A = m_X x N_A.**

I-4-2 Molecular molar mass

Molecular molar mass: is the mass of one mole of molecules. It is the sum of the atomic masses that make up a body.

Exemple : Molar mass of water H_2O: MH_2O= 2.1+16=18 $g.mol^{-1}$ (The molecular molar mass of the H2O molecule is the sum of the atomic molar mass of oxygen and twice the atomic molar mass of hydrogen).

I-4-3 Le molar volume

The molar volume of a perfect gas is the volume occupied by one mole of any perfect gas under Normal Conditions of Temperature and Pressure.

(to be precise: $1{,}013.10^5$ Pa [1013 hPa] et 0° Celsius [273,15 Kelvin]). This condition is noted CNTP or **TPN.**

his volume is 22.41 L = 0.02241 m^3 under NTP conditions..

- Unless otherwise stated, the molar volume of a gas is always expressed according to CNTP!

1 mole of compound in the gaseous state will occupy a volume of 22.4 L

Exemple : One mole of (O2) or (CO2) will always occupy a volume of 22.4 L under TPN conditions and a volume of 24.79 L under CNTP conditions.

Propriété :

- Its unit is the litre per mole (L-mol-1). In the units of the international system, molar volume is expressed in cubic meters per mole (m^3-mol^{-1}).
- The molar volume can be calculated using the formula: Vm = V/n

Note: This formula applies to gases only, where V is the volume in litres and n is the quantity of substance in moles.

I-5- Weight rules

The law of definite proportions is a law of weights laid down by Joseph Louis Proust, according to which when two or more simple bodies combine to form a definite compound, they always combine in the same weight ratio (relative to the weights and therefore to the mass).

I-5-LAVOISIER Law (1789)

In a chemical reaction, the mass of the reactants lost is equal to the mass of the products formed (Lavoisier's Law). ; ***Reactants (R)*** → ***Products (P)***

- **Σ of the mass of reactants = Σ of the mass of products**
- **In a chemical reaction, the elements are conserved**

I-5-2 law of definite proportions (PROUST's law)

Proust's law or the law of definite proportions teaches us that: "during the formation of a given pure substance, the ratio between the masses of each reagent consumed in the chemical reaction is constant.

I-5-3 Multiple proportion law

When two simple bodies can form several compounds. The masses of one of the constituents unite with the same mass of the other are always in ratios of whole numbers.

Exemple : a chemical compound made up of two elements A and B, for example oxygen and nitrogen, r is the ratio $\frac{m_{(A)}}{m_{(B)}}$ the masses of A and B measured for a certain quantity of this compound. Consider two different chemical compounds A and B, with respective ratios r1 and r2. The law of multiple proportions states: The ratio $\frac{r_1}{r_2}$ is the ratio of two small integers.

I-5-4 Dalton's atomic hypothesis and its consequences:

Dalton based his theory on two laws: the law of conservation of mass (which states that in a closed system matter can be neither created nor destroyed) and the law of definite proportions. It is based on 4 important points:

- Matter is made up of small, invisible, indivisible particles called atoms (H for hydrogen, C for carbon, etc.).
- The atoms of a given element are identical (they have the same properties and the same mass).
- Atoms of different elements have different properties and masses.

- Atoms can combine to form a new substance (the molecule produced has different properties to the atoms that make it up).

I-6- Qualitative aspect of the matter

I-6-1 The Pure *substance*:

- ***A pure* substance** is a substance made up of a single type of chemical entity (atom, ion or molecule).
- ***A pure substance*** is either an element (a simple pure substance, e.g. Cu, Fe, H2, O2, etc.) or a compound (made up of several elements, e.g. pure water H2O).

Among pure substances, a distinction is made between simple pure substances and compound pure substances.

I-6-2 Les corps purs simples :

On appelle corps purs simple, une substance chimique qui n'est composée que d'un type d'élément chimique.

Example: Oxygen (O2), formed from two oxygen atoms, and dinitrogen (N2), formed from two nitrogen atoms, are simple pure bodies.

I-6-3 Pure Compound bodies:

Are made up of different types of atoms combined into molecules, salts, complexes or any other polyatomic structure, such as water (H2O), sodium chloride (NaCl), ...

I-6-4 the Blends

Matter is a mixture of particles, atoms and/or molecules ***(Figure I-6).*** There are two types of mixture:

- Homogeneous mixtures, in which the various constituents are indistinguishable and evenly distributed throughout the sample.
- ***Example***: air (a mixture of oxygen and nitrogen), salt in water, And heterogeneous mixtures, whose components are not equally distributed throughout the sample and whose individual components can be identified. (Oil in water, sugar in salt, .).

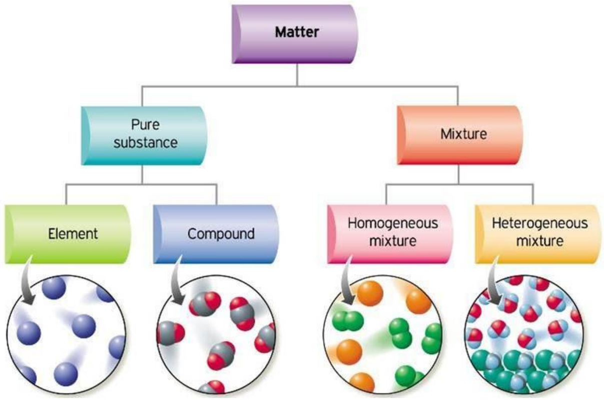


Figure I-6: Classification of matter

I-6-4-1 Liquid-liquid mixtures

Some liquids mix together: they are miscible. ... If two liquids are miscible, then the mixture is homogeneous. If two liquids are immiscible, then the mixture is heterogeneous.

I-6-4-1-1 Homogeneous mixture :

If, after stirring, the bodies cannot be distinguished from one another, the mixture is said to be homogeneous, i.e. a homogeneous solution.

I-6-4-1-1 Miscibility

Miscibility usually refers to the ability of different liquids to mix. If the mixture obtained is homogeneous, the liquids are said to be miscible.

Example: Water and vinegar.

Liquids are said to be immiscible if they cannot mix and form a heterogeneous mixture: there are then several phases.

Example: The liquid of lower density will then be positioned above the other. This is the case, for example, with water and oil.

I-6-4-2 Heterogeneous mixture

If, after stirring, the substances brought together can be distinguished from one another, the mixture is heterogeneous.

I-6-4-2-1 Liquid-solid mixtures

Some solids (such as salt or sugar) are soluble in water. The mixture is then clear: it is a homogeneous mixture also known as a solution. Other solids (such as sand) are insoluble: the mixture is then cloudy. This is a heterogeneous mixture, also known as a suspension.

I-6-4-2-2 the dissolution

Dissolution is the physico-chemical process by which a solute incorporated into a solvent (the solute is said to be dissolved) forms a homogeneous mixture called a solution. Conversely, a solution is obtained by dissolving a chemical species in a solvent. Formally, dissolution is defined as the mixing of two phases to form a new homogeneous phase.

I-6-4-3The Other Mixture

- There are a number of situations where the type of mixture obtained from two chemical species is predictable:
- Direct mixing of two solids (without intermediate melting) always results in a heterogeneous mixture.
- A mixture of gas and solid is always heterogeneous.
- Two aqueous solutions (in the absence of chemical transformation) form a homogeneous mixture.

Two gases always form a homogenous mixture.

In other cases, the type of mixture obtained may depend on the proportions of the constituents and sometimes on their chemical nature.

I-6-4-3-1 Solid-solid mixtures

Two solids always form a heterogeneous mixture if they are in the solid state at the time of mixing, but if the mixture is obtained by solidifying a mixture of liquids, then it is possible to obtain a homogeneous mixture (this is the case with alloys, for example).

Note :

- ***Two initially solid bodies → heterogeneous mixture***
- ***Solidification of a homogeneous mixture of two molten solids → homogeneous mixture***

I-6-4-3-2 The mixture gas-gas

n the absence of chemical transformation, the mixture of two gases is always homogeneous. Gases always mix together as long as their molecules are not linked.

Note: ***Two gases → homogeneous mixture***

I-6-5-The solutions

A solution is a homogeneous mixture composed of a solvent which is in large excess compared with the other constituents of the mixture and one or more solutes. Solutions are usually in liquid form.

I-6-5-1 The solvent

Solvents are substances that are used to dissolve, extract or suspend other substances to form a generally liquid solution. In other words, a solvent is any liquid substance that has the power to dissolve other substances.

I-6-5-2 The solute

Is a chemical species (molecular or ionic) dissolved in a solvent.

Note ***:*** ***The solvent is always in much greater quantity than the solute(s).***

I-6-6 Aqueous solution

An aqueous solution is a liquid phase containing several majority chemical species, water (H2O, the solvent), and minority species, the solutes or "dissolved chemical species". The study of aqueous solutions constitutes the major part of chemistry.

I-6-6-1 Aqueous solution, solute and solvent

This homogeneous mixture (solvent + solute) is called an aqueous solution if the solvent is water. The substance in question is referred to as the solute and the water as the solvent. When the limit to the quantity of solute that water can dissolve is reached, we speak of a saturated aqueous solution.

I-6-6-2 Saturation of a solution

Saturation is the concentration above which a substance cannot dissolve in a solvent. This is the solubility limit and the solution is therefore a saturated solution.

Note ***: This solubility limit can be pushed back by heating the solution.***

I-6-6-3 Dilution of a solution

Dilution is a process that consists of obtaining a final deconcentrated solution that is smaller than the initial solution, either by adding solvent or by removing part of the solution and replenishing it with solvent to maintain the same volume. Dilution is characterised by its dilution ratio. This presupposes that the diluted substance is soluble in the solvent used.

Note

The initial solution is called the mother solution and the diluted solution is called the daughter solution. During a dilution, the quantity of dissolved chemical species does not change

$$N_{mother}= n_{daughter} \Rightarrow C_mV_m= C_dV_d \quad \text{Avec} \quad n_{mother} = C_0V_0$$

Where n: quantity of substance; V: volume and C: concentrationm:

- Initial, i.e. relative to the mother solution.
- d: final, i.e. relative to the dilute (daughter) solution.

Note

The problem is to determine the volumes: Vm: volume of stock solution to be taken and Vf: volume of dilute solution corresponding to that in the volumetric flask.

Example :

To prepare a volume V1= 100ml of a potassium hydroxide solution with a concentration of $2.5.10^{-3}$ mol/ l from a potassium hydroxide solution with a concentration of 5.10^{-2} mol/l. a volume V1 of the initial or stock solution must be taken.

$$N_{mother} = C_0V_0 = n_{daughter} = C_1V_1 \Rightarrow V_0 = C_1V_1/V_1 \Rightarrow V_0 = 2,5.10^{-3} x\ 0,1/5.10^{-2} = 5\ ml$$

I-7- Quantitative aspect of the Matter

See Table I.1 : Concentration formulas below

I-7-1 Quantity of matter

The quantity of matter is a quantity used to count elementary chemical or physical entities. The corresponding unit is the mole. This concept allows us to move from the microscopic to the macroscopic.

I-7-2 Number of mole

It is the quantity of matter containing N identical entities (entities = molecules, atoms or ions).Also defined as the number of carbon12 atoms contained in 12g of carbon12.

$$1\ mol = \frac{12g}{1.9926*10-23} = 6.023\ 10^{23}.$$

***The mole number** is the ratio between the mass of the compound and its molar mass:*

$$n = \frac{m}{M}$$

n: number of moles**;** **m:** mass of compound in g**;** **M:** molar mass of compound in g/mol

I-7-3 Molar concentration or molarity

Molarity (CM): expresses the number of moles of solute per litre of solution.

I-7-4 Molalité

Molality (Cm): expresses the quantity of solute contained in 1000 g of solvent.

I-7-5 Mass concentration (Weight concentration)

The mass concentration of a chemical substance in solution is the mass of solute present per litre of solution. The mass concentration is called Cm and is expressed in $g.L^{-1}$.

I-7-6 Weight or mass fraction (Mass fraction/ Weight fraction (wt/wt)

The mass fraction w_i of component i is the ratio of the mass m_i of this component to the total mass m_{tot} of the mixture.

I-7-7 Solution title

The titre (T) is calculated using the mass of the solute (m) expressed in grams divided by the volume of the solution (V) expressed in litres.

I-7-8 The mole fraction x_i

Mole fraction (Xi): indicates the ratio between the number of moles and the total number of moles in the solution.

I-7-9 Normal concentration or Normality

Normality (N): expresses the number of gram equivalents of solute per litre of solution (eq.g/l). The gram equivalent is the quantity of substance comprising one mole of the particles in question (H+, OH-, e-...... etc.).

I-7-10 Volumic Mass

Density is the mass of a substance per unit volume at a given temperature. SI unit $Kg.m^{-3}$, usually: $g.L^{-1}$

I-7-11 Density

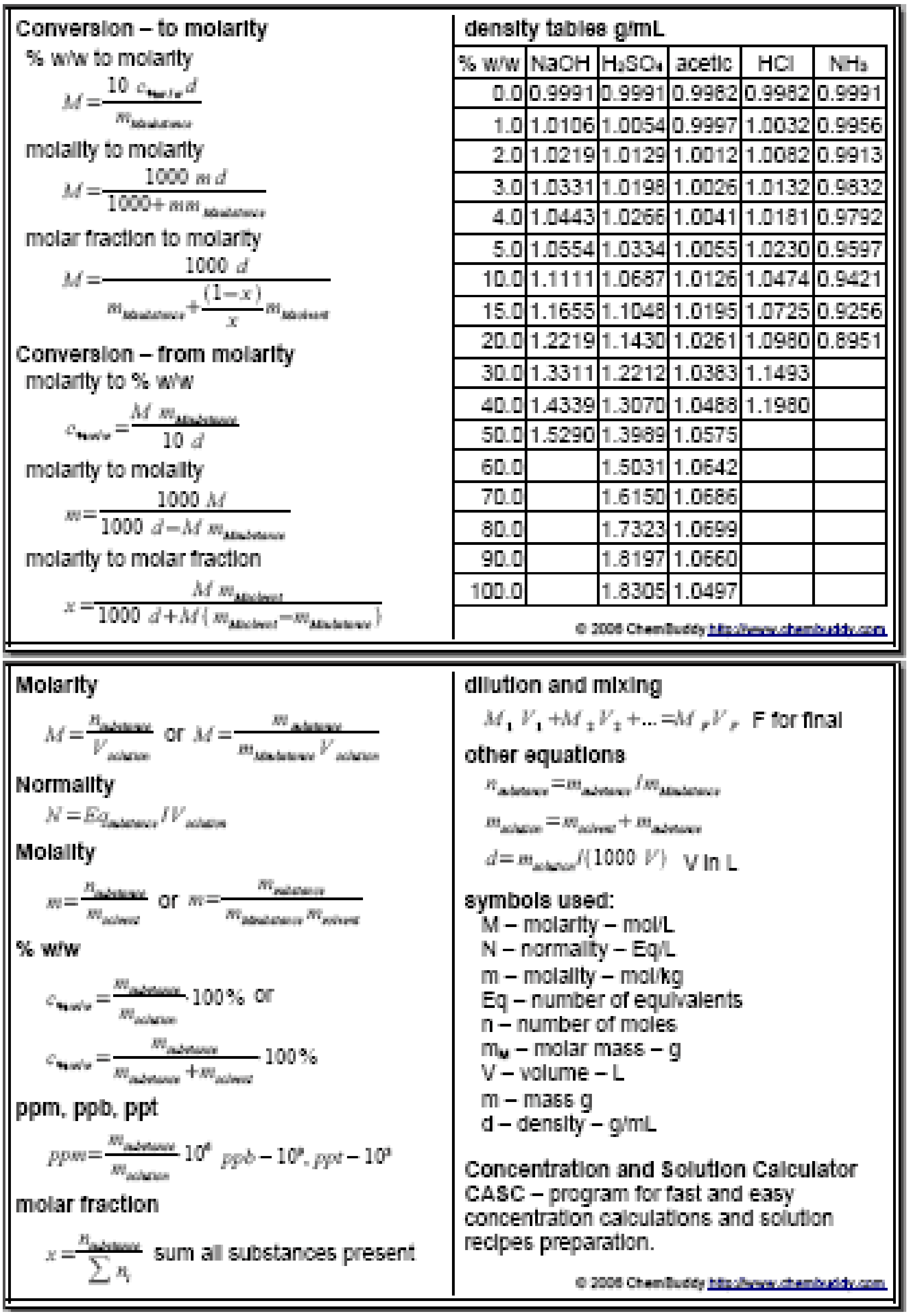
The density of a substance is equal to the density of the substance divided by the density of the reference body at the same temperature $d = \rho_{substance} / \rho_{water}$

I-7-11-1 Liquid density

Number without unit, expressing the ratio of the mass of a certain volume of a body to that of the same volume of water. $d = \rho_{body} / \rho_{water}$

I-7-12 The laws of dilute solutions: Raoult's laws

Raoult's law states that in an ideal solution, at constant temperature, the partial pressure in the vapour phase of a component is proportional to its mole fraction in the liquid phase.



Conversion – to molarity

% w/w to molarity

$$M=\frac{10\ c_{\%w/w}\,d}{m_{Msubstance}}$$

molality to molarity

$$M=\frac{1000\ m\,d}{1000+m\,m_{Msubstance}}$$

molar fraction to molarity

$$M=\frac{1000\ d}{m_{Msubstance}+\frac{(1-x)}{x}m_{Msolvent}}$$

Conversion – from molarity

molarity to % w/w

$$c_{\%w/w}=\frac{M\ m_{Msubstance}}{10\ d}$$

molarity to molality

$$m=\frac{1000\ M}{1000\ d-M\ m_{Msubstance}}$$

molarity to molar fraction

$$x=\frac{M\ m_{Msolvent}}{1000\ d+M(m_{Msolvent}-m_{Msubstance})}$$

density tables g/mL

% w/w	NaOH	H_2SO_4	acetic	HCl	NH_3
0.0	0.9991	0.9991	0.9982	0.9982	0.9991
1.0	1.0106	1.0054	0.9997	1.0032	0.9956
2.0	1.0219	1.0129	1.0012	1.0082	0.9913
3.0	1.0331	1.0198	1.0026	1.0132	0.9832
4.0	1.0443	1.0266	1.0041	1.0181	0.9792
5.0	1.0554	1.0334	1.0055	1.0230	0.9597
10.0	1.1111	1.0687	1.0126	1.0474	0.9421
15.0	1.1655	1.1048	1.0195	1.0725	0.9256
20.0	1.2219	1.1430	1.0261	1.0980	0.8951
30.0	1.3311	1.2212	1.0383	1.1493	
40.0	1.4339	1.3070	1.0488	1.1980	
50.0	1.5290	1.3989	1.0575		
60.0		1.5031	1.0642		
70.0		1.6150	1.0686		
80.0		1.7323	1.0699		
90.0		1.8197	1.0660		
100.0		1.8305	1.0497		

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Molarity

$$M=\frac{n_{substance}}{V_{solution}}\ \text{or}\ M=\frac{m_{substance}}{m_{Msubstance}V_{solution}}$$

Normality

$$N=Eq_{substance}/V_{solution}$$

Molality

$$m=\frac{n_{substance}}{m_{solvent}}\ \text{or}\ m=\frac{m_{substance}}{m_{Msubstance}m_{solvent}}$$

% w/w

$$c_{\%w/w}=\frac{m_{substance}}{m_{solution}}\cdot 100\%\ \text{or}$$

$$c_{\%w/w}=\frac{m_{substance}}{m_{substance}+m_{solvent}}\cdot 100\%$$

ppm, ppb, ppt

$$ppm=\frac{m_{substance}}{m_{solution}}10^6\quad ppb-10^9,\ ppt-10^{12}$$

molar fraction

$$x=\frac{n_{substance}}{\sum n_i}\ \text{sum all substances present}$$

dilution and mixing

$$M_1V_1+M_2V_2+...=M_FV_F\quad \text{F for final}$$

other equations

$$n_{substance}=m_{substance}/m_{Msubstance}$$

$$m_{solution}=m_{solvent}+m_{substance}$$

$$d=m_{solution}/(1000\ V)\quad \text{V in L}$$

symbols used:

M – molarity – mol/L
N – normality – Eq/L
m – molality – mol/kg
Eq – number of equivalents
n – number of moles
m_M – molar mass – g
V – volume – L
m – mass g
d – density – g/mL

Concentration and Solution Calculator
CASC – program for fast and easy concentration calculations and solution recipes preparation.

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Tableau I.1 : *Concentration formulas* [1]

[1]*LA PAGLIA S.R., Introductory quantum chemistry, Harper & Row, New York, 1971.*

II-1- Introduction

His concept of the atom dates back more than 2,500 years, when Greek scientists proposed that the objects around us were made up of tiny particles they called atoms. However, it was not until the 19th century, notably with J. Dalton and A. Avogadro, for the atom to move from a philosophical to a scientific concept. It was not until the early twentieth century that we had the technical means to probe matter on a subatomic scale.

All natural objects are made up of combinations of atoms with a limited number of species. John Dalton, a 19th-century British chemist, formalised the modern atomic theory in seven points:

1) Ordinary matter is made up of "particles" called atoms.
2) These atoms are too small to be seen with the naked eye.
3) The different chemical substances are made up of specific atoms, characterised by their atomic mass.
4) All atoms of the same chemical element are identical.
5) Atoms combine in simple proportions to form new substances.
6) Atoms, however, remain unchanged.
7) Atoms cannot be divided, created or destroyed.

Apart from a minor correction to point 4 to take account of isotopes (see below), the first five points are correct. During the 20th century, point (7) was shown to be wrong: atoms can be divided into even more fundamental particles: the proton, neutron and electron

II-2- Faraday experiment: the relationship between matter and electricity

Faraday noted with "wonder" that the destruction of chemical bonds by electrolysis involved considerable quantities of electricity.

II-2-1 The discovery of the electron

Historical:

In 1833, Faraday established the laws of electrolysis, which stated that in a solution of water and salt, each atom or molecular fragment had a fixed electrical charge. The formulation of the laws of electrolysis was a major asset for atomic theory throughout the 19th century, until the discovery of the electron at the end of the century.

The discovery of the electron. By studying the decomposition of solutions by electric current, Faraday had established that, for the same quantity of electricity, the weight of matter deposited by the ions varied in ratios similar to those involved in chemical reactions. Example: electrolysis of water: $H_2O \rightarrow H_2 + 1/2\ O_2$.

II-3 Highlighting the constituents of matter and therefore of the atom and some physical properties (mass and charge)

II-3-1 Electron:

II-3-1-1 Electrons highlighted

The concept of the electron, or "atom of electricity", was introduced by G. Stoney. The experimental demonstration and characterisation of this particle came with J.J. Thomson. He proved that matter is made up of heavy positive parts and electrons, lighter negative parts, for which he was able to determine the charge and mass.

II-3-1-2 J.J.Thomson experiment: Determination of the ratio |e| / me

Under the effect of a very high electrical voltage (40,000V) applied between two parts of a gas tube, a beam is emitted from the cathode, called cathode rays, and collected by the anode. The trajectory of the rays is straight and perpendicular to the surface of the cathode.

The application of an electric or magnetic field deflects the trajectory of the cathode rays in the opposite direction to the field. The cathode ray is therefore made up of negatively charged particles called electrons. ***(Figure II-1).***

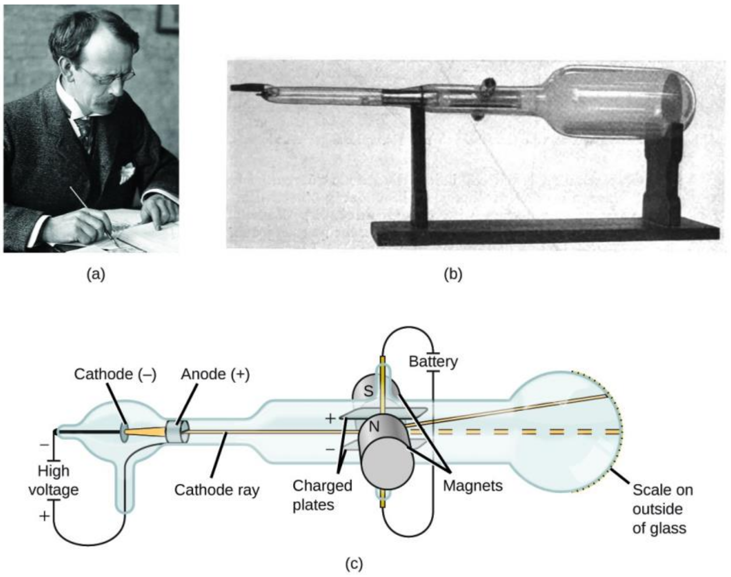


Figure II-1 : Cathode rays and the deflection path of the electron

J.J. Thomson thus came up with the notion of splittable atoms. To respect the classical vision of continuous matter, he proposed the "plum pudding" model. (Figure II-2)

He imagined that the electrons, the "plum", moved in a positively charged medium: the "pudding".

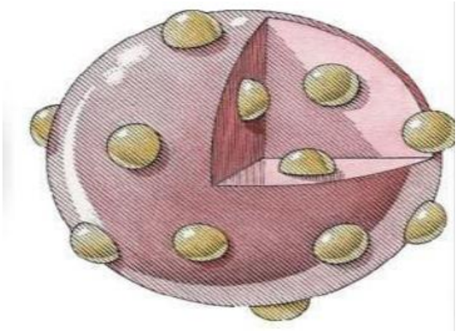
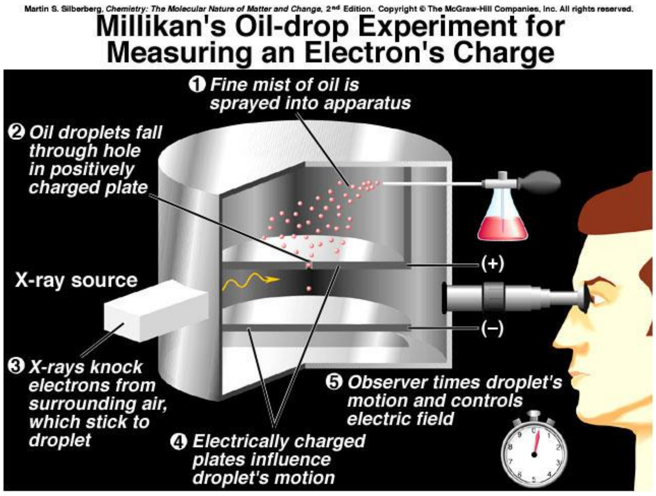


Figure II-.2 : Diagram of a plum pudding

II-3-1-3 Millikan experiment: Determination of the charge |e| of the electron and deduce its mass

Millikan's experiment contains a sprayer P that produces oil droplets in the upper chamber. The microscope M is used to follow the evolution of the droplets once they have penetrated between the plates of the condenser. An X-ray beam irradiating the space between the plates creates ions that attach themselves to the droplets. All the forces acting on a charged droplet ***(Figure II-2)***



Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Millikan's Oil-drop Experiment for Measuring an Electron's Charge

Figure II-2: Millikan experiment

The values of q determined in this way are always multiples of a certain value e, which is the smallest electrical charge that a charged droplet of oil can carry.

This is the elementary electric charge e. with: $e = 1.602.10^{-19}$ Coulomb

Knowing the values (|e|/me) and (e), we can deduce the mass of the electron: $m_e = 9.108.10^{-31}$ Kg.

II-3-2 Proton:

The proton is a tiny particle. It is about one hundred thousand times smaller than the hydrogen atom (1/100,000 = 10^{-5}), which itself measures about one ten-billionth of a metre, or 10^{-10} m. The proton carries a single positive charge (+ 1 e) and its mass is one unit of atomic mass (1 amu or 1 u). This is a tiny unit: 1 u = 1.66×10^{-27} kg.

A proton weighs 1.0073 u, which we usually round up to 1 u.

Goldstein experiment: demonstration of the positive charge of the nucleus

In a discharge tube, we place a cathode pierced with channels. Radiation is visible on the fluorescent screen: these are channel rays, positive ions obtained by tearing electrons from the gas molecules contained in the enclosure. The positive ions, attracted by the cathode and with sufficient kinetic energy, pass through the channel and strike the fluorescent screen, revealing the existence of positive particles in the nucleus, protons. These are protons ***(Figure II-3).***

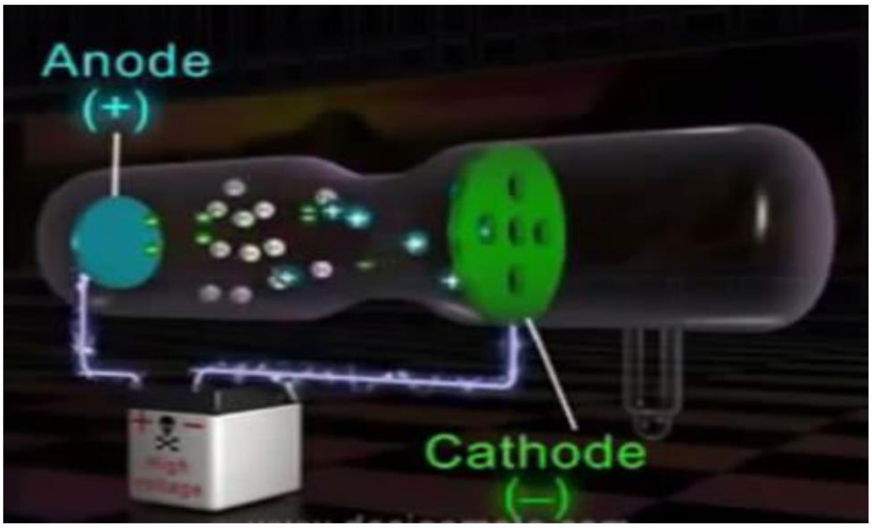


Figure II.3: Goldstein experiment

II-3-3 Neutron:

Un neutron est une particule neutre (dépourvue de charge électrique) de la même taille que le proton. It weighs 1.0087 u, 2½ electron masses more than the proton. We usually round its mass to 1 u.

II-3-3-1 Chadwick's experience

It was first demonstrated by James Chadwick (1932). The bombardment of a beryllium target by helium nuclei emits neutrons. Since the beam from the beryllium was not deflected by electric or magnetic fields, it could only be electromagnetic radiation or a beam of neutral particles. During an experiment in which he bombarded beryllium with alpha particles, he noticed an unknown type of radiation that ejected protons from the nucleus. Chadwick concluded that this radiation was made up of particles with a mass approximately equal to that of the proton but with no electric charge; neutrons.... ***(Figure II-4)***

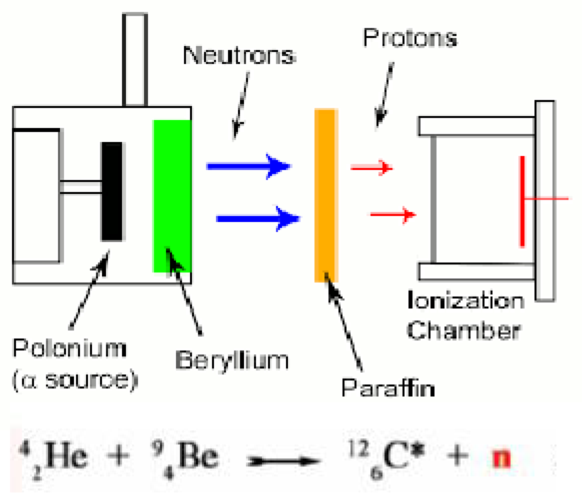


Figure II-6: Chadwick's neutron discovery experiment

II-4 Rutherford planetary model

The Rutherford atomic model or planetary model of the atom is a physical model proposed in 1911 by Ernest Rutherford to describe the structure of an atom. This model follows the Thomson atomic model (or "plum pudding model"), proposed in 1904 by Joseph John Thomson, which was invalidated following Rutherford's experiment or "gold foil experiment" in 1909. The Rutherford-Bohr atomic model represents the atom by indicating the number of protons in the nucleus as well as the number of electrons in each electron shell. Rutherford's model was a significant advancement in understanding the structure of the atom.

II-4-1 Discovery of the core

The discovery of the atomic nucleus is attributed to Ernest Rutherford, Hans Geiger and their student Ernest Marsden. Their measurements took place in Manchester in 1909. The experiment involved measuring the scattering of alpha particles (i.e. helium nuclei) by a foil of gold.

II-4-1-1 The gold foil experiment

The gold leaf experiment, also known as the Rutherford experiment, is a nuclear physics experiment carried out by New Zealand physicist Ernest Rutherford in 1911. The experiment involved bombarding a thin sheet of gold with alpha particles (helium nuclei) emitted by a radioactive source.

The alpha particles were directed at the gold foil and the scientists measured the angles of deflection of the alpha particles as they passed through the foil (Figure II-7). Rutherford expected the alpha particles to pass easily through the gold foil with little or no deflection, as he believed that atoms were mainly composed of vacuum with a small positively charged nucleus in the centre. However, the results of the experiment revealed that some alpha particles were deflected at significant angles, and some even bounced backwards..

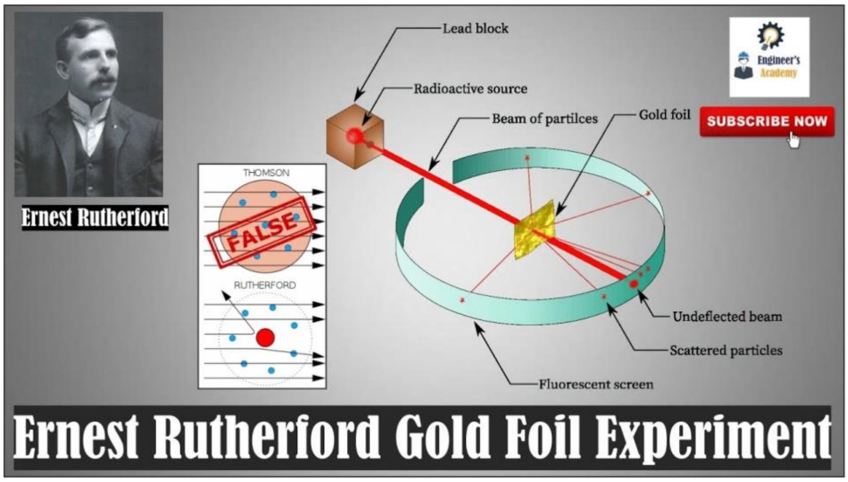


Figure II-7 : Ernest Rutherford Gold Foil Experiment

These results led Rutherford to conclude that atoms are not composed mainly of vacuum, but rather that the positive charge is concentrated in a small, dense nucleus at the centre of the atom, and that most of the space in an atom is in fact empty, in other words Rutherford deduced that the atom is made up of a positively charged nucleus, around which negatively charged electrons are in motion and remain inside a sphere. The nucleus is 10^4 to 10^5 times smaller than the atom and concentrates most of its mass ***(Figure II-8).***

In the light of these results, Rutherford proposed his model: Matter is concentrated in a nucleus of very small dimensions, about 10^{-14} m in radius, charged with positive electricity. The electrons of the atom move around this nucleus like planets around the Sun, and the attractive electric force (the - charge of the electron attracting the + charge of the nucleus) plays the role of the gravitational force for the planets; hence the name planetary atom model. The electron is subject only to the electromagnetic force ***(Figure II-8).***

This discovery has had a significant impact on our understanding of the structure of the atom and nuclear physics in general..

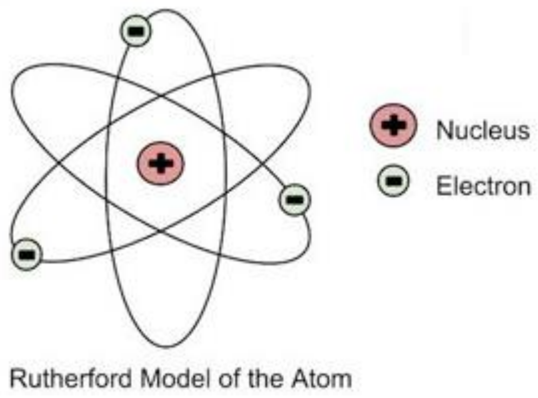


Figure II-7 : Rutherford Model of the Atom

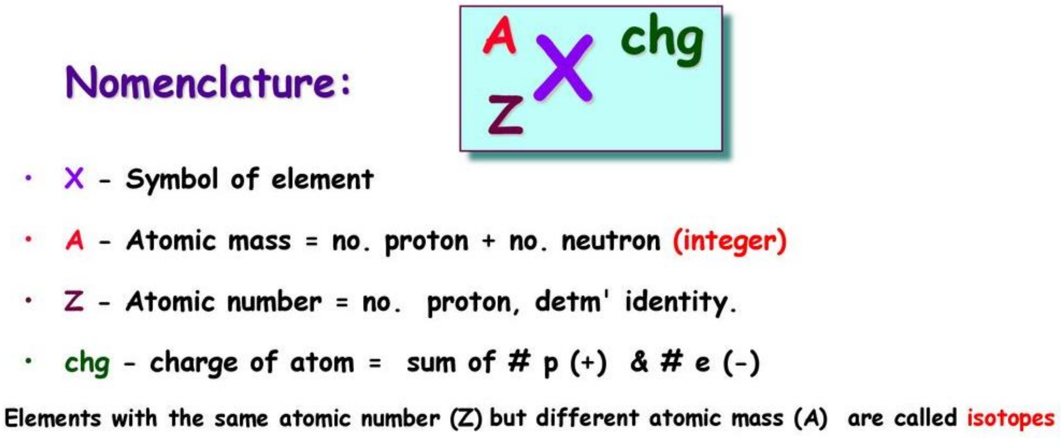
II-5 Presentation of the atom

The atom is the smallest particle of matter that has the chemical properties of an element. It consists of a central nucleus containing protons and neutrons, and electrons that orbit the nucleus. In an atom, there are as many positively charged protons as negatively charged electrons: an atom is electrically neutral. The number of protons is the atomic number Z. The sum of protons and neutrons is the mass number A.

An atom is made up of a nucleus of protons and neutrons, and a cloud of electrons, all of which are electrically neutral; it is characterised by an atomic number, which corresponds to its number of protons, which is also the number of electrons. Each atom is defined by its atomic number, which corresponds to the number of protons in the nucleus.

II-5-1 Nomenclature

The atom is made up of three types of subatomic particles: protons, neutrons and electrons. The number of protons in the nucleus of an atom determines its atomic number, which is used to identify the chemical element to which the atom belongs. The nucleus of an atom is represented by the symbol:



Nomenclature:

$^{A}_{Z}X^{chg}$

- X - Symbol of element
- A - Atomic mass = no. proton + no. neutron (integer)
- Z - Atomic number = no. proton, detm' identity.
- chg - charge of atom = sum of # p (+) & # e (-)

Elements with the same atomic number (Z) but different atomic mass (A) are called isotopes

A: Number of protons or mass number;

Z: Charge number or atomic number (atomic number) this is very important because it characterises the chemical element.

X: chemical symbol of the element, for example: X = O: oxygen, X = Cl: chlorine,

X= Cl. If we note Cl the number of neutrons in the **nucleus**, we have: **A = Z+N.**

The name of an element is generally derived from its atomic number. For example, the element with an atomic number of 8 is oxygen, the element with an atomic number of 6 is carbon and the element with an atomic number of 1 is hydrogen.

$$^{A}_{Z}X \quad ^{12}_{6}C \ ; \ ^{16}_{8}O \ ; \ ^{1}_{1}H$$

What's more, some elements can have several isotopes; some elements can have several isotopes, which are atoms with the same number of protons but a different number of neutrons

II-5-2 The atom's characteristics

The atom is the smallest unit of matter that has the chemical properties of an element. An atom contains a nucleus at its centre and electrons that "revolve" around the nucleus. The nucleus contains nucleons, i.e. protons and neutrons. Electrons have a negative electrical charge. Protons have a positive electrical charge, the same value as that of the electron ***(Figure II-9).***

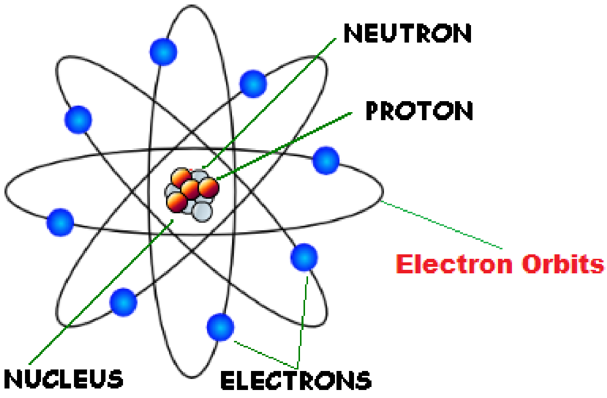


Figure II-9: Rutherford's nuclear model of atom

The proton, which has a charge of $+1.60 \times 10^{-19}$ Coulomb, corresponding to the elementary charge for a mass of 1.673×10^{-27} Kg...

The neutron has zero charge and a mass of 1.675×10^{-27} Kg.

The nucleus (Core) has a positive charge. The neutrons and protons make up the nucleons, which are held together by strong interaction.

The electron An electron has a charge of -1.60 x10^{-19} C, which is negative and opposite to that of the proton, and a mass of 9.109 x 10^{-31} Kg, so it is 1800 times lighter than the proton. The mass of an atom is therefore roughly the same as the mass of its nucleus. An atom has as many electrons as protons, so its overall charge is zero.

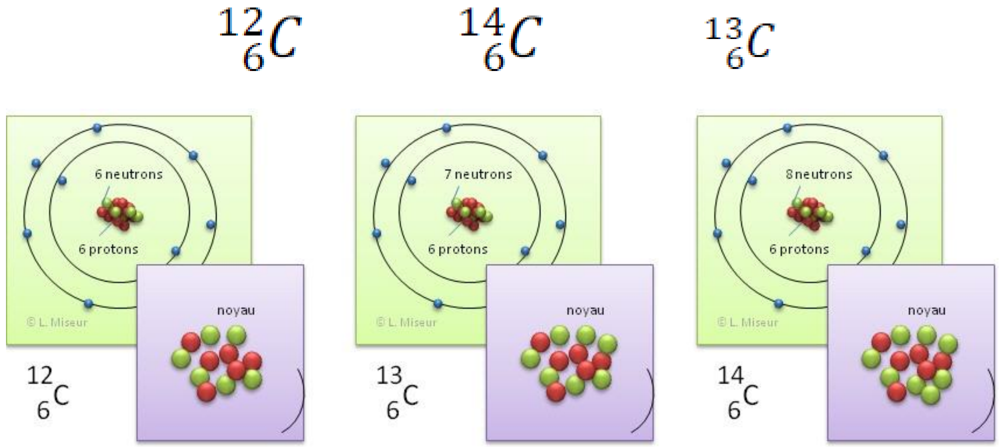
II-5-2-1 The Nucleus

The nucleus of an atom is the central region of the atom that contains the protons and neutrons that make up the nucleons. Protons are positively charged particles, while neutrons are particles with no electrical charge. Together, protons and neutrons form the nucleus of the atom. The nucleus is surrounded by electrons, which are negatively charged particles that move in space around the nucleus. The whole atom is electrically neutral, because the number of positive protons in the nucleus is equal to the number of negative electrons orbiting the nucleus.

II-6 Isotopy and relative abundance of different isotopes

The isotopes are atoms of the same element that have the same number of protons in their nucleus, but a different number of neutrons. This means that isotopes have different atomic masses but similar chemical properties. Therefore, they are sets of atoms that only differ in the number of their neutrons.

Example **:** Carbon isotopes



II-6-1-1 The natural abundance of isotopes (AN)

Isotopy is the property of different isotopes of the same element. The relative abundance of isotopes is the proportion of each isotope in a sample of an element. The relative abundance of isotopes varies according to the element and the sample in question. For example, carbon has three natural isotopes: carbon-12, carbon-13 and carbon-14. Carbon-12 is the most abundant, accounting for about 98.9% of all carbon atoms in nature; carbon-13 accounts for about 1.1% of all carbon atoms; and carbon-14 is extremely rare, accounting for only about one carbon atom in a trillion.

This abundance is equivalent to the mole fraction of each stable isotope. Since an element is made up of a mixture of various isotopes and the proportions of these various isotopes are constant, we can define an average molar mass for each element, taking into account its composition.

$$M = \sum x_i M_i \; ; \sum_i^n x_i = 1$$

M : Molar mass of element.

X $_i$: is the natural abundance of isotope i.

M $_i$: Molar mass

<u>for example</u>: In the example of oxygen:

Isotope	Abundance (molar percentage)	Range of variation
^{16}O	99,757 (16) %	99,738 – 99,776
^{17}O	0,038 (1) %	0,037 – 0,04
^{18}O	0,205 (14) %	0,188 – 0,222

$M(O) = 0{,}99757 \text{ x } M(_{16}O) + 0{,}00038 \text{ x } M(_{17}O) + 0{,}00205 \text{ x } M(_{18}O)$.

$M(O) = 0{,}99757 \text{ x } 16 + 0{,}00205 \text{ x } 18 = 15.99 \text{ g /mol}^{-1}$

.

II-7 Separation of isotopes and determination of the atomic mass and average mass of an atom

II-7-1 Spectrométrie de masse

Mass spectrometry is a chemical analysis technique used to determine the molecular weight and composition of a sample. It is used in many fields, including chemistry, biochemistry, pharmacology, medicine, geology and astronomy.

A mass spectrometer is used to separate and measure the mass of isotopes of the same element. There are many different types of mass spectrometer:

ASTON mass spectrometer

DEMPSTER mass spectrometer

BAINBRIDGE mass spectrometer

Isotopes are subjected to the effects of electric and magnetic fields

The most practical method is to measure the ratio (q/m)

q: the charge of the isotope; **m:** the mass of the isotope.

II-7-1-1 Mass spectrometer description

A mass spectrometer is a complex instrument that analyses the molecular composition of a sample using the principle of mass spectrometry. The mass spectrometer consists of several important parts:

The source of ions: it produces ions from the sample by vaporising and ionising it. There are several techniques for ionising samples, including electrospray ionisation (ESI), matrix-assisted laser desorption/ionisation (MALDI) and electron impact ionisation (EI) mass spectrometry.

The analysis chamber: once the ions have been produced, they are directed into the analysis chamber, where they are separated according to their mass by an electromagnetic field. The analysis chamber is also equipped with a detector that records the signal from each ion.

The mass analyser: this may be a quadrupole, time-of-flight, ion trap or orbiter type analyser, which is used to separate ions according to their mass. The type of analyser used depends on the needs of the experiment and the desired resolution.

The detector: the detector records the signal generated by each ion, which is separated and identified by the mass analyser. The signal is amplified and transmitted to the computer for analysis and the creation of a mass spectrum.

The computer: the signal recorded by the detector is analysed by specialised software to generate a mass spectrum that can be used to identify the molecules present in the sample..

II-7-1-1-1 Bainbridge spectrograph

This spectrograph consists of four parts:

1- The source of ions

2- velocity filter

3- The analyser

4- The ion detector
the application of this spectrograph is the precise determination of atomic masses and concentrations in a solution ***(Figure II-10).***

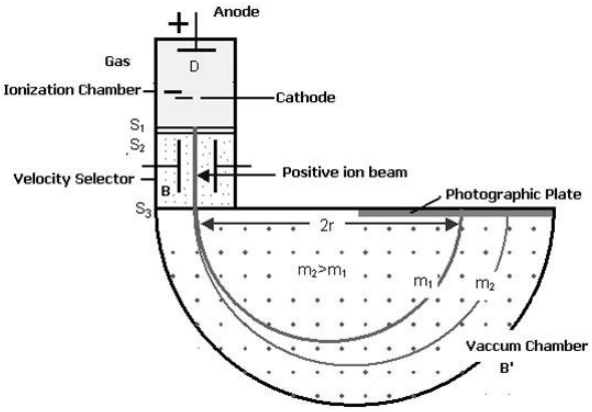


Figure II-10: Bainbridge spectrograph schematic diagram

The source of ions:

When a heated filament emits a flow of electrons, these have the effect of positively ionising the atoms of a gas.

Speed filter:

Ions moving at different speeds are subjected to the simultaneous action of mutually orthogonal electric and magnetic fields. As a result, these ions are subjected to forces consisting of:

The electric force: $\vec{\mathbf{F}}_{\mathbf{E}} = q\,\vec{E}$

The magnetic force: $\vec{\mathbf{F}}_{\mathbf{m}} = q\,\vec{v}_o\vec{B}$

$\vec{F}_E$ et $\vec{F}_m$ have parallel and opposite directions, the ion will pass through the analyser if:

$$|\vec{F}_E| = |\vec{F}_m| \,.\, \vec{v}_o \wedge \vec{B} \Rightarrow q\,E = qv_0B \Rightarrow v_0 = q/B$$

The ions leaving the speed filter have the same speed

In the velocity filter : $F_B = F_A \Rightarrow \mathrm{q}\,\mathrm{E} = \mathrm{q}\,v_0\,B_0 \Rightarrow v_0 = E/B_0$

The ions enter the analyser at the same speed $\mathbf{v_0}$ and describe circular trajectories created by the magnetic field.$\vec{B}$ (***Figure II-11***).

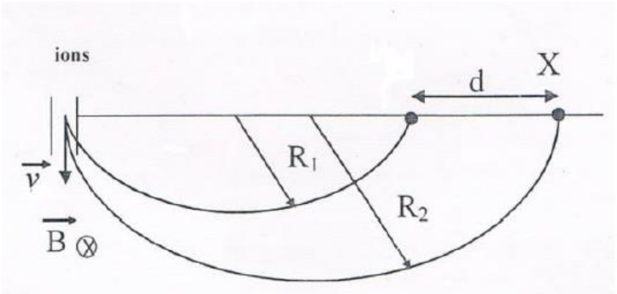


Figure II-11: Diagram of the circular trajectories of ions in the analyser

$$F_m = m\,g = m\frac{v_0^2}{R} = q\,B_0 v_0 \Rightarrow R = \frac{m\,v_0}{qB} \Rightarrow m = \frac{RqB}{v_0}$$

- **Isotope R_1:** $R_1 = \frac{m_1\,v_0}{qB}$
- **Isotope R_1:** $R_2 = \frac{m_2\,v_0}{qB}$
- **Isotope R_i:** $R_i = \frac{m_i\,v_0}{qB}$ *avec* $R_i = \frac{D_i}{2}$, $m_2 > m_1 \Rightarrow$
- $d = 2\,(R_2 - R_1) = \frac{2\,v_0}{qB}(m_1 - m_2)$ *on a* $m_1 = \frac{q\,B\,R_1}{v_0}$ *et* $m_2 = \frac{q\,B\,R_2}{v_0}$

et $v_0 = E/B_0 \Rightarrow \frac{q}{m} = \frac{E}{R\,.B.B_0}$

- $M_i = m_i\,N_A$; M_i: *molecular mass,* m_i : *mass of the isotope ;*

  N_A: *Avogadro Number*

$$\Rightarrow R_1 = \frac{N_A\,q\,B\,R_1}{v_0}\ ;\ R_2 = \frac{N_A\,q\,B\,R_2}{v_0}$$

The ion detector: When deflected, the ion is projected onto a photographic plate where it is detected by an electrode that acts as an ion collector.

II-7-1-1-2 Spectrograph of DEMPSTER

The first mass spectrographs were invented almost 100 years ago, by A.J. Dempster, F.W. Aston and others, and have therefore undergone continuous development over a very long period. The following description of Dempster's original mass spectrograph is a simple illustration of these physical principles ***(Figure II-12)***. Dempster's research during his career focused on the mass spectrometer and its applications, leading in 1935 to his discovery of the uranium isotope ^{235} U.

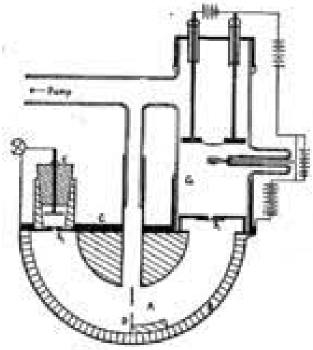


Figure II-12: DEMSTER magnetic sector spectrograph

The atoms/molecules are first ionised by the electrons emitted by the hot filament (F), then accelerated towards the entrance slit (S1). The ions then follow a semi-circular trajectory established by the Lorentz force in a uniform magnetic field. The radius of the trajectory, r, is defined by three slits (S1, S2 and S3). Ions following this trajectory are then detected by detector D.

III-1 Introduction

Matter is formed from elementary grains: the atom is an electrically neutral whole with a central part, the nucleus (protons + neutrons), where practically all its mass is centred, and around which are electrons. Physicists and chemists currently believe that an atom can be modelled by a structure with a nucleus around which there is a spherical zone centred on the nucleus and in which there is a certain probability of finding electrons.

The mass of matter is essentially concentrated in the nucleus, and this nucleus is 100,000 times smaller than the atom. So the rest is empty: matter is incomplete. It is necessary to develop a model to be able to explain various phenomena and predict their consequences. These are subject to experiment, which validates the model, improves it or rejects it. However, it is not always necessary to use the most complex model to explain a number of observations in a simple way. You just need to be aware of its limitations. The atomic model evolved as phenomena appeared that could not be explained by the previous model, and it took the intervention of many scientists before the atomic model became satisfactory. We will follow its development over time.

III-2 Wave-particle duality

Wave-particle duality is a fundamental concept in quantum physics that describes the behavior of subatomic particles such as electrons, photons and atoms. According to this theory, these particles can have both wave and particle characteristics. This means that, in certain situations, these particles can behave like waves, propagating and interfering with each other. In other situations, they may behave like particles, exhibiting properties such as position and velocity. This principle was first formulated by Louis de Broglie in 1924, who proposed that particles could be described as both waves and particles. This idea was confirmed by experiments such as the double slit experiment. This wave-particle duality is at the root of many strange phenomena in quantum physics, such as the tunnel effect, electron diffraction, interference and quantum observation It was discovered at the beginning of the 20th century by physicists such as Max Planck, Albert Einstein, Louis de Broglie, Erwin Schrödinger and Niels Bohr, and remains an active area of research in quantum physics today.

As far as light is concerned, many experiments show that it is wave-like: diffraction, interference. Others demonstrate corpuscular behavior and see light as a jet of particles (photons): photoelectric effect (A.EINSTEIN 1921). The wave and corpuscular aspects must then be considered as complementary: light sometimes manifests the character of a wave, sometimes that of a corpuscle. This is known as Wave-particle duality

III-2-1 wave aspect of light

Light is a progressive electromagnetic plane wave (electric field $\vec{E}$ and magnetic field $\vec{B}$ dependent on space and time). These vectors are themselves orthogonal,

are perpendicular to the direction of propagation ***(Figure III-1)***. Light radiation is characterised by: Its energy **E** (in J)

Its wavelength λ (in m), or spatial period. This is the length, at a fixed time, after which the wave repeats itself identically.

Its period T (in s), or temporal period. This is the time, at a fixed position, after which the wave repeats itself identically. In parallel, we use the frequency of the wave, defined by : $\nu = \frac{c}{\lambda}$ and expressed in hertz (Hz) or s^{-1} when T is expressed in seconds.

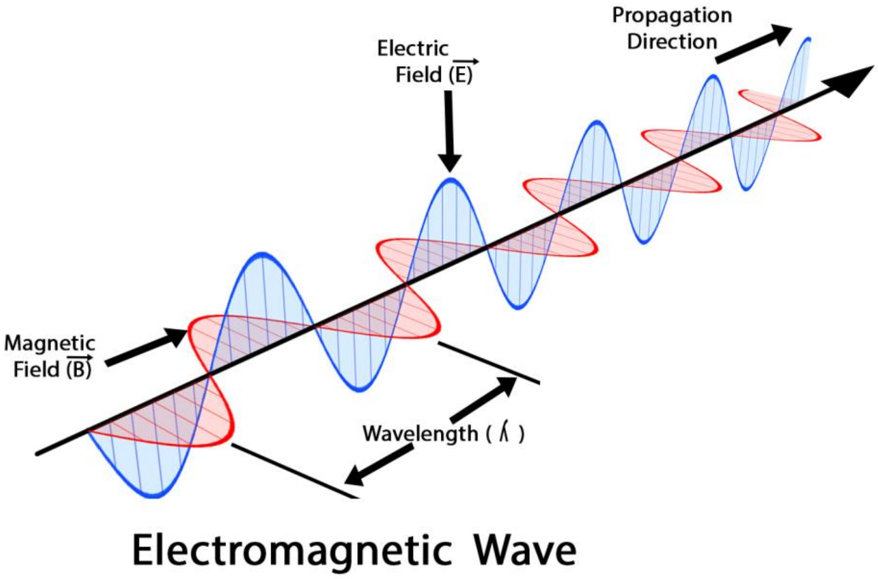


Figure III-1: Wave character of light

We have the following relationships between the energy of light radiation, frequency, period and wavelength: $E= h\upsilon$; ***E*** is energy expressed in joules (J), υ is the frequency in hertz (Hz) and h is the PLANCK constant, h= 6.62 10^{-34} J.s.

The distance (in meters m) travelled by light over a period T, at speed c (celerity of light in a vacuum, c = 3108 m.s-1) is equal to the wavelength...

As a result, the following can be noted: **E=** $h\ \frac{c}{\lambda}$.

The very nature of electromagnetic radiation depends on its wavelength and therefore the energy it carries. Visible radiation has a wavelength of between 400 nm (blue light) and 750 nm (red light). (***Figure III-2)*** shows the electromagnetic spectrum, which illustrates the nature of radiation as a function of wavelength.

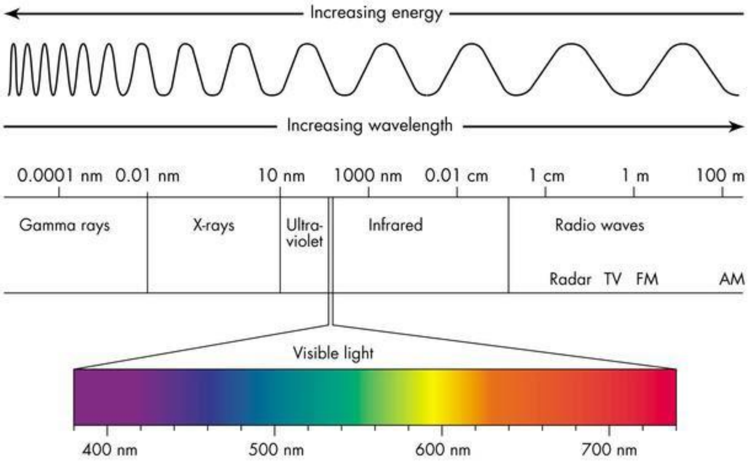


Figure III-2: Wave character of light

The wave model is essential for studying the propagation of light, but is not sufficient to describe the exchanges between light and matter. The energies exchanged between matter and light cannot take on arbitrary values: energy transfers are discontinuous or quantified: they can only take place in packets or quanta of well-defined energy, which constitutes the corpuscular aspect.

III-2-2 Corpuscular aspect of light

The corpuscular aspect of light is a theory according to which light is made up of particles called photons. This theory was first proposed by Albert Einstein in 1905, in his paper on the photoelectric effect. According to this theory, light is made up of discrete particles that have a specific energy and momentum. Photons have zero mass and travel at the speed of light in a vacuum. They interact with matter in a quantum manner, meaning that their behavior is described by the laws of quantum mechanics. The particle aspect of light is in opposition to the wave aspect of light, which describes light as an electromagnetic wave. These two aspects are not mutually exclusive and are both necessary to explain the behavior of light.

White light is a set of wavelengths (or colors) emitted by the sun.

These colors go from red to violet (infrared/ultraviolet) and everything in between, and each color has its own energy, frequency and wavelength. The corpuscular aspect of light radiation can be considered as a set of particles each carrying a quantum (quanta) of energy called photons, the value of which is proportional to the frequency associated with it.

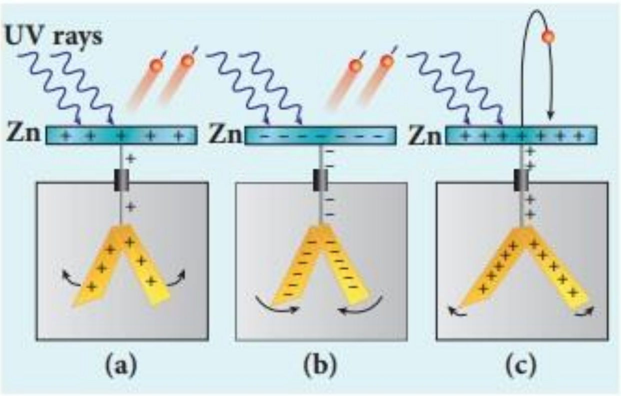
$$E = h\,\frac{c}{\lambda}$$

III-2-2 -1 Photoelectric effect

The photoelectric effect is a physical phenomenon in which electrons are ejected from a material when it is exposed to light of sufficiently high frequency. It is one of the first observed phenomena that led to the quantum theory of light. When light strikes a surface, it transfers energy to electrons in the material. If the frequency of the light is high enough, this energy can be sufficient to eject the electrons from the surface of the material. The electrons ejected are called photoelectric electrons, and the energy required to eject them is called the binding energy of the material.

The phenomenon was discovered by the German physicist Heinrich Hertz in 1887. Later, in 1905, Albert Einstein proposed a theory of the photoelectric effect that provided a more complete understanding of the observations. According to Einstein's theory, light is made up of particles called photons that carry a discrete amount of energy. The energy of a photon is proportional to its frequency, and when light strikes a surface, the energy of the photons can be sufficient to eject electrons.

The photoelectric effect is an experiment that demonstrates the photoelectric effect. It was first performed by Heinrich Hertz in 1887. The experiment involves bombarding a metal plate (zinc) ***(Figure III-3)*** with light of sufficiently high frequency to cause the photoelectric effect. The electrons ejected from the surface of the metal are collected and measured using a device called an electrometer.



Irradiation of ultraviolet light
on (a) uncharged zinc plate (b) negatively
charged plate (c) positively charged plate

<u>Figure III-3: The zinc blade experiment (Heinrich Hertz in 1887)</u>

To extract an electron from a metal, energy must be supplied, known as the extraction energy. Einstein interpreted the photoelectric effect by formulating the following hypotheses:

- Light is made up of a set of corpuscles, called photons, carrying a quantum of energy. Each photon of monochromatic radiation at the frequency υ carries a quantum of energy.: $\mathbf{E = h\upsilon} = h\,\frac{c}{\lambda}$
- The photoelectric effect is the interaction between an incident photon with a higher frequency υ and an electron in the metal at the threshold frequency υ_0.
- The excess energy in relation to the characteristic energy of the metal $\mathbf{E_0 = h\upsilon_0}$ is dissipated in the form of kinetic energy taken up by the electrons ***(Figure III-4).***

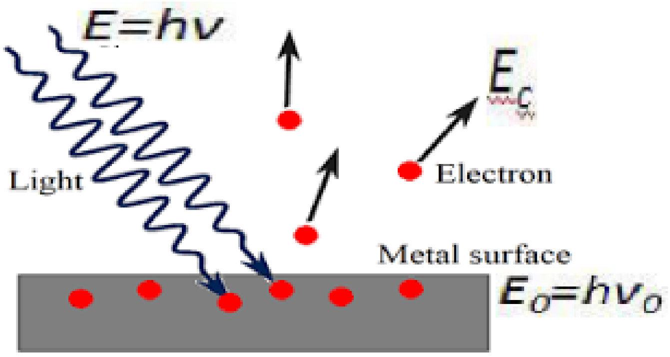


Figure III-4: The different energies making up the photoelectric effect

The photoelectric effect only occurs if the energy of the incident photon $\mathbf{E = h\upsilon}$ is higher than the extraction work $\mathbf{W_0 = h\upsilon_0}$ of an electron from the metal, the extraction energy depending solely on the nature of the metal υ_0 is the threshold frequency ($\upsilon_0 = \mathbf{C_0/\lambda_0}$; λ_0 the threshold wave length).

- If the photons energy is not sufficient ($\upsilon < \upsilon_0$ ou $\lambda > \lambda_0$), the photon is reflected and the electron is not ejected from the metal.
- If the photon has sufficient energy ($\upsilon > \upsilon_0$ ou $\lambda < \lambda_0$), all the photon's energy is transferred to the electron, which leaves the metal at an ejection velocity.
- $\mathbf{E = E_C + h\upsilon_0 \Rightarrow E_C = E - h\upsilon_0 = E - W_0 = h(\upsilon - \upsilon_0) = h\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right) \Rightarrow}$

$\frac{1}{2}m_e v^2 = \mathbf{h(\upsilon - \upsilon_0) = h\,c\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)}$; m_e is the electron mass = $\mathbf{9{,}109.\ 10^{-31}Kg}$

Note:

The results of the experiment show that the number of electrons ejected from the metal surface depends on the frequency of the light and not on its intensity. If the frequency of the light is below a certain threshold value, no electrons are ejected, regardless of the intensity of the light.

III-3 Interaction between light and matter

The interaction between light and matter is a complex subject that is being studied in various areas of physics, including optics, quantum physics and chemistry. In general, the interaction between light and matter can manifest itself in different ways, including:

1. Absorption: matter can absorb light energy, which can lead to electronic, molecular or atomic excitation.
2. Emission: matter can emit light energy in the form of fluorescence, phosphorescence, luminescence or thermal radiation.
3. Scattering: light can be scattered by matter, giving rise to phenomena such as Rayleigh scattering, Raman scattering or elastic light scattering.
4. Refraction: light can be deflected when it passes through a transparent medium, such as glass or a lens.
5. Reflection: light can be reflected by a surface, such as a mirror.

These different types of interaction between light and matter are governed by physical laws, such as Beer-Lambert's law for absorption, Snell-Descartes' law for refraction and Fresnel's law for reflection. Understanding these laws is essential for many fields, including optics, medical imaging, spectroscopy, optical communication and photovoltaic technologies..

III-3-1 the emission spectrum of the hydrogen atom

The emission spectrum of the hydrogen atom is made up of several light lines, each corresponding to a specific electronic transition between different energy levels of the hydrogen atom. The hydrogen atom played an important role in the development of quantum physics, as it was one of the first examples of the use of quantum theory to understand the properties of matter.

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-5),*** the spectrum of the hydrogen atom is obtained by placing a sealed tube containing hydrogen under low pressure in front of the slit of a spectrograph and in which an electrical discharge is produced. This discharge excites the hydrogen atoms. When the atoms return from the various excited states to states of lower energy, electromagnetic radiation is emitted.

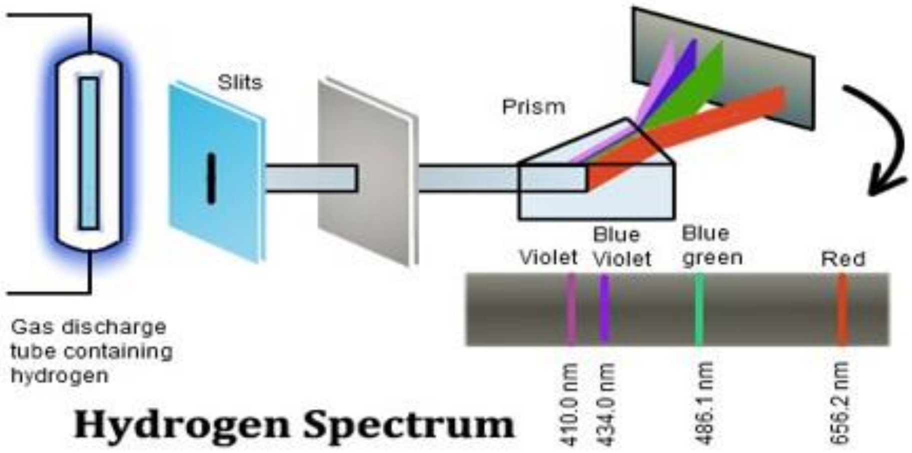
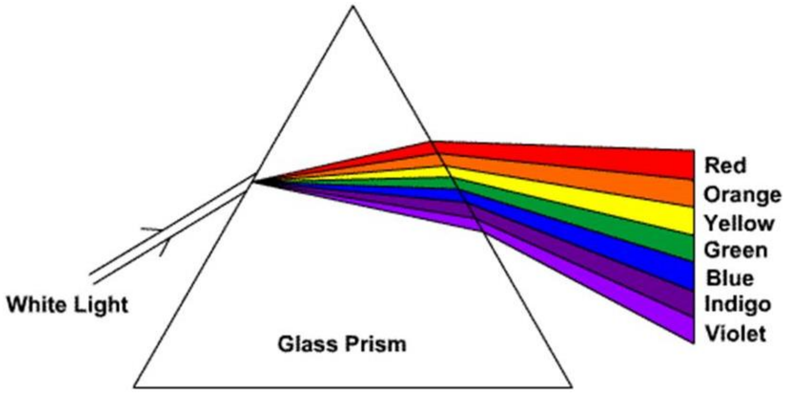


Figure III-5: Hydrogen Atom Emission Spectrum

The radiation emitted is made up of a series of lines of different wavelengths. These spectra show dark lines which indicate that the light has been absorbed (Absorption Spectrum), unlike the white light which represents a (Continuous Spectrum) ***(Figure III-6).***



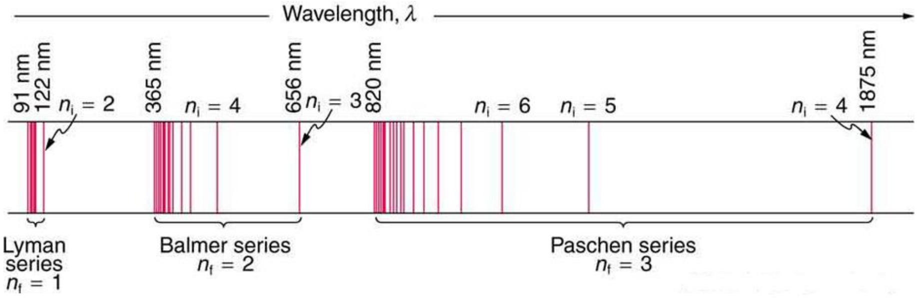
Continuous Spectrum of all the colours of the visiblelight region

Figure III-7: the decomposition of white light: a Continuous Spectrum

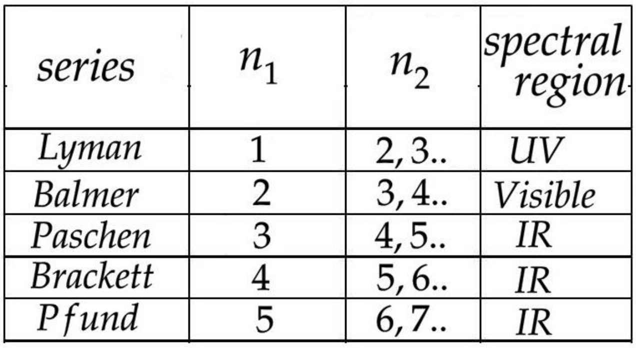
Note:** **White light is the only continuous spectrum visible to the human eye. If a light has a specific color, this means that certain wavelengths are missing from the spectrum, making it non-continuous.

Le spectre d'émission de l'atome d'hydrogène est constitué de plusieurs raies lumineuses, chacune correspondant à une transition électronique spécifique entre différents niveaux d'énergie de l'atome d'hydrogène. Les raies les plus connues du spectre d'émission de The emission spectrum of the hydrogen atom is made up of several light lines, each corresponding to a specific electronic transition between different energy levels of the hydrogen atom. The best-known lines in the hydrogen emission spectrum are the **Balmer** lines, which correspond to the electronic transitions between the n ≥ 3 energy levels and the n = 2 level. Balmer lines have wavelengths in the visible region of the electromagnetic spectrum, making them easy to observe with optical instruments. There are also Lyman lines, which correspond to electronic transitions between energy levels n ≥ 2 and the n = 1 level. These lines are in the ultraviolet and are therefore less easily observed. Other series of lines also exist, such as the **Paschen** series (transitions towards the n = 3 level) and the **Bracket** and **Pfund** series successively (transitions towards the n = 4,5 level...) (Figure III-7), but these lines are in the infrared and require special instruments to be observed.

- Within the same series, the lines are not separated by the same wavelength: the lines come closer together as the wavelength decreases and seem to tend towards a limit line.



spectral lines for hydrogen



series	n_1	n_2	spectral region
Lyman	1	2, 3..	UV
Balmer	2	3, 4..	Visible
Paschen	3	4, 5..	IR
Brackett	4	5, 6..	IR
Pfund	5	6, 7..	IR

__*Figure IV-7 : Series of lines in the hydrogen atom spectrum*__.

III-3-2 The empirical Balmer-Rydberg relationship

The empirical Balmer-Rydberg relationship is a mathematical formula that describes the wavelengths of the spectral lines of hydrogen. This formula was developed by Johann Balmer in 1885, and then improved by Johannes Rydberg in 1890.

Balmer first demonstrated that the graphical representation of the inverse of the wavelengths as a function of $\frac{1}{n^2}$ (where n is an integer between 3 and 6) is a straight line.

The Balmer-Rydberg relationship can be written as follows: $\frac{1}{\lambda} = 1{,}097\ .10^7\ [(\frac{1}{2^2}) - (\frac{1}{n^2})]$

By applying this equation to n = 3, we obtain the wavelength of one of the hydrogen lines, i.e. a calculated value of 656.3 nm, which also corresponds to the observed wavelength.

The other values of n, 4, 5 and 6, provided the Balmer series, the first series of wavelengths of hydrogen lines in the visible range.

III-3-3 RITZ-RYDBERG formula

The Ritz-Rydberg formula is an empirical relationship that describes the frequencies of the spectral lines of different chemical elements. The formula was proposed independently by two physicists, Walther Ritz and Johannes Rydberg, in 1908.

The Rydberg equation was eventually generalised to take account of the discovery of other lines in the ultraviolet and infrared parts of the hydrogen spectrum.

The Ritz-Rydberg formula can be written as follows : $\frac{1}{\lambda} = 1{,}097\ .10^7\ [(\frac{1}{n^2}) - (\frac{1}{n'^2})]$

Or λ is the wavelength of the spectral line, R is the Rydberg constant **(1.097 x 10^7 m^{-1})**,

n' > n avec n= 1, 2, 3,4…….. And n' = n+1, n+2 ………

This is how the wavelength values of the other series of lines were calculated, namely those of Lyman (n = 1) and Balmer (n = 2) in the ultraviolet, and those of Paschen (n = 3), Brackett (n = 4) and Pfund (n = 5) in the infrared.

<u>Note</u>

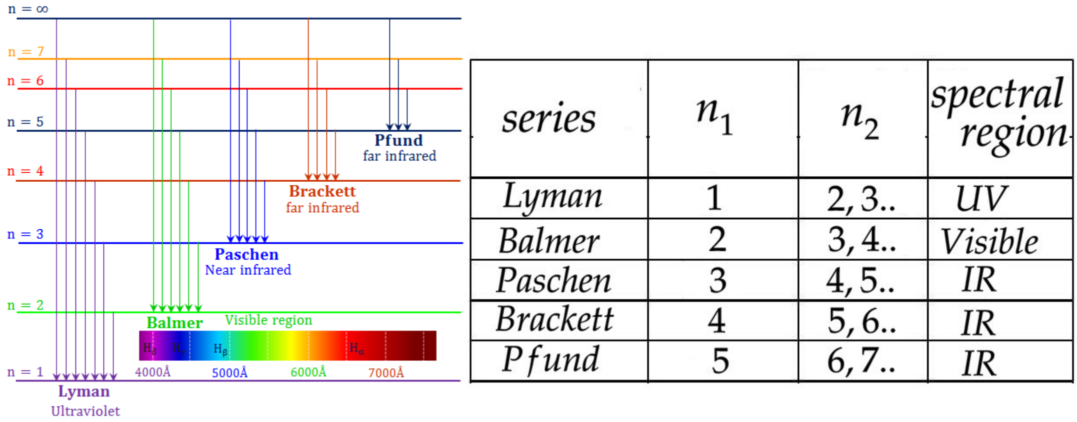
This equation is completely empirical, meaning that it is based solely on experimental measurements and is not linked to any particular theory. However, it can be used to accurately predict the position of the lines in the spectrum of hydrogen, the only element to which it applies.

III-3-4 The concept of a series of lines

A line series is a sequence of spectral lines in the electromagnetic spectrum emitted or absorbed by an atom or molecule. Spectral lines are narrow bands of light of different wavelengths that result from the transition of an electron from one energy level to another in an atom or molecule.

The best-known series of lines are the hydrogen spectral series, which were discovered and studied by the German physicist Johann Balmer in the 1880s. These series include the Balmer series, the Lyman series, the Paschen series, the Brackett series and the Pfund series. Each of these series corresponds to specific electronic transitions in the hydrogen atom.

A line series is the set of all the lines that cause the electron to return to a given, fixed n level. Each series is named after its discoverer, as shown in the diagram (Figure III-8).



series	n_1	n_2	spectral region
Lyman	1	2, 3..	UV
Balmer	2	3, 4..	Visible
Paschen	3	4, 5..	IR
Brackett	4	5, 6..	IR
Pfund	5	6, 7..	IR

Figure III-8 : Emission spectrum of H

III-4 Classical atomic model

The classical model of the atom is also known as the Rutherford model, after the physicist Ernest Rutherford who proposed it in 1911. The atomic model has evolved, been modified and challenged throughout history.

III-4-1 The Rutherford model

The Rutherford model is a scientific theory proposed in 1911 by the British physicist Ernest Rutherford. It was developed following the gold leaf experiment, in which alpha particles were sent through a gold leaf and observed to see how they moved.

Rutherford's model postulates that the atom is mainly composed of vacuum, with a small positively charged nucleus at the centre, surrounded by electrons that orbit the nucleus at a relatively distant distance. The electrons are held in orbit around the nucleus by the electrostatic force between the opposite charges of the negative electrons and the positive nucleus, like planets around the sun under the effect of gravitational attraction. This model is also called the **Rutherford Planetary** Model ***(Figure III-9).***

He used classical mechanics as a physical law to study the movement of the electron:

- He used classical mechanics as a physical law to study the movement of the electron. The electron is subject to two equal and opposing forces: the columbic attraction of the nucleus and the centrifugal force (repulsion).
- The total energy E of a system is simply the sum of its internal, kinetic, an potential energies:

Total system energy = kinetic energy + potential energy

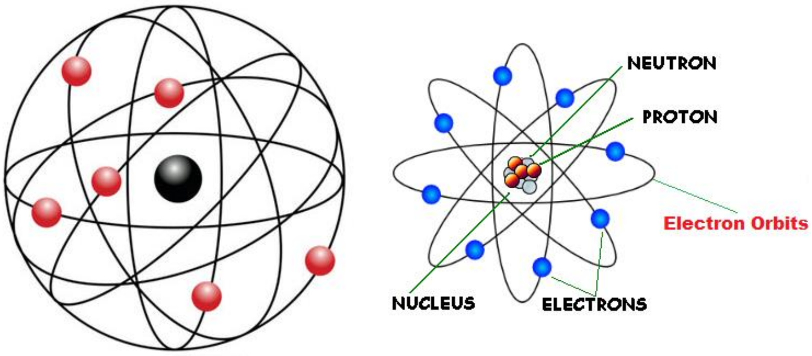


Figure III-9: Rutherford's planetary model of the atom

III-4-1-1 Application to hydrogen atoms

The hydrogen atom is made up of an electron and a planetary nucleus containing a proton. The electron rotates around the nucleus at speed V ***(Figure III-10).***

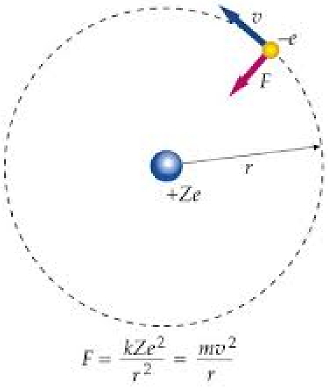


Figure III-10: Different forces exerted on the electron of an atom

The electron is subject to :

The columbic attraction of the nucleus: $|\overrightarrow{F_a}| = \frac{Ze^2}{4\pi r^2 \varepsilon_0}$ and

A repulsive or centrifugal force : $|\vec{F}_c| = \frac{mV^2}{r}$

Condition of stability $|\vec{F}_a| = |\vec{F}_c| \Rightarrow \frac{Ze^2}{4\pi r^2 \varepsilon_0} = \frac{mV^2}{r} \Rightarrow mv^2 = \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r}$

With ε_0 is the permittivity of a vacuum.

Total energy of the system E_T = potential energy E_P + kinetic energy E_c

$$E_P = \int_{\infty}^{r} F_a\, dr \Rightarrow E_P = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \quad \text{and } E_c = \frac{1}{2}mv^2 \text{ or } \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} = \frac{1}{2}mv^2$$

$\Rightarrow E_c = -\frac{1}{8\pi\varepsilon_0}\frac{Ze^2}{r} = -\frac{Ze^2}{8\pi\varepsilon_0}\frac{1}{r} \Rightarrow E_T = -E_c \Rightarrow E_T = f(r)$. This means that the total energy of the electron is a continuous function over the interval] 0,+∞[That's to say ; the electron can have any energy value". This means that the electron is not limited to a specific energy value and can possess a range of different energy values. In other words, when an electron loses energy, it moves closer to the nucleus of the atom. If the electron loses enough energy, it will eventually fall into the nucleus ***(Figure III-11).***

In summary, according to Rutherford's theory, the electron is in circular motion and emits radiation that leads to a loss of energy. This loss of energy can take the form of a slowing down of the movement or a reduction in the radius of the orbit. However, in both cases, the theory predicts that the electron should eventually fall into the nucleus. This contradicts the reality of atomic structure. "This contradiction was resolved by Bohr's theory.

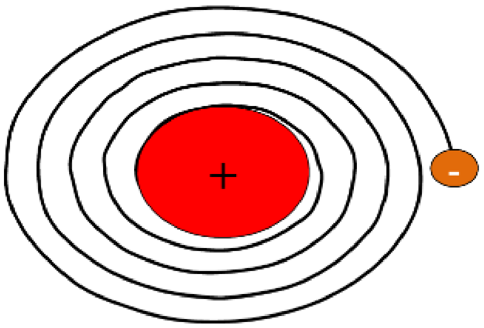


Figure III-11: Electron trajectory according to Rutherford's model

III-4-2- Bohr atomic model: hydrogen atom

"Bohr's model resolved an important contradiction in Rutherford's atomic theory, introducing the notion of quantized orbits and explaining how electrons absorb and emit energy as they jump from one orbit to another." previous atomic theory by introducing new ideas about atomic structure and electron behavior.

In 1913, Niels Bohr proposed a new atomic model based on the quantification of energy. This model made it possible to explain the structure of the hydrogen atom and its spectrum, and provided a theoretical basis for the Rydberg equation. The Bohr model was developed to explain previous experimental results using classical concepts. The main features of this model are summarised in three postulates.

III-4-2-1 Bohr's postulates

In 1913, Bohr set out three postulates that served as the basis for his explanation of the interpretation of the emission line spectrum of the hydrogen atom. These postulates made it possible to propose an explanation of the atomic structure and the behavior of electrons in hydrogen atoms.

The first postulate Bohr's statement was that the atom cannot undergo continuous energy variations; it can only exist in a series of stationary states corresponding to energy levels E_1, E_2, E_3… in which the electron does not radiate. In other words, the energy of the electron in an atom must be quantified and cannot take on any value. The electron must occupy one of the possible stationary states of the atom, each corresponding to a specific energy level, and cannot exist between two of these states. In a stationary state, the electron does not radiate energy and does not lose energy.

The second postulate stated by Bohr was that the orbital angular momentum L of the electron with respect to the centre of the orbit is quantized. This moment is defined as the vector product of the position vector **r** and the momentum vector **p** of the electron, according to the relation **L = r x p** ;

$\vec{L} = \vec{r} \wedge \overrightarrow{p}\,;$ $\vec{L} = m(\vec{r} \wedge \overrightarrow{v}) = L = m\,v\,r \sin(\vec{v}, \vec{r})$. $L = m\,v\,r \sin(90°) = m\,v\,r$

According to quantum mechanics, the electron's orbital angular momentum is quantized and can only take discrete values. This quantization is linked to the quantization of the electron's energy and is determined by the orbital quantum number (l), which can take values ranging from 0 to n-1 (where n is the principal quantum number). Each value of l corresponds to a possible orbit for the electron.

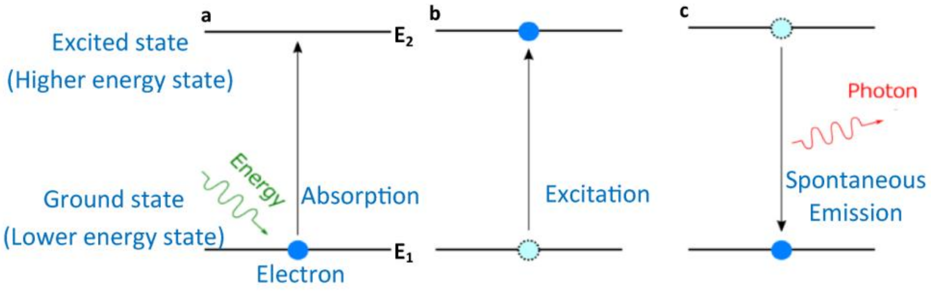
$\overrightarrow{L}$ is perpendicular to the plane of the orbit. This moment can therefore only take on integer values $\frac{n\,h}{2\pi}$. As a result, angular momentum is quantified $m\,v\,r = \frac{n\,h}{2\pi}$

With **h**: Planck's constant**;** **m**: mass of the electron and **n**: quantum number.

<u>The third postulate of Bohr is</u> often referred to as the "quantization postulate". It states that electrons in an atom can only occupy well-defined and discrete orbits (or energy levels) around the nucleus, and that these orbits have specific and fixed energy levels. According to this postulate, an electron cannot be located anywhere in the atom or have any amount of energy. Instead, it can only exist in certain quantified energy states, and when it moves between these states, it emits or absorbs energy in the form of photons. This postulate helped to explain the structure of the hydrogen atom and led to the development of the theory of quantum mechanics. In other words, when a system passes from a stationary state of energy En1 to another state of energy En2, it can emit or absorb a quantity of energy equal to the difference in energy between the two states, represented by :

$$\Delta E = |En_2 - En_1| = h\upsilon = \frac{hc}{\lambda}$$

This amount of energy can also be expressed in terms of Planck's constant h= 6.623 10-^{34} j.s (Planck's constant) and the frequency of the radiation involved, represented by ν. During the emission process, an electron of energy En_2 can return to a lower energy state En_1, releasing its excess energy in the form of light. The radiation emitted will have an energy corresponding to the energy difference between the two states, which is negative ($En_1 - En_2 < 0$). ***(Figure III-12).*** During the absorption process, an electron of energy En1 can absorb radiation if it allows a higher energy state En2 to be reached. The absorbed radiation will have a positive energy corresponding to the energy difference between the two states (**En_2 - En_1** > **0**).



<u>Figure III-12 Photon absorption or emission corresponds to a change in the electron's orbit..</u>

III-4-2-2 Radius of stationary orbits

The radius of the stationary Bohr electron orbit is a characteristic of a hydrogen atom in its basic configuration, as described by the Bohr model. In this model, the electron is assumed to move around the nucleus in a stationary circular orbit, and the distance from this orbit to the nucleus is called the orbit radius. ***Figure (III-13)***

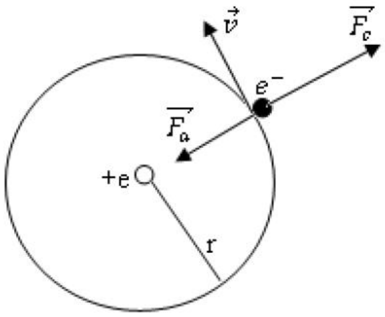


Figure III-13 Bohr's stationary electron orbit

According to Bohr's first postulate, the system is in equilibrium

$\vec{F}_a + \vec{F}_c = 0 \Rightarrow |\vec{F}_a| = |\vec{F}_c|$ with :

$|\vec{F}_c| = \frac{m v^2}{r}$ **et** $|\vec{F}_a| = K\frac{|q||q'|}{r^2} = K\frac{e^2}{r^2}$ **with k =** $\frac{1}{4\pi\varepsilon_0}$

Or : $|\vec{F}_a| = |\vec{F}_c| \Rightarrow \frac{m v^2}{r} = K\frac{e^2}{r^2} \Rightarrow m v^2 = K\frac{e^2}{r}$ (1)

According to Bohr's second postulate describing the quantization of orbital angular momentum: $m v r = \frac{n h}{2\pi} \Rightarrow (m v r)^2 = (\frac{n h}{2\pi})^2 \Rightarrow m v^2 = \frac{n^2 h^2}{4 m r^2 \pi^2}$ (2)

Equating equation (1) with equation (2) gives us the radius of the orbit:

$$K\frac{e^2}{r} = \frac{n^2 h^2}{4 m r^2 \pi^2} \Rightarrow r_n = \frac{h^2}{4 K \pi^2 e^2} n^2 \Rightarrow r_n = Constant\ n^2 \Rightarrow$$

We can see that the electron can only exist on a discontinuous series defined by the quantum number n and the radius r.

Since **h, π, k, m** and e are constant then r depends only on the value of the positive number **n** called the principal quantum number, or: $r_n = \frac{h^2}{4 K \pi^2 e^2} n^2$ (3)

with : [**k =** $\frac{1}{4\pi\varepsilon_0}$ **=** $9,10^9 \left(\frac{N \cdot m^2}{C^2}\right)$] ;[**m =** $9,110.10^{-31}$ **Kg]** **et** **[e =** $1,602 \cdot 10^{-19}$ **C]**

h : Planck constant = **$6,623\ 10^{-34}$ j.s .**

2

For n = 1, **r_n = r_1 = 0,5290** Å : the first Bohr radius for the hydrogen atom, which is given by:

$a_0 = r_1 = \frac{h^2}{4 K \pi^2 e^2}(1)^2 =$ **0,5290 Å [1 Å (Angström) = 10^{-10} m)].**

For **n = 2**, The 2nd Bohr orbit r2= 4×a_0 ;

For **n = 3**, The 3rd Bohr orbit **r_3**= 9× a_0;

For **n = 4**, The 4rd Bohr orbit **r_4**= 16× a_0 ;

For n **= 5**, The 5rd Bohr orbit r_5= 25× a_0 … ***Figure (III-14)***

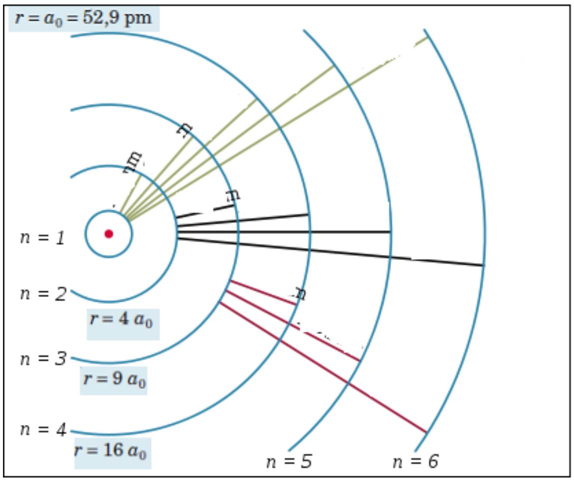


Figure (III-14): Representation of the partial circular orbits of the hydrogen atom

III-4-2-3 Energy of the electron in a stationary orbit

The energy of the electron in a stationary orbit is the amount of energy required to maintain the electron in that specific orbit around the atomic nucleus. This energy is related to the electron's distance from the atomic nucleus and is determined by the principal quantum number (n) of the orbit. Orbits with higher values of n have higher energies and are therefore further from the nucleus. These orbits are also less stable and the electron is more likely to move to a lower orbit by emitting energy in the form of photons.

The total energy of the system under consideration is the sum of the potential energy Ep and the kinetic energy E_c; $E_T = Ep + Ec$ with:

$$E_c = \frac{1}{2} mv^2 \quad \text{et} \quad E_P = -\frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} = -K\frac{e^2}{r} \quad \text{with } E_T = E_c + E_p \Rightarrow$$

$$E_T = -\frac{Ze^2}{8\pi\varepsilon_0}\frac{1}{r} \quad (4)$$ And from equation (3) we have $$r_n = \frac{h^2}{4\,K\,\pi^2 e^2}\, n^2 \quad (3)$$

By replacing the expression for **r** in equation (4), the total energy of the system as a function of **n** will be: $$E_T = -\frac{2mK^2\pi^2e^4}{h^2}\frac{1}{n^2} \quad (5)$$

With $$\frac{-2mK^2\pi^2e^4}{h^2} = -21,76.10^{-19}j = -13.6\,eV$$

The energy of the electron in a given orbit depends exclusively on the principal quantum number n, which means that the energy is quantised and can only take on certain discrete values. This can be expressed by a specific mathematical formula (equation 5):

For n = 1, $E_n = E_1 = -13,6\frac{1}{n^2} = -13,6\frac{1}{1^2} = -13.6\ eV$. This value represents the energy of the ground state of the hydrogen atom

The quantized energy value corresponding to the ground state of the hydrogen atom is the minimum energy that the electron can have, and is reached when the principal quantum number n is equal to 1. This electronic state is called the ground state of the hydrogen atom.

Effectively, the energy of an electron in the ground state of the hydrogen atom is (-13.6 eV). When the electron receives excess energy, it is possible to move to a higher electronic state with a higher value of the principal quantum number n. These states are called excited states and have higher energy levels than the ground state.

From where: $E_n = E_1 = -13,6\frac{1}{n^2} = \frac{-13.6}{n^2}$

Effectively, Bohr's model explains that the energy of the electron in an atom is quantized and depends on a principal quantum number n, which is a positive integer. The different quantized states of energy for an electron in an atom are determined by the different possible quantum numbers for that electron. The quantized states are generally designated by the following electron symbols:

- **n = 1** : $E_n = E_1$ (ground state (lowest energy state)
- **n = 2, 3, 4, ...**$\frac{E_1}{4}, \frac{E_1}{9}, \frac{E_1}{16}, \frac{E_1}{25}$ …… excited states (higher energy than the ground state)

Each quantized state corresponds to a specific orbit around the atomic nucleus, and the electron's energy increases with the value of n.

The algebraic value of the energy is minimal for the most stable system, which corresponds to an energy of **-13, 6 eV.**

• A stationary state is a state in which the electron of an atom is in a fixed position relative to the nucleus, without undergoing any movement or change in its energy state.

• The ground state is the lowest energy state that an electron can occupy in an atom. It is the state in which the electron is in the orbit closest to the nucleus.

• The excitation energy of the hydrogen atom is the energy required to move the electron from an n1 orbit to an n2 orbit (where n1< n2). When the electron absorbs this amount of energy, it can move to an orbit further away from the nucleus.

• The ionization energy of the hydrogen atom corresponds to the energy required to completely remove the electron from the atom, moving it from the n=1 orbit to a position infinitely far from the nucleus (n=∞). This energy is great enough to free the electron from the electrostatic attraction of the nucleus and make it free to move.

- Le niveau d'énergie correspondant à cette situation est **E=0**.

Example: The ionization energy of the hydrogen atom is:

$$\mathrm{H} \rightarrow H^{+} + 1\mathrm{e}^{-} \qquad E_i = E_\infty - E_1 \Rightarrow E_i = 0 - (-13{,}6) = +13{,}6\ \mathrm{e}V$$

According to Bohr's third postulate, the electron in the hydrogen atom can pass from an initial energy level Eni to a final energy level Enf by absorbing or emitting a quantum of energy, which has the expression : $\Delta E = E_{nf} - E_{ni} = \frac{2mK^2\pi^2e^4}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$ **(6)**

Where; ΔE is the energy involved and is measured in joules (J), Eni and Enf represent the initial and final energy levels of the electron respectively, expressed in joules (J).

From where, $\Delta E = \left|En_f - En_i\right| = h\upsilon = \frac{hc}{\lambda}$ **(7)**

Equality between the equation **(6)** et **(7)** $\Rightarrow$

$$|\Delta E| = \left|En_f - En_i\right| = h\upsilon = \frac{hc}{\lambda} = \frac{2mK^2\pi^2e^4}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) \Rightarrow$$

$$\upsilon = \frac{\left|En_f - En_i\right|}{h}\ ; \quad \bar{\upsilon} = \frac{1}{\lambda} = \frac{\left|En_f - En_i\right|}{hc} = \frac{1}{hc}\frac{2mK^2\pi^2e^4}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) \Rightarrow$$

$$\bar{\upsilon} = \frac{1}{\lambda} = \frac{1}{hc}\frac{2mK^2\pi^2e^4}{h^2}\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) = 10973740\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$$

We can deduce: $R_H = \frac{1}{hc}\frac{2mK^2\pi^2e^4}{h^2} = 10973740\ m^{-1} \Rightarrow$

$$\bar{\upsilon} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) \qquad \textbf{(8)}$$

<u>Ritz Empiric Formula</u>

Ritz's empirical formula for calculating the line frequencies in the hydrogen emission spectrum is based on the same relationship as Bohr's third postulate. This formula relates the frequency of each line emitted by the hydrogen atom to the energy difference between the initial and final energy levels: $\bar{\upsilon} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right)$

Where; λ is the wavelength of the emitted line, R is the Rydberg constant; ni and nj are the principal quantum numbers of the initial and final energy levels, respectively.

Using this formula, it is possible to calculate the frequencies of the different lines emitted by the hydrogen atom, which are grouped into spectral series (Lyman series, Balmer series, Paschen series, etc.) as a function of the values of the quantum numbers n1 and n_2. ***(Figure III- 15).*** The Rydberg constant R, is a fundamental constant that is linked to the properties of the hydrogen atom and the structure of its energy levels. Its calculated value is close to the experimental value given empirically by Balmer, RH=109677.6 cm-1 which confirms the validity of Bohr's theory and Ritz's empirical formula for describing the hydrogen emission spectrum..

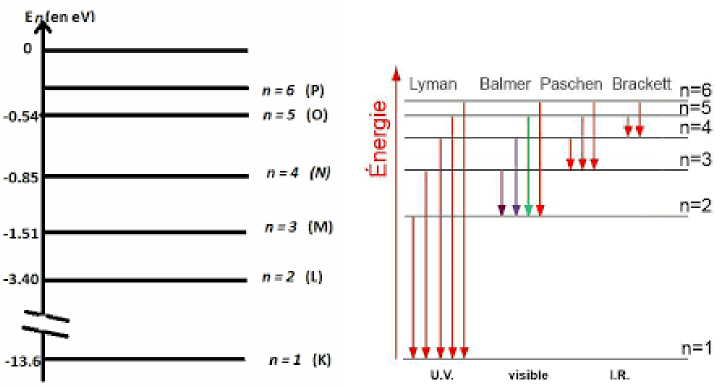


Figure III- 15: Energy diagram of the hydrogen atom.

III-4-2-4 Quantifying the energy of the hydrogen atom

The hydrogen atom is an example of a quantum system in which the energy is quantized, i.e. the possible energy levels are discrete and determined by quantum numbers.

Bohr's model shows that the energy of the electron in the hydrogen atom is quantized and depends only on the value of the principal quantum number n. The energy levels of the hydrogen atom are therefore evenly spaced and determined by the value of n. The larger n is, the higher the energy of the electron. In other words, each layer has a specific energy level that is identical for all hydrogen atoms. The energy diagram shows these different levels ***(Figure III-16)***

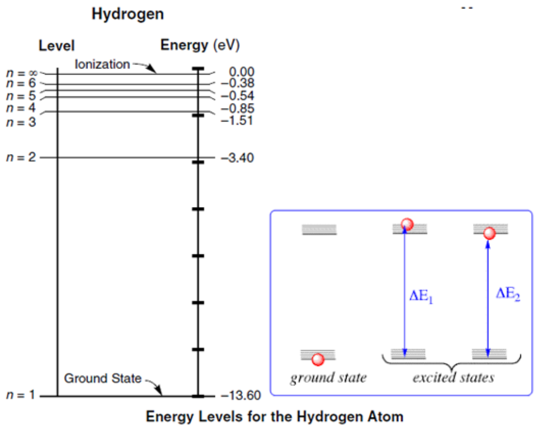


Figure III-16: Energy quantization diagram for the hydrogen ato

III-4-2-5 Applications to hydrogenoides

Hydrogenoids ions are monatomic ions with an electronic structure similar to that of the hydrogen atom. These ions have a positively charged nucleus, which contains a proton, and one or more electrons that orbit the nucleus. As with the hydrogen atom, the energy levels of these ions are quantized.

The main difference between Hydrogenoids ions and the hydrogen atom is their electrical charge. Hydrogenoids ions have a different positive electrical charge (Z) to neutral hydrogen, which changes the electronic structure of the ion. The electric charge of the ion affects the electrostatic force between the nucleus and the electron, which modifies the value of the energy levels..

These are called hydrogen ions,, cations with a single electron and Z protons.

Example : ${}_{2}He^{+}$; ${}_{3}Li^{+2}$; ${}_{4}Be^{+3}$…

Calculating the radius and energy of the electron of a Hydrogenoids ion in an orbit n gives the following expressions:

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\,\frac{z^2}{n^2} = -13.6\,\frac{z^2}{n^2}\,eV \qquad (9)$$

$$r_n = -\frac{\varepsilon_0 h^2}{\pi m_e e^2}\,\frac{n^2}{z} = 0.529\,\frac{n^2}{z}\,A^\circ = r_1\,\frac{n^2}{z}\,A^\circ \qquad (10)$$

- ***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 of the series observed in the spectrum of hydrogen ions are given by :*** $\bar{\upsilon} = \frac{1}{\lambda} = R_H\, Z^2\left(\frac{1}{n_i^2} - \frac{1}{n_j^2}\right) \qquad (11)$

III-4-2-6 Inadequacy of the Bohr model

Bohr's model was indeed a great success in understanding the hydrogen atom and its electronic spectra, but it also showed certain limitations and inconsistencies. Here are some of the main shortcomings of Bohr's model:

1. Bohr's model could not explain the spectra of atoms more complex than hydrogen. Hydrogen is the only atom with a single electron, so its energy levels and electronic transitions are relatively simple to predict. But for atoms with several electrons, the electron-electron and electron-nuclear interactions are complex, and Bohr's model could not take them into account.

2. Bohr's model could not explain the fine structure of spectral lines. The fine structure is due to the interaction between the electron spin and its orbital angular momentum, and is

important for accurate measurements of the frequency of spectral lines. Bohr's model could not take this interaction into account.

3Bohr's model could not explain the splitting of spectral lines in the presence of a magnetic field. This phenomenon is called the Zeeman effect, and is due to the interaction between the electron's magnetic moment and the external magnetic field. Bohr's model could not take this interaction into account either.

These shortcomings of Bohr's model were resolved by quantum mechanics, which is a more complete and precise theory of atomic structure. Quantum mechanics describes electrons as wave particles, and orbitals as regions of space where the probability of finding an electron is high. Quantum mechanics also makes it possible to explain the fine structure, the Zeeman effect and other phenomena observed in complex atoms.

In short, Bohr's model could not describe the spectra of atoms other than hydrogen. This model was replaced by the fundamental theory of atomic physics formulated by De Broglie, Heisenberg and Schrödinger: it was quantum mechanics (or wave mechanics) that led to the current conception of atomic structure.

III-5 Atomic model in wave mechanics

III-5-1-1- Wave-corpuscle duality and the de Broglie relation

Wave-corpuscle duality is a fundamental concept in quantum physics that describes the behavior of subatomic particles as waves and particles at the same time. This concept was developed in the early 20th century by physicists such as Louis de Broglie, Erwin Schrödinger and Werner Heisenberg. In short, wave-corpuscle duality is a key concept in quantum physics that shows that the nature of matter and light is fundamentally different from that of macroscopic objects, and that understanding quantum mechanics is essential to understanding the behavior of subatomic particles.

Since Einstein's discovery of the photon, wave-corpuscle duality has been established for light radiation. In 1924, Louis de Broglie proposed the hypothesis that wave-corpuscle duality is a universal property of physics. He argued that any particle in motion is linked to a wave, called an "associated wave", with a wavelength λ.

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

λ = the Broglie wavelength**;** ***h*** = Planck's constant ($6{,}626 \times 10^{-34}$ J.s) **;** ***p*** **:** momentum of the particle = ***m.v***. Where: ***m*** is the mass of the particle and ***V*** is its velocity.

Light is mainly presented in the form of waves, but it also has a corpuscular character, as shown by its quantification according to Planck's equation. Similarly, according to De Broglie, matter is mainly in particle form, but can also be wave-like under certain conditions. He suggested that not only light but also matter were governed by the equation mentioned above, in which $\boldsymbol{mv}$ represents the particle's momentum, which is the product of its rest mass (in kg) and its speed (in m/s), provided its speed is not too close to that of light.

De The de Broglie equation makes it possible to recover the quantization condition used by Bohr:

By considering the electron as a wave, we now have a theoretical basis for one of Bohr's postulates: the electron can only move in orbits for which

$$\boldsymbol{m\,v\,r = \frac{n\,h}{2\pi}}$$

In fact, by isolating the term mv from this equation as well as from the De Broglie equation, it can be shown that the circumference of the orbit, 2πr, corresponds to an integer number of wavelengths, λ ***(Figure III-17).***

$$\boldsymbol{m\,v\,r = \frac{n\,h}{2\pi} \Rightarrow m\,v = \frac{n\,h}{2\,\pi\,r}} \quad (1)$$

$$\{(\mathbf{1}) = (\mathbf{2})\} \Rightarrow \boldsymbol{\frac{n\,h}{2\,\pi\,r} = \frac{h}{\lambda} \Rightarrow 2\,\pi\,r = nh}$$

$$\boldsymbol{\lambda = \frac{h}{p} = \frac{h}{mv} \Rightarrow m\,v = \frac{h}{\lambda}} \quad (2)$$

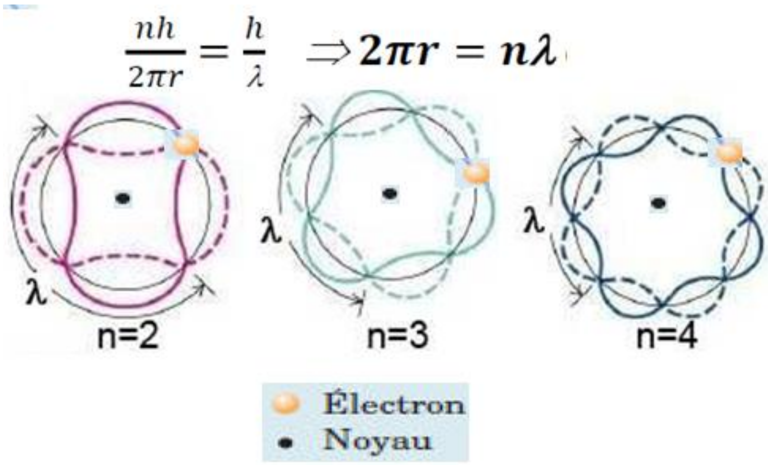


figure III-17 representation of the electron as a standing wave

When we consider the electron as a standing wave, it can be represented by a wave function that indicates the probability of finding it in a region of space around the atomic nucleus. This wave function can be visualised in the form of an orbital, which is a probability cloud representing the region of space where the electron has the greatest probability of being found.

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

Microscopic particles**:** Electron mass $m = 9{,}11.10^{-31}$Kg and speed $V= 10^7$ m/s

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6{,}626 \times 10^{-34}}{9{,}11.10^{-31}\times 10^{7}} = \mathbf{0{,}736 \times 10^{-10}\ m}$$

$0{,}736.10^{-10}$ m ; Measurable value corresponding to the wavelength λ of X-rays

- ***Macroscopic*** particle: a tennis ball of mass 0,05 kg and speed 40 m/s

$$\lambda = \frac{h}{p} = \frac{h}{mv} = \frac{6{,}626 \times 10^{-34}}{0{,}05 \times 40} = \mathbf{3{,}3 \times 10^{-34}\ m}$$

$3{,}3 \times 10^{-34}$ m. This value is not verifiable. It makes no sense

III-5-1-2- Principe d'incertitude d'Heisenberg

The uncertainty principle, also known as Heisenberg uncertainty, is a fundamental concept in quantum physics, which states that it is impossible to measure two complementary physical quantities, such as position and momentum, or energy and time, with absolute precision.

The uncertainty principle was first enunciated by Werner Heisenberg in 1927, and derives from the wave-corpuscle duality of subatomic particles. Because of the wave nature of these particles, their position and momentum cannot be known simultaneously with absolute precision. In 1927, Werner Heisenberg generalised this problem of imprecision in the position and momentum of an electron in the form of a statement:

Statement: The position x and the momentum p of a particle cannot be determined simultaneously with greater accuracy than that given by this relationship

$$:\Delta X.\ \Delta P \geq \frac{h}{4\pi} \quad \Rightarrow \quad \Delta X.\ m\ \Delta V \geq \frac{h}{4\pi} = \frac{\bar{h}}{2} \qquad \text{Avec ;} \quad \bar{h} = \frac{h}{2\pi}$$

Δx : uncertainty about the position

Δp = m ΔV uncertainty about the momentum and;

h is Planck's constant. This equation states that the product of the uncertainty in the position and the uncertainty in the momentum of a particle is greater than or equal to a fundamental constant, determined by Planck's constant.

This equation shows that the more precisely we measure the position of a particle, the greater the uncertainty about its momentum, and vice versa. In other words, the more precisely we know the position of a particle, the less precisely we can know its momentum, and vice versa. This fundamental limitation has important implications for the measurement and understanding of quantum phenomena.

In short, the relationship established by Heisenberg is known as the uncertainty principle, and justifies the use of wave functions to describe the electronic structure of the atom.

III-5-2- Wave function

In quantum physics, the wave function is a mathematical function that describes the quantum state of a system. It is used to calculate the probability of finding a particle in a certain position or with a certain momentum, as well as to describe the quantum properties of a system, such as superposition and interference.

The wave function is usually denoted **$\psi(x,t)$**, where x represents the position of the particle and t represents time. It is defined so that the square of its modulus **$|\psi(x,t)|^2$** represents the probability density of finding the particle at position x and time t. In other words ;

To any particle at time t at point M with coordinates **(x,y,z)**, a wave function is associated with **$\Psi(x,y,z,t)$** which is a real, complex, positive, negative or zero function, with the square of its modulus ($|\Psi(\vec{r},t)|^2$) represents the probability of the particle being present in a volume element ***$dV = dx\,dy\,dz$***

$$dp = \Psi(x, y, z, t)^2\, dV$$

The probability of finding the electron in a volume V is obviously 1

$$:p = \int dP = \iiint_{l'espace}^{tout} \Psi^2(x, y, z, t)\, dx\, dy\, dz = 1$$

The wave function is said to be ***normalized***

In quantum mechanics, the electron's trajectory no longer exists as a well-defined physical concept. Instead, it is replaced by the notion of the probability of the electron's presence in space. This idea involves abandoning the notion of a precise orbit for the electron around the nucleus and replacing it with that of atomic orbitals **(AO)**, which define a region of space where the particle has a probability of presence ***dP,*** described mathematically by the wave function **ψ**.

The wave function is subject to the Schrödinger equation, which describes the temporal evolution of the quantum state of a system. This equation is used to calculate the wave function at different moments in time, and therefore to predict the evolution of a quantum system.

III-5-3- Schrödinger equation

The Schrödinger equation is a fundamental equation in quantum physics that describes the time evolution of the wave function of a quantum system. It was proposed by the Austrian physicist Erwin Schrödinger in 1926.

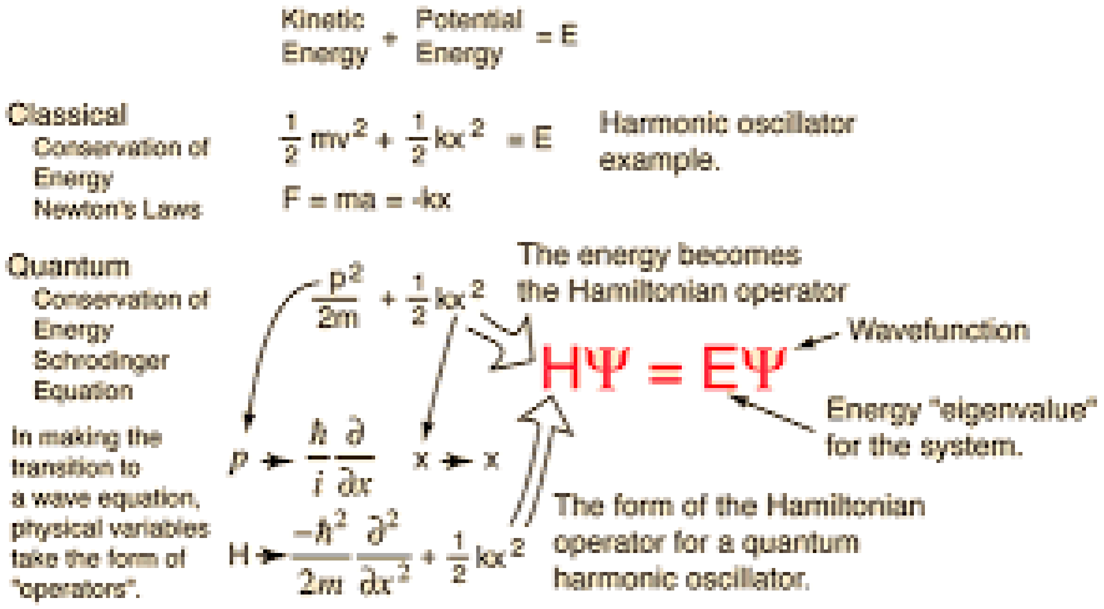
The wave functions associated with electrons are not determined experimentally but can be calculated. They are the solutions of a differential equation, known as the Schrödinger equation: **H Ψ = E Ψ**

Où **E** is Energy Eigen of System and

H is the corresponding operator: the Hamiltonian of the system $\hat{H} = -\frac{h^2}{8m\pi^2}\Delta + V$ avec,

Δ is The Laplacian = $\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$,   ***V*** : Potential energy,   ***m*** : Electron mass

h : Planck constant ; **Ψ** is the wave function of the system,



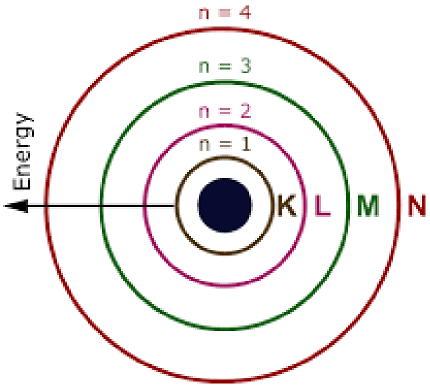
The solution to Schrödinger's equation reveals quantisation: the solutions depend on parameters that can only take discrete values, the quantum numbers. $R(r)$ depends on the principal quantum number, n, and the azimuthal quantum number, ***l***.$Y(\theta, \phi)$ depends on the azimuthal quantum number, l, and the magnetic quantum number, $\boldsymbol{m_l}$. ***l*** can vary from 0 to n - 1. $\boldsymbol{m_l}$ can vary from **-*l*** to **+*l*.**

III-5-4- Nombres quantiques

Quantum numbers are numbers used to describe the quantum properties of subatomic particles, in particular the electrons in an atom. There are four main quantum numbers: the principal quantum number **(n)**, the secondary quantum number **(l)**, the magnetic quantum number **(m)** and the spin quantum number **(s).**

III-5-4-1- Principal quantum number « n »

The principal quantum number (n): This represents the electron's energy level and corresponds to the electron's average distance from the nucleus. The possible values of n are positive integers. It is usual to designate these layers by the letters K, L, M, N when n takes the values 1, 2, 3, 4 respectively. However, the different energy levels of the atom can be represented in the form of electronic layers, as shown in the diagram below:

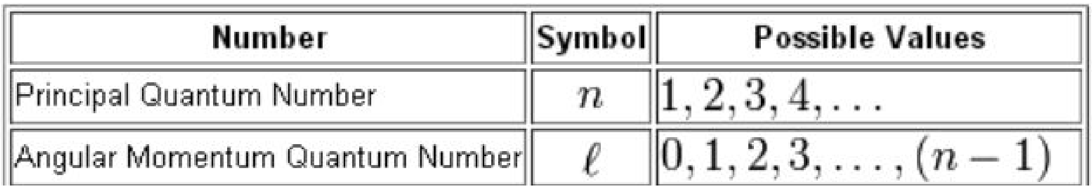


Principal quantum number (n)

III-5-4-2- Secondary quantum number or Azumutal "l".

Le nombre quantique secondaire **(l)** : Il représente le moment angulaire orbital de l'électron et détermine sa forme orbitale. Les valeurs possibles de l dépendent de la valeur de **n** et sont des entiers allant de **0 à (n-1)**. C'est un entier positif ou nul qui définit la sous-couche électronique et la symétrie de cette sous-couche. Comme vous l'avez indiqué, sa valeur est telle que :

$$\mathbf{0 \leq l \leq n-1.}$$

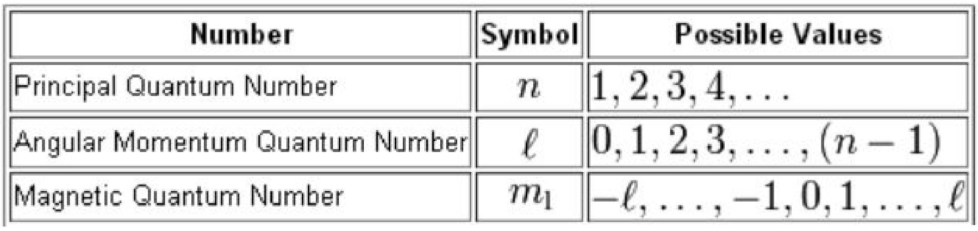


Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$

III-5-4-3- Magnetic quantum number « m »

The magnetic quantum number **(m)**: This represents the spatial orientation of the electron's orbit in relation to an external magnetic field. The possible values of m depend on the value of l and range from ***-l*** to ***+l***. It is a zero or positive negative integer. It defines the atomic orbital (AO) or quantum bin (represented by a square). It is an integer such that: $-l \leq m \leq +l$, i.e. (2l+1) different values for each value of ***l***.

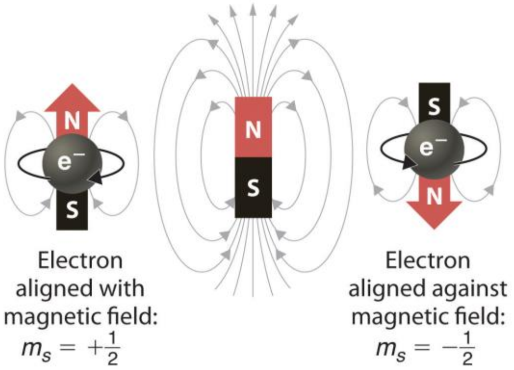
To sum up, each state (n ,l ,m) of the system corresponds to a wave function **Ψn ,l ,m (r,** $(\boldsymbol{\theta}, \boldsymbol{\phi})$ called an atomic orbital, which defines the spatial distribution of the electron's electric charge around the nucleus



Number	Symbol	Possible Values
Principal Quantum Number	n	$1, 2, 3, 4, \ldots$
Angular Momentum Quantum Number	ℓ	$0, 1, 2, 3, \ldots, (n-1)$
Magnetic Quantum Number	m_l	$-\ell, \ldots, -1, 0, 1, \ldots, \ell$

III-5-4-4- Quantum spin number « s »

The spin quantum number (s): This represents the amount of spin movement of the electron about its own axis. To describe atomic orbitals (AO), the first three quantum numbers (n, l, m) are sufficient. However, to quantify the electron's intrinsic angular momentum, it is assigned a fourth spin quantum number, ms (or s). This quantum number represents the orientation of the electron's intrinsic angular momentum about its own axis, as shown in the diagram below:



The spin quantum number can only take two values: +1/2 or -1/2, which means that the electron has two possible orientations of intrinsic angular momentum. So the state of an electron is characterised by the four quantum numbers n, l, m and ms. The four quantum numbers are necessary to fully describe the electronic distribution in an atom and to predict its chemical properties.

In short, these quantum numbers are used to describe the electronic structure of atoms and to predict the chemical properties of elements.

III-6- Electronic structure of atoms

The Schrödinger equation for a quantum system, **H Ψ = E Ψ**, is the fundamental equation of quantum mechanics that describes the behavior of subatomic particles. In this equation, H represents the Hamiltonian operator, ψ is the wave function and E is the total energy of the system. However, for most quantum systems, the Hamiltonian operator contains repulsion terms between the particles, which makes the equation **H Ψ = E Ψ** very difficult to solve analytically. In the case of single-electron atoms such as hydrogen and hydrogenoids, the repulsion term is absent, so the Schrödinger equation for these systems can be solved exactly.

II-6-1- Hydrogen atom in quantum mechanics

Since the hydrogen atom contains only one proton and one electron, the study of this system focuses on the interaction between these two charges, which are separated by a distance r. Potential energy of the system, **V(r),** is determined by the interaction.

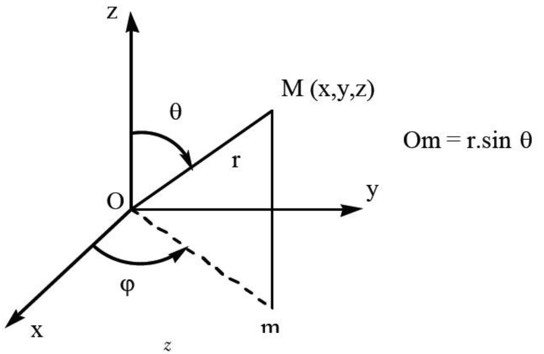
$$\mathbf{V(r)} = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

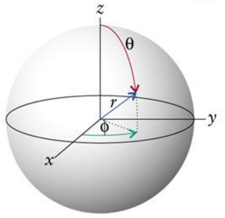
Avec $\hat{H} = -\frac{h^2}{8m\pi^2}\Delta + \mathbf{V(r)}$ et $\Delta = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}$

The Schrödinger equation in Cartesian coordinates is then written as: **H Ψ = E Ψ(x, y, z)**

$$\Rightarrow \left(-\frac{h^2}{8m\pi^2}\left[\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right] - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right)\Psi = \mathbf{E}\,\Psi(\mathbf{x},\mathbf{y},\mathbf{z}) \qquad (1)$$

To solve this equation, it is preferable to switch to spherical coordinates **r**, **θ** et **ϕ**, The proton is placed at the origin of the electron's frame of reference at the point M with coordinates as in the diagram below:





$$\begin{cases} x = r.\sin\theta.\cos\varphi \\ y = r.\sin\theta.\sin\varphi \\ z = r.\cos\theta \end{cases} \qquad \begin{cases} r \in [0,\ \infty[\\ \theta \in [0,\ \Pi] \\ \varphi \in [0,\ 2\,\Pi] \end{cases}$$

The Cartesian coordinates in the equation(1) are replaced by spherical coordinates

(**r**, **θ** et **ϕ**) this last one becomes:

équation (1) $\Rightarrow$

$$\left(-\frac{h^2}{8m\pi^2}\left[\sin\theta\,\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{\partial}{\partial r}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin\theta}\left(\frac{\partial^2\Psi}{\partial\varphi^2}\right)\right]-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\right)\Psi=\mathbf{E}\,\Psi(\mathbf{x},\mathbf{y},\mathbf{z})$$

with $\Delta=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin\theta^2}\;\frac{\partial^2}{\partial\varphi^2}$

Solutions to this equation are of the form :

$\boldsymbol{\Psi}_{(n,l,m)}(\mathbf{r},\boldsymbol{\theta},\boldsymbol{\varphi}) = \mathbf{Rn,l(r)\ x\ \Theta_{l,m}x\ (\theta)\ x\ \Phi_{,m}(\varphi) = Rn,l(r)\ x\ Y_{l,m}x\ (\theta,\varphi)}$ **with ;**

$\mathbf{Rn,l(r)}$ **: Radial part**

$\mathbf{Y_{l,m}x\ (\theta,\varphi)}$ **: Angular part**

We see that $\boldsymbol{\Psi}_{(n,l,m)}(\mathbf{r},\boldsymbol{\theta},\boldsymbol{\varphi})$ can be expressed in the form of a product:

$$\psi\,(r,\theta,\phi)=R(r)\,Y(\theta,\phi) \qquad (2)$$

III-6-2- Atoms with multiple electrons

III-6-2-1 Multi-electron Schrödinger equation

The handling of the atom or ion containing N electrons is more difficult than that of the hydrogen atom because of the complexity of the expression of the potential energy of the system. This expression includes negative terms resulting from the attraction of the electrons towards the nucleus as well as positive terms resulting from the mutual repulsion of the electrons. The presence of these terms complicates the problem.

Consider the example of the **helium atom with 2 electrons (Z=2).** Assuming that the nucleus is stationary, the distances of the two electrons from the nucleus can be given as r1 and r2, while the distance between the two electrons can be given as $\mathbf{r_{12}}$**.**

The potential energy of the 3-charge system is equal to:

$$\mathrm{V(r)}=-\frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r_1}-\frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r_2}+\frac{Z}{4\pi\varepsilon_0}\frac{e^2}{r_{12}}=-\frac{2}{4\pi\varepsilon_0}\frac{e^2}{r_1}-\frac{2}{4\pi\varepsilon_0}\frac{e^2}{r_2}+\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r_{12}}$$

$$\mathbf{V(r)} = -\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{r_{12}}\right)$$

The kinetic energy will be the sum of the kinetic energies of the 2 electrons:

$E_c = \frac{1}{2m}\,(p_1^2 + p_2^2)$ **;** This gives the Hamiltonian H of the **He** atom:

$$\hat{H} = -\frac{\hbar^2}{2m}\,(\Delta_1+\Delta_2)+\mathbf{V(r)} = -\frac{\hbar^2}{2m}\,(\Delta_1+\Delta_2)-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2}{r_1}+\frac{2}{r_2}-\frac{1}{r_{12}}\right)$$ with ;

Δ_1 et Δ_2 being the Laplacians of the 2 electrons.

The Schrödinger equation in this case is written as: **H Ψ = E *Ψ*(x$_1$, y$_1$, z$_1$, x$_2$, y$_2$, z$_2$)** because; **Ψ** depends on the coordinates of the 2 electrons, which can be written more simply as follows: $\Psi = \Psi_{(1,2)}$

It is impossible to solve such a problem mathematically and we have to resort to approximations.

III-6-2-2 Approximate resolution:

One of the assumptions we have used is the Born-Oppenheimer approximation, which consists of considering the nucleus as immobile. The second assumption is to return to a result similar to that of hydrogenoids. To illustrate this, let's take the example of the helium atom. Each electron is attracted by the positively charged nucleus of (+2e) and repelled by the other negatively charged electron of (-e). We can replace these forces with a single force due to the attraction of the nucleus to the electron, but the effective charge of the nucleus would then be fictitious and equal to **(2 – *σ*).** We call (***σ***) screen constant.

Moyennant cette approximation, l’Hamiltonien s’écrit :

$$\hat{H} = -\frac{\hbar^2}{2m}\,(\Delta_1+\Delta_2)-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2-\sigma_1}{r_1}+\frac{2-\sigma_2}{r_2}\right).$$

Here $\sigma\,1 = \sigma\,2$ screen constant for the two electrons. $\hat{H}$ is the sum of two terms:

Hamiltoenian 1 depends only on electron 1 and Hamiltonian 2 depends only on electron 2.

$$\widehat{H_1} = -\frac{\hbar^2}{2m}\,(\Delta_1)-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2-\sigma_1}{r_1}\right) \quad \textbf{et} \quad \widehat{H_2} = -\frac{\hbar^2}{2m}\,(\Delta_2)-\frac{e^2}{4\pi\varepsilon_0}\left(\frac{2-\sigma_2}{r_2}\right)$$

Sow we have : $\hat{H} = \widehat{H_1} + \widehat{H_2}$ **et** $(\widehat{H_1} + \widehat{H_2})\,\Psi = \mathrm{E}\,\Psi\,(1,2)$

this leads us to ask $\Psi\ (1,2) = \ \varphi\ (1)\varphi\ (2)$ that is the wave function $\Psi\ (1,2)$ appears as the product of two functions $\varphi\ (1)\ \text{et}\ \varphi\ (2)$ which depends solely on the electron (1) and (2) respectively.

For the energies E = $E_1 + E_2$, we can easily obtain;

$\widehat{H_1}\varphi_1 = E_1\varphi_1$ **et** $\widehat{H_2}\varphi_2 = E_2\varphi_2 \quad \Rightarrow$ We therefore need to solve the hydrogenoids problem.

En général, n atome d'un numéro atomique Z donné, une simplification courante consiste à considérer que le potentiel auquel chaque électron est soumis est de type :

$$-\frac{Z^{*}}{4\pi\varepsilon_0}\frac{e^2}{r} \qquad \textbf{Avec} \qquad Z^{*} = Z - \sigma$$

Z* is called the fictitious nuclear charge**;** σ is the electron's screen constant.
This approximation simplifies the mathematically impossible solution of the polyelectronic Schrödinger equation. In fact, it reduces it to the solution of N monoelectronic Schrödinger equations of the hydrogenoid type. For electron i :

$$\left(-\frac{\hbar^2}{2m}(\Delta_i) - \frac{Z^{*}e^2}{4\pi\varepsilon_0}\right)\varphi(i) = E_i\varphi(i) \qquad \text{Avec} \qquad Z^{*} = Z - \sigma$$

The wave function can be written as Ψ (1, 2, 3,…i……..N) = $\varphi\ (1)\varphi\ (2) \ldots.\ \varphi\ (i) \ldots.\ \varphi\ (N)$

The total energy $\mathbf{E_T}$ **=** $E_1 + E_2 + \ldots + E_i + \ldots E_N$

You can even give the energy value $\mathbf{E_i}$ of several i electrons

$$E_i = -13.,6\ \frac{Z^{*2}_{i}}{n^2}\ \mathbf{eV}$$

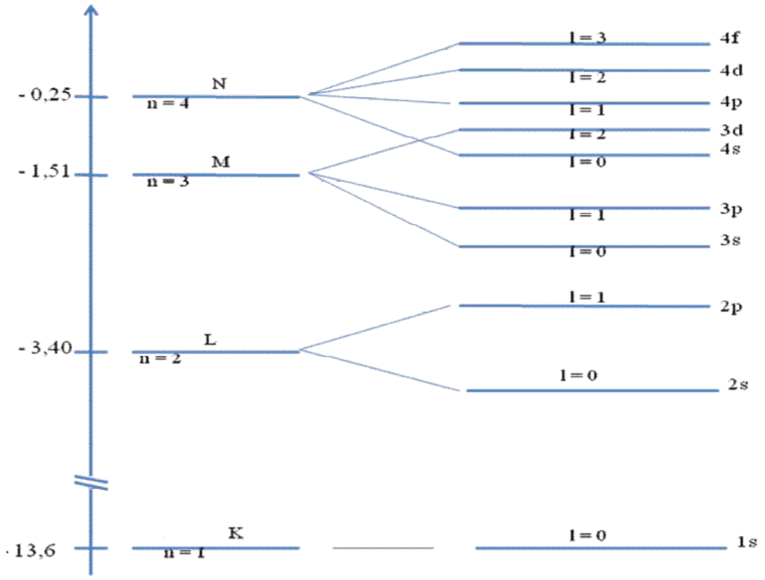
Calculations show that the energy of an electron depends not only on its principal quantum number n, but also on its secondary quantum number l, because **0 ≤ l ≤ n-1.**

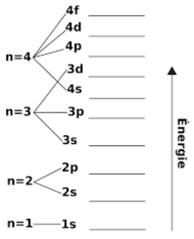
Thus, for any electron of quantum number n and l, the energy is given by

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

By observing, in relation to the level of the hydrogen atom of energy $E_n = -13{,}6\ Z^2/n^2$, sub-levels of energy $E_{n,l}$ appear. Whereas for n = 2, for example, we would have $n^2 = 4$ 4 O.A. of the same energy.

In the case of an atom with several electrons (4 O.A) but with different energies (sub-levels), we have the O.A. (2s) on the one hand and the 3 O.A. (2p) on the other. The 3 O.A. (2p) will have the same energy, but this energy will be different from that of the O.A. (2s). We say that the energy degeneracy is partially lifted. This means that the sub-layers of the same n level of these atoms will have different energies, hence the following energy diagram:

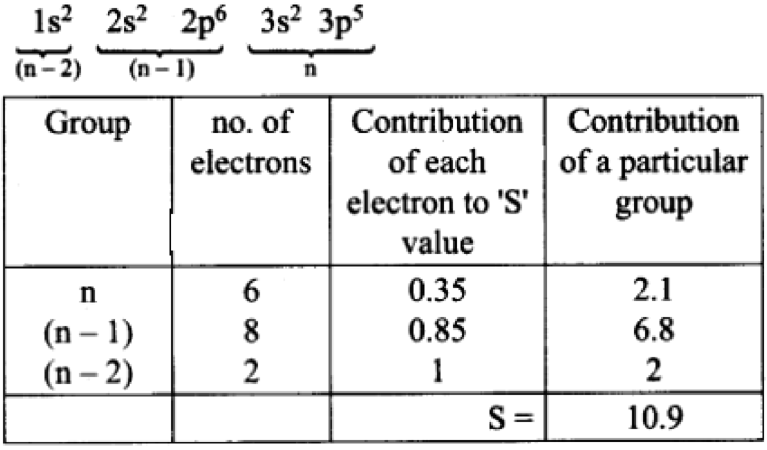




In summary, for any electron of quantum number n and l, the energy is given by: $E_{n,l} = -13.,6\,\frac{Z_i^{*2}}{n^2}$ Avec $Z^* = Z - \sigma$ **et** σ : the screen constant is calculated using Slater's rules of empiric.

The Slater screen constant is a numerical value used in quantum chemistry to take into account the effect of electron repulsion on the electrostatic force of attraction between the nucleus and a given electron. It is denoted **"σ"** and is calculated as a function of the number and electronic configuration of the electrons in the atom under consideration. The Slater screen constant represents an approximation of the electron repulsion effect by considering that each electron in the inner layer of the atom exerts a partial repulsion on the electrons in the outer layer. This approximation simplifies calculations of the electronic structure of atoms and molecules. The Slater screen constant is therefore an important concept in quantum chemistry. In the general case, the screen effect **σ** j on electron j is the sum of the screen effects **σ j....i** exerted on electron j by any other electron i, taking into account the situation of electron j. According to Slater the effects of other electrons are determined by the following rules:

- Each electron in the same group as electron j exerts a shielding effect equivalent to 0.35 (electronic charges), with the exception of group 1s for which the shielding of one electron on the other is 0.30.
- An electron j in a group ns np is screened by 0.85 by each electron of main quantum number (n -1), and by 1.00 by each electron of lower main quantum number.
- An electron j of a group nd or nf is screened by 1.00 by each electron of a lower group, either with a lower value of n, or with the same value of n as electron j and a lower value of l..

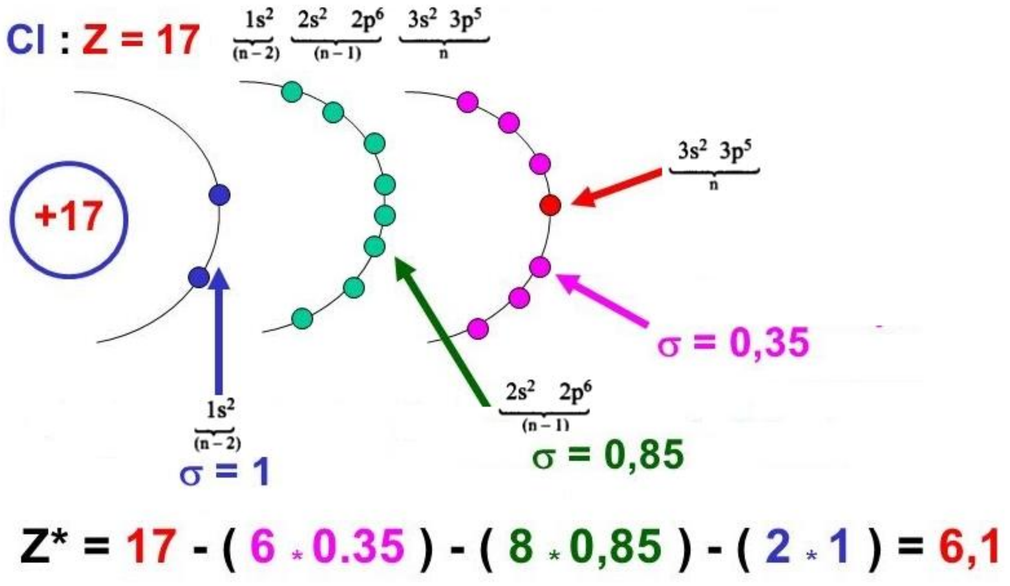


$$\underbrace{1s^2}_{(n-2)}\ \underbrace{2s^2\ \ 2p^6}_{(n-1)}\ \underbrace{3s^2\ \ 3p^5}_{n}$$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	6	0.35	2.1
(n − 1)	8	0.85	6.8
(n − 2)	2	1	2
		S =	10.9

<u>Note :</u> These rules of thumb are applicable for the first few periods but become very random when n > 4.

<u>Exemple : **Cl**</u>$_{17}$



III-6-3 Atomic orbitals : O.A

Atomic orbitals (A.O.) are regions of space around an atomic nucleus where the probability of finding an electron is highest. A.O.s are determined by the quantum numbers n, l and m, which describe the size, shape and spatial orientation of the A.O.s respectively. Atomic orbitals are classified according to their principal quantum number (n), which determines the energy of the electron and the average distance of the electron from the nucleus. Atomic orbitals with the same principal quantum number form an electronic layer. The mathematical resolution of $H\Psi = \mathbf{E\Psi}$ led to pose $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$ being the product of a function of θ with a function of Ψ.

The calculation shows: $\boldsymbol{\Psi}_{(n,l,m)}(\mathbf{r},\boldsymbol{\theta},\boldsymbol{\varphi}) = \mathbf{Rn,l(r)}\,\mathbf{Y}_{l,m}\mathbf{x}\,(\boldsymbol{\theta},\boldsymbol{\varphi})$

The radial part $\mathbf{Rn,l(r)}$ de l'O.A depends only on **n** and **l** and. (defines the layer)

The angular part $\mathbf{Y}_{l,m}\mathbf{x}\,(\boldsymbol{\theta},\boldsymbol{\varphi})$ de l'O.A depends only on **l** and **m**. (geometry defined)

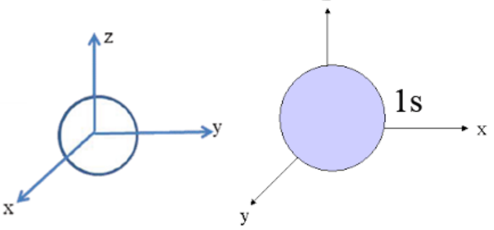
For **n = 1 ;** Only state (1, 0, 0) is possible, and it is described by the wave function:

$\boldsymbol{\Psi}_{(1,0,0)} = \mathbf{R}_{1,0}(\mathbf{r})\,\mathbf{Y}_{0,0}\,(\boldsymbol{\theta},\boldsymbol{\varphi})$, It is an atomic orbital (1s) with a spherical shape. Its energy : E_1 = -13,6 eV.

So ; $\boldsymbol{\psi}_{1,0,0}$ ou $\boldsymbol{\psi}_{1s}$ ou (1S) : corresponds to n=1, l=0 (and therefore $m_l = 0$).

$\boldsymbol{\psi}_{1,0,0} = \boldsymbol{\psi}_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} exp\left(\frac{-r}{a_0}\right)$ **with** a_0 the Bohr atom radius (a_0 = 0,529 Å).

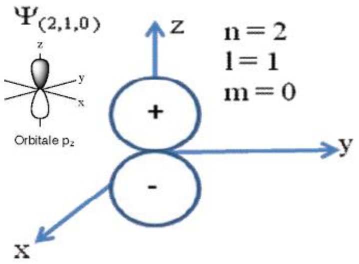
$$\Psi_{1,0,0} = 1s = \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}} exp\left(\frac{-r}{a_0}\right)$$

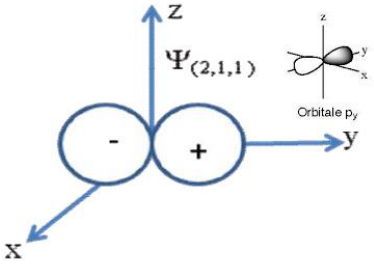


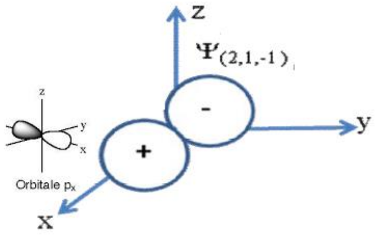
orbital atomic 1s

The shape of each A.O. is given by the representation of its angular part:

- The O.A. is formed by two spheres tangent at O. They are carried by the axis Oz, this A.O. is: 2Pz (n= 2, l = 1, z = direction Oz)
- The O.A. is formed by two spheres tangent at O. They are carried by the axis Oy, this O.A. is: 2Py
- The O.A. is formed by two spheres tangent at O. They are carried by the Ox axis, this A.O. is: 2Px





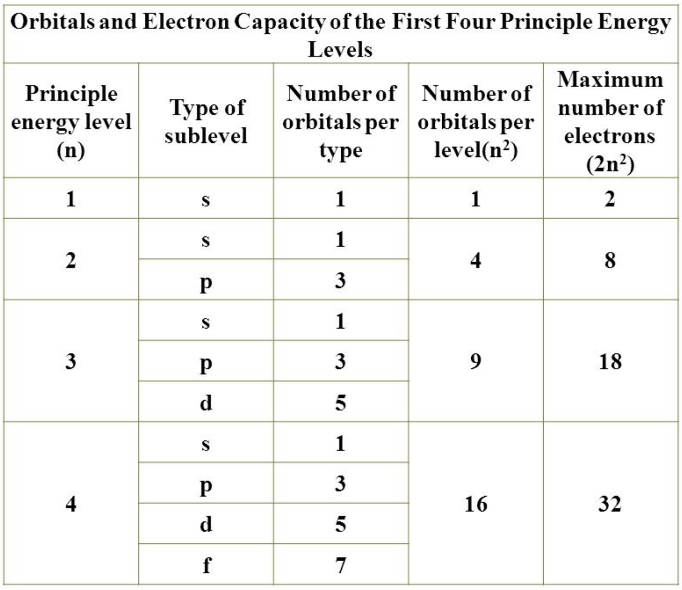


III-7- Electronic structures of atoms

The electronic configuration of an atom describes how the electrons are distributed in the atom's different atomic orbitals. It is determined by the number of electrons in the atom and how they are distributed in the different electron layers.

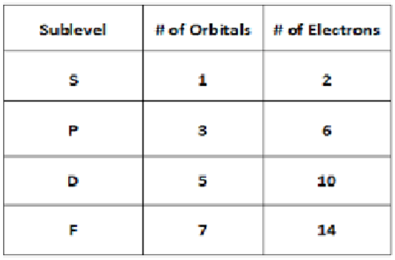
The electronic configuration can be written using Schrödinger notation, which consists of writing the atomic orbitals occupied by the electrons in the form of symbols. The symbols used for the orbitals are letters that represent the shape of the orbital, followed by an index that indicates the number of electrons in that orbital.

In summary, the state of each electron is defined by the four quantum numbers n, l, m and s. The representation of the different OAs is the same as that of the hydrogen atom. The electronic configuration (or structure) of an atom ZX is the way in which the Z electrons are distributed in the different OAs. ***(Figure III-18).***

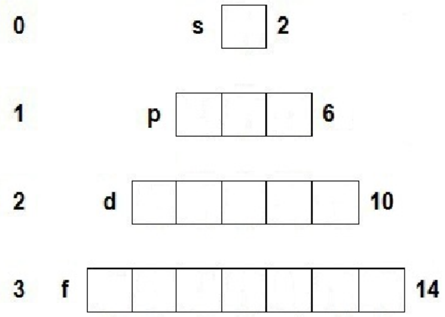


Orbitals and Electron Capacity of the First Four Principle Energy Levels

Principle energy level (n)	Type of sublevel	Number of orbitals per type	Number of orbitals per level(n^2)	Maximum number of electrons ($2n^2$)
1	s	1	1	2
2	s	1	4	8
	p	3		
3	s	1	9	18
	p	3		
	d	5		
4	s	1	16	32
	p	3		
	d	5		
	f	7		



Sublevel	# of Orbitals	# of Electrons
S	1	2
P	3	6
D	5	10
F	7	14



<u>Figure III-18: Organisation of the electronic cloud into layers, sublayers and atomic orbitals</u>

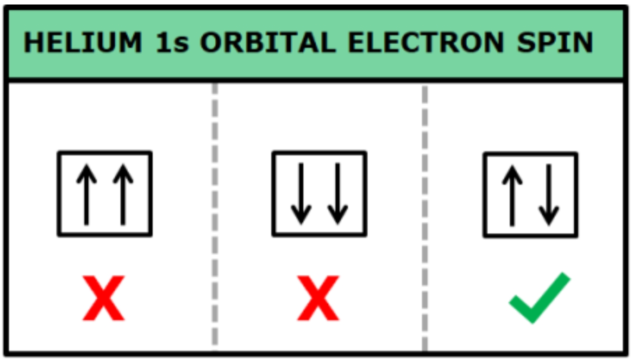
When electrons are distributed in the different atomic orbitals, it is crucial to observe the following rules:

1. Orbital filling principle (stability principle):

The electrons first fill the lowest energy orbitals available before moving on to the highest energy orbitals.

2. Pauli exclusion principle: each electron must have a unique spin, so two electrons in the same orbital must have opposite spins. In other words, no two electrons in an atom can have the same four quantum numbers.

Example :

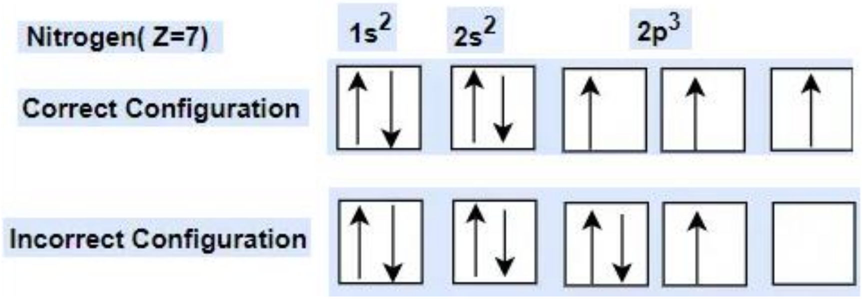


Note:** **An electronic layer of rank n comprises n^2 atomic orbitals and contains a maximum of $2n^2$ electrons. The maximum capacity of the ns, np, nd and nf sublayers is therefore 2, 6, 10 and 14 electrons respectively.

3. Hund's rule or maximum multiplicity :

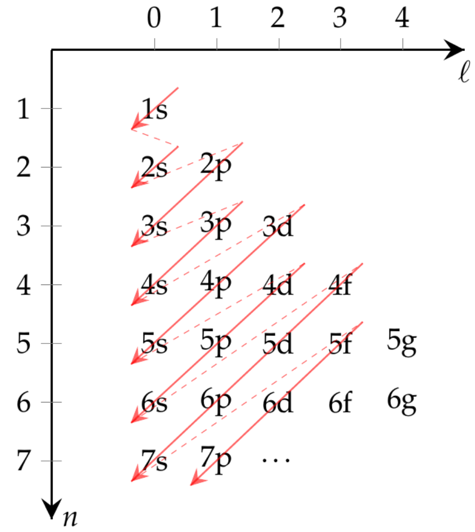
Lorsqu'il y a plusieurs orbitales d'une même sous-couche électronique, les électrons occupent chaque orbital individuellement avant de commencer à les apparier. De plus, les électrons appariés ont des spins opposés pour minimiser la répulsion électrostatique.

Exemple :



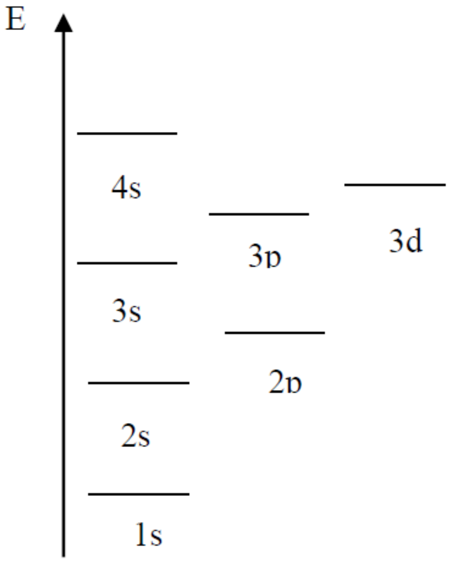
4- Klechkowski's rules

For the atom to reach its lowest energy ground state, the electronic layers and sublayers must be filled in ascending order of the sum of the principal (n) and secondary (l) quantum numbers. If several sublayers have the same sum (n+l), then the sublayer with the lowest value of n must be filled first. This approach ensures that the electrons are evenly distributed across the different electron layers and sublayers, minimising the total energy of the atom..



The order in which the electronic sublayers are filled is :

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p…

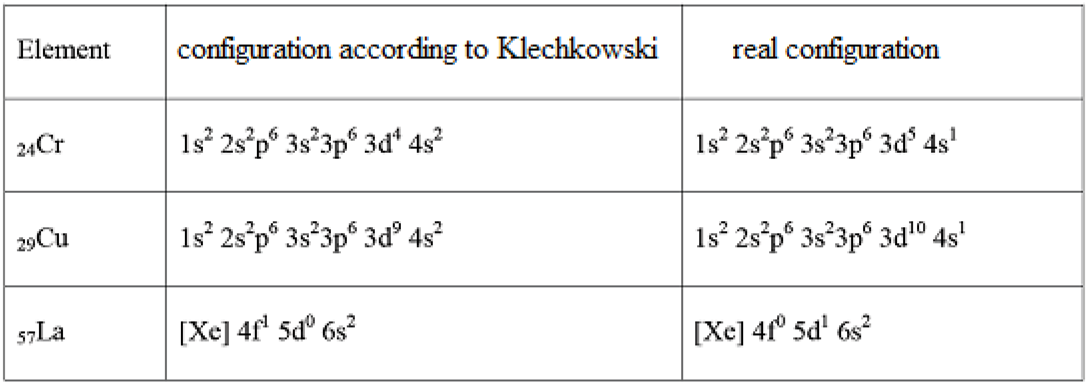


Note

- ***The order of increasing energies is the order of increasing values of the sum (n+l)***
- ***If two sub-layers correspond to the same value of (n+l), the sub-layer with the lowest value of n has the lowest energy.***
- ***The 8th energy level does not exist. The configuration of the elements of the 7th level end with the configuration: 7s 5f 6d.***

5- Exceptions to the Klechkowski rule

When a sublayer is empty, partially filled or symmetrically filled, this gives the atom a lower total electronic energy, which makes it more stable. This explains why atoms with particular electronic configurations, such as (n-1) d9 ns2 (Cu, Ag and Au) and (n-1) d4 ns2 (Cr, Mo), transform into (n-1) d10 ns1 and (n-1) d5 ns1 respectively (one electron from the s sublayer transits to the d sublayer to complete it with 5 or 10 electrons): the configuration thus obtained will be more stable than the expected Klechkowski configuration, as the table below shows:



Element	configuration according to Klechkowski	real configuration
$_{24}Cr$	$1s^2\ 2s^2p^6\ 3s^23p^6\ 3d^4\ 4s^2$	$1s^2\ 2s^2p^6\ 3s^23p^6\ 3d^5\ 4s^1$
$_{29}Cu$	$1s^2\ 2s^2p^6\ 3s^23p^6\ 3d^9\ 4s^2$	$1s^2\ 2s^2p^6\ 3s^23p^6\ 3d^{10}\ 4s^1$
$_{57}La$	$[Xe]\ 4f^1\ 5d^0\ 6s^2$	$[Xe]\ 4f^0\ 5d^1\ 6s^2$

As far as the f sublayers are concerned, the d level is first filled with an electron before the f level begins to fill. This is due to the complex shape of the f orbitals, which require more energy to fill and are therefore less stable than the s, p and d orbitals.

By following these rules, we can determine the electronic configuration of an atom and how the electrons are distributed in the different atomic orbitals

6- Valence layer

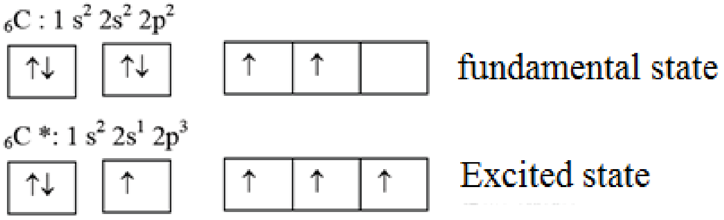
The layer with the highest principal quantum number in the ground state of an atom is called the outer or peripheral layer. This is the layer that contains the electrons furthest from the atomic nucleus. The electrons located in this layer are called valence electrons and they play a crucial role in the chemical properties of the element.

Valence electrons are involved in chemical bonds and chemical reactions. They determine the reactivity of the atom and how it interacts with other atoms to form molecules.

7- Excited state

The excited state of an atom is a state in which one or more electrons have been excited to a higher energy level than their ground state. This can occur when the atom absorbs energy in the form of light, heat or collision with another atom or particle. When the atom is in an excited state, the electrons occupy atomic orbitals further from the nucleus and have a higher energy.

Example :



III-7- 1- Periodic classification of D. Mendeleev

In the XIX century, chemists were faced with a growing number of chemical elements that they had to classify in a comprehensible way. By organising atoms according to their increasing atomic mass, a periodicity in their properties became apparent. In 1869, D. Mendeleïev demonstrated this periodicity by studying the 63 elements then known. He noticed that the properties of the elements followed a trend when they were classified according to their increasing atomic mass. The periodic table is a crucial tool for comparing chemical elements and understanding their properties. It allows groups of elements to be distinguished by showing the relationship between their atomic structure and their chemical properties. In addition, the periodic table is useful for predicting the formulae of compounds and the types of bonds that unite the components of a molecule.

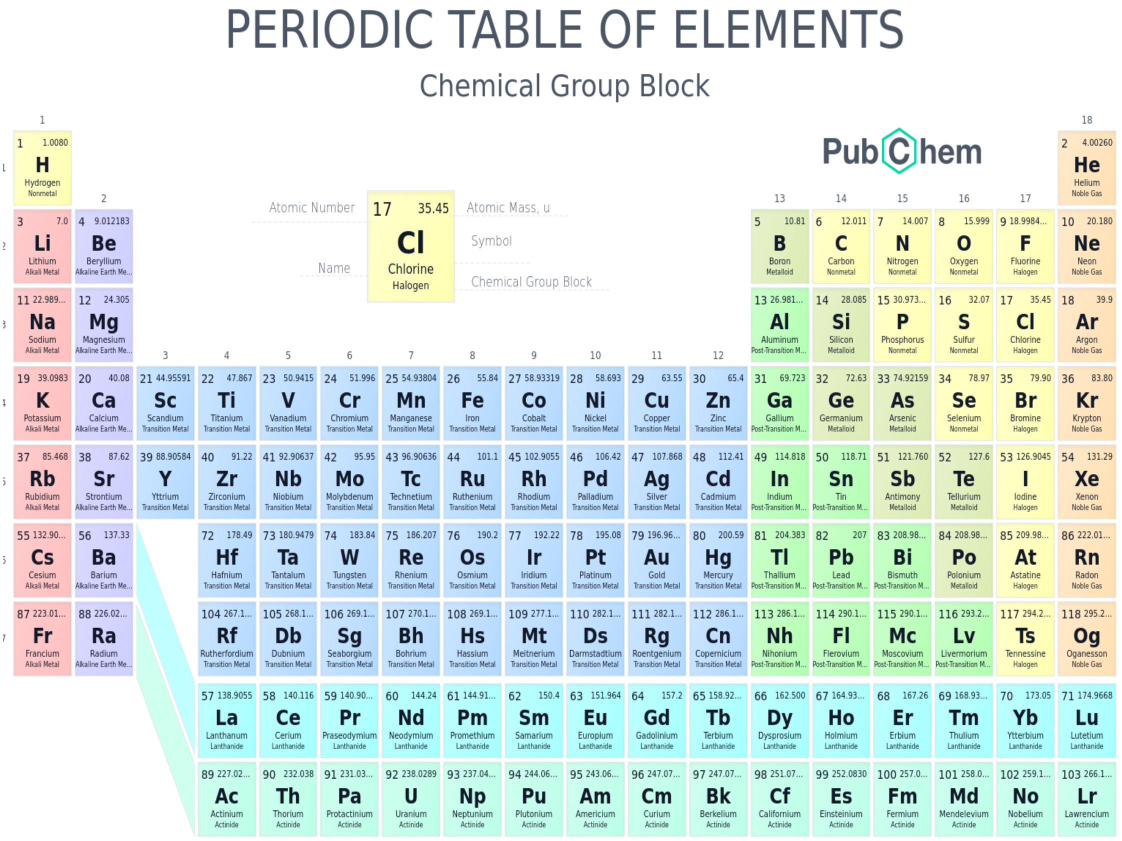
III-7-2- Principle of the periodic table

D. Mendeleïev's periodic table is a method of classifying chemical elements according to their common physical and chemical properties. It was first proposed by the Russian chemist Dmitri Mendeleïev in 1869.

Mendeleïev organised the elements in ascending order of atomic weight, placing elements with similar properties in vertical columns called groups and placing them in horizontal rows called periods according to their physical and chemical properties. In other words ;

- The elements are classified in increasing order of Z.
- Each horizontal row in the periodic table occupied by elements with the same value of n (ns subshells) is called a period.
- The periods are classified from top to bottom in increasing order of n.
- All elements in the same period have the same core electron configuration.
- The periodic table contains 7 periods (7 rows) and 18 columns.
- All elements in the same column (group) have the same valence electron configuration.

Chemical elements have properties that are related to their electronic structure, and some have properties in common: they are classified by family. The columns with the subscript A represent the main families, while those with the subscript B represent the transition elements. The atoms in the periodic table are arranged in ascending order of atomic number Z. A distinction is made between columns or groups and rows or periods. ***Figure III-18***



PERIODIC TABLE OF ELEMENTS

Chemical Group Block

PubChem

Atomic Number: 17
Atomic Mass, u: 35.45
Symbol: Cl
Name: Chlorine
Chemical Group Block: Halogen

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 1.0080 H Hydrogen Nonmetal																	2 4.00260 He Helium Noble Gas
2	3 7.0 Li Lithium Alkali Metal	4 9.012183 Be Beryllium Alkaline Earth Me...											5 10.81 B Boron Metalloid	6 12.011 C Carbon Nonmetal	7 14.007 N Nitrogen Nonmetal	8 15.999 O Oxygen Nonmetal	9 18.9984... F Fluorine Halogen	10 20.180 Ne Neon Noble Gas
3	11 22.989... Na Sodium Alkali Metal	12 24.305 Mg Magnesium Alkaline Earth Me...											13 26.981... Al Aluminum Post-Transition M...	14 28.085 Si Silicon Metalloid	15 30.973... P Phosphorus Nonmetal	16 32.07 S Sulfur Nonmetal	17 35.45 Cl Chlorine Halogen	18 39.9 Ar Argon Noble Gas
4	19 39.0983 K Potassium Alkali Metal	20 40.08 Ca Calcium Alkaline Earth Me...	21 44.95591 Sc Scandium Transition Metal	22 47.867 Ti Titanium Transition Metal	23 50.9415 V Vanadium Transition Metal	24 51.996 Cr Chromium Transition Metal	25 54.93804 Mn Manganese Transition Metal	26 55.84 Fe Iron Transition Metal	27 58.93319 Co Cobalt Transition Metal	28 58.693 Ni Nickel Transition Metal	29 63.55 Cu Copper Transition Metal	30 65.4 Zn Zinc Transition Metal	31 69.723 Ga Gallium Post-Transition M...	32 72.63 Ge Germanium Metalloid	33 74.92159 As Arsenic Metalloid	34 78.97 Se Selenium Nonmetal	35 79.90 Br Bromine Halogen	36 83.80 Kr Krypton Noble Gas
5	37 85.468 Rb Rubidium Alkali Metal	38 87.62 Sr Strontium Alkaline Earth Me...	39 88.90584 Y Yttrium Transition Metal	40 91.22 Zr Zirconium Transition Metal	41 92.90637 Nb Niobium Transition Metal	42 95.95 Mo Molybdenum Transition Metal	43 96.90636 Tc Technetium Transition Metal	44 101.1 Ru Ruthenium Transition Metal	45 102.9055 Rh Rhodium Transition Metal	46 106.42 Pd Palladium Transition Metal	47 107.868 Ag Silver Transition Metal	48 112.41 Cd Cadmium Transition Metal	49 114.818 In Indium Post-Transition M...	50 118.71 Sn Tin Post-Transition M...	51 121.760 Sb Antimony Metalloid	52 127.6 Te Tellurium Metalloid	53 126.9045 I Iodine Halogen	54 131.29 Xe Xenon Noble Gas
6	55 132.90... Cs Cesium Alkali Metal	56 137.33 Ba Barium Alkaline Earth Me...		72 178.49 Hf Hafnium Transition Metal	73 180.9479 Ta Tantalum Transition Metal	74 183.84 W Tungsten Transition Metal	75 186.207 Re Rhenium Transition Metal	76 190.2 Os Osmium Transition Metal	77 192.22 Ir Iridium Transition Metal	78 195.08 Pt Platinum Transition Metal	79 196.96... Au Gold Transition Metal	80 200.59 Hg Mercury Transition Metal	81 204.383 Tl Thallium Post-Transition M...	82 207 Pb Lead Post-Transition M...	83 208.98... Bi Bismuth Post-Transition M...	84 208.98... Po Polonium Metalloid	85 209.98... At Astatine Halogen	86 222.01... Rn Radon Noble Gas
7	87 223.01... Fr Francium Alkali Metal	88 226.02... Ra Radium Alkaline Earth Me...		104 267.1... Rf Rutherfordium Transition Metal	105 268.1... Db Dubnium Transition Metal	106 269.1... Sg Seaborgium Transition Metal	107 270.1... Bh Bohrium Transition Metal	108 269.1... Hs Hassium Transition Metal	109 277.1... Mt Meitnerium Transition Metal	110 282.1... Ds Darmstadtium Transition Metal	111 282.1... Rg Roentgenium Transition Metal	112 286.1... Cn Copernicium Transition Metal	113 286.1... Nh Nihonium Post-Transition M...	114 290.1... Fl Flerovium Post-Transition M...	115 290.1... Mc Moscovium Post-Transition M...	116 293.2... Lv Livermorium Post-Transition M...	117 294.2... Ts Tennessine Halogen	118 295.2... Og Oganesson Noble Gas
				57 138.9055 La Lanthanum Lanthanide	58 140.116 Ce Cerium Lanthanide	59 140.90... Pr Praseodymium Lanthanide	60 144.24 Nd Neodymium Lanthanide	61 144.91... Pm Promethium Lanthanide	62 150.4 Sm Samarium Lanthanide	63 151.964 Eu Europium Lanthanide	64 157.2 Gd Gadolinium Lanthanide	65 158.92... Tb Terbium Lanthanide	66 162.500 Dy Dysprosium Lanthanide	67 164.93... Ho Holmium Lanthanide	68 167.26 Er Erbium Lanthanide	69 168.93... Tm Thulium Lanthanide	70 173.05 Yb Ytterbium Lanthanide	71 174.9668 Lu Lutetium Lanthanide
				89 227.02... Ac Actinium Actinide	90 232.038 Th Thorium Actinide	91 231.03... Pa Protactinium Actinide	92 238.0289 U Uranium Actinide	93 237.04... Np Neptunium Actinide	94 244.06... Pu Plutonium Actinide	95 243.06... Am Americium Actinide	96 247.07... Cm Curium Actinide	97 247.07... Bk Berkelium Actinide	98 251.07... Cf Californium Actinide	99 252.0830 Es Einsteinium Actinide	100 257.0... Fm Fermium Actinide	101 258.0... Md Mendelevium Actinide	102 259.1... No Nobelium Actinide	103 266.1... Lr Lawrencium Actinide

<u>Figure III-18 : Periodic Table of Elements</u>

III-7-3- Description of the lines (periods)

The periodic table of the elements contains seven horizontal lines called periods. Each period represents a complete electronic configuration around the atomic nucleus, which contains an increasing number of electrons as you move from left to right.

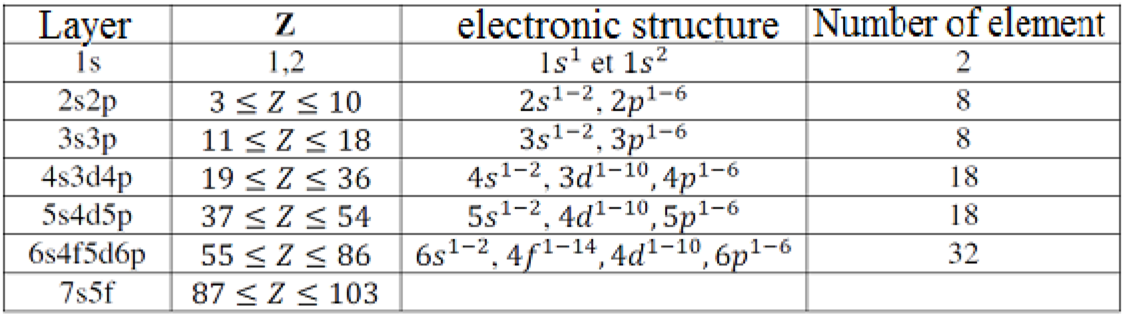
The first period contains only one element, hydrogen, which has one electron in its outermost electronic configuration.

The second period contains two elements, lithium and beryllium, which have two and four electrons respectively in their outermost electronic layer. As we move through the periods, the number of electrons in the outermost electronic layer continues to increase, reaching eight electrons in the third period.

The third period. This complete electronic layer is called the valence layer, and it is the layer that determines the chemical properties of an element..

The fourth period contains 18 elements, including the transition elements. These elements have complex electronic configurations and can form compounds with various degrees of oxidation. The following periods also contain transition elements, as well as elements from the lanthanide and actinide families.

In summary, each period of the periodic table corresponds to a complete electronic configuration around the atomic nucleus, with an increasing number of electrons in the valence shell as the period progresses ***(Table III-7-1) :***



Layer	Z	electronic structure	Number of element
1s	1,2	$1s^1$ et $1s^2$	2
2s2p	$3 \leq Z \leq 10$	$2s^{1-2}, 2p^{1-6}$	8
3s3p	$11 \leq Z \leq 18$	$3s^{1-2}, 3p^{1-6}$	8
4s3d4p	$19 \leq Z \leq 36$	$4s^{1-2}, 3d^{1-10}, 4p^{1-6}$	18
5s4d5p	$37 \leq Z \leq 54$	$5s^{1-2}, 4d^{1-10}, 5p^{1-6}$	18
6s4f5d6p	$55 \leq Z \leq 86$	$6s^{1-2}, 4f^{1-14}, 4d^{1-10}, 6p^{1-6}$	32
7s5f	$87 \leq Z \leq 103$		

Table III-7-1: The electronic distribution of the elements in the periodic table

The 6th period comprises 32 elements, including the lanthanides corresponding to the filling of the 4f sublayer***:*** $58 \leq Z \leq 71$; [Xe] $6s^2$ $4f^{2-14}$ $5d^0$.

The 7th period is incomplete. It begins with the filling of the 7s sublayer (Fr, Ra). This is followed by the actinide series ($Z \geq 90$), corresponding to the filling of sublayer 5f. Most of these elements are radioactive. Uranium (Z=92) is the heaviest natural element. Artificially heavier elements have been obtained, up to Z=103.

III-7-4- Periodic table analysis

II-7-4-1-Group blocks

The periodic table is made up of 4 blocks: s, p, d and f. These blocks correspond respectively to the filling of the sub-layers s, p, d and f. In the center of the periodic table appears the d block, which forms the 3 series of transition elements. On the right of the periodic table is the p block, on the left the s block. The f block contains the lantanides and actinides (Table III-8-2):

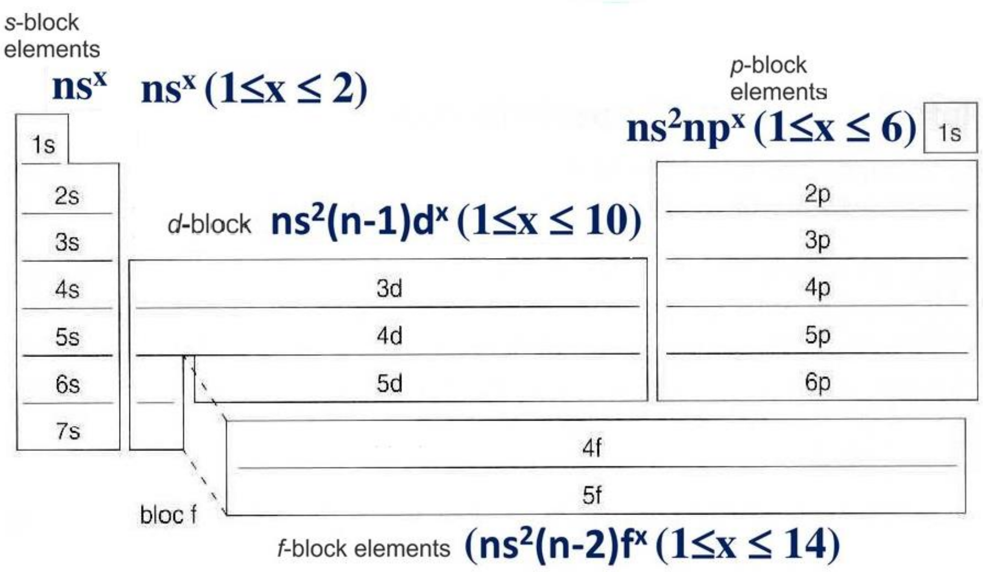


Table III-7-2: Blocks s, p, d and f in the periodic table

III-7-4-2-Description of columns (chemical groups)

Elements in the same column with the same electronic configuration of the outer layer form a family or group. The periodic table is made up of 18 columns or groups.

The columns are divided into 8 groups, which are grouped into 8 subgroups A and 8 subgroup B.

III-7-4-2-1-Subgroup A

The elements of subgroup A contain whose outer layer the configuration:

$ns1$ or $ns2$ for block S and $ns2\ npx\ 1 \leq x \leq 6$ for block p. these are summarized in the following table **(Table III-8-3)**

Subgroup	I_{A}	II_{A}	III_{A}	IV_{A}	$VIII_{\text{A}}$
Electronic configuration external	ns^1	ns^2	$ns^2np^1 \ldots$ ..	ns^2np^2 ….	ns^2np^6
Number of valence electrons	1	2	3	4	8

Example	$_3$Li [He] $2s^2$	$_{12}$Mg [Ne] $3s^2$	$_{13}$Al [Ne] $3s^2p^1$	$_6$C He] $2s^2$ P^6	$_9$Ne [He] $2s^2$ P^6

Table III-8-3: The A subgroups of the periodic table

In summary; The s block: It contains the elements of the first column $ns1$ which corresponds to the IA group, these elements are monovalent called the alkalines and the second column $ns2$ which corresponds to the IIA group these elements are divalent called the alkaline earths.

The p block: It contains the elements, $ns2$ $np1$ which belongs to the trivalent groups, $ns2$ $np2$, $ns2$ $np3$, $ns2$ $np4$ which group together the metalloid elements ($groupes$: $\boldsymbol{IVA}$**,** $\boldsymbol{VA}$**,** $\boldsymbol{VI}$**A**) , $ns2$ $np5$ which represent the halogens (group: VIIA) and rare gases of saturated external electronic configuration $ns2np6$ of the $\boldsymbol{VIII}$**A** group.

III-7-4- 2-2-Subgroup B

The d-block elements whose d-sublayer is incompletely filled are the transition metals: (n - 1) dx nsy with: $0 \leq 0 \leq x \leq 10$, $y \leq 2$

These are the elements of block d (columns 3, 4, 5, 6, 7, 11,12, and triads 8, 9,10). These elements differ in their structure only in the filling of their d sublayer.

Their electronic configuration ends with (n - 1) dx nsy with: $0 \leq 0 \leq x \leq 10$, $y \leq 2$

They are good electronic conductors with the existence of multiple oxidation states. Ionization of transition elements occurs through the departure of electrons from the s then d layer. these are summarized in the following table (Table III-8-4)

subgroups	IB	IIB	$IIIB$	$VIIB$	$VIIIB$
External electronics configuration	$(n-1)d^{10}$ ns^1	$(n-1)d^{10}$ ns^2	$(n-1)d^1$ ns^2	$(n-1)d^5$ ns^2	$3d^64s^2$ $3d^74s^2$ $3d^84s^2$
Numbers of valence electrons	1	2	3	7	8
Example	$_{29}$Cu : $[Ar]3d^{10}$ $4s^1$	$_{49}$Cd: $[Ar]3d^{10}$ $4s^2$	$_{21}$Sc $[Ar]3d^1$ $4s^2$	$_{25}$Mn $[Ar]3d^5$ $4s^2$	$_{26}$Fe $[Ar]3d^5$ $4s^2$

Table III-8-4: The B subgroups of the periodic table

Block d:

The first series of elements with d sublayers corresponds to the period of n=4. Filling of the 3d sublayer begins when the 4s sublayer is saturated at $4s2$. There are three series of transition elements $3dx$, $4dx$, $5dx$ with $0 \leq x \leq 10$

Block f: This corresponds to the Lanthanides and Actinides, known as rare earths. When the 6s orbital is completely filled, the 4f orbitals appear, which fill before 5d according to Klechkowski's rule.

Note:

Triad family: These elements make up Group VIII. There are three types of triad:

- Iron triad (Fe, Co, Ni).

- Palladium triad (Ru, Rh, Pd).

- Platinum triad (Os, Ir, Pt).

III-7-4-3- Family of groups

The group family of the periodic table refers to the vertical columns of the periodic table. Each column is a group and is numbered from 1 to 18. Elements in a group have similar chemical properties due to their similar electronic configuration.

Groups are generally divided into two categories: metals and non-metals. Groups 1, 2 and 13 to 18 are the metal groups, while groups 14 to 17 are the non-metal groups.

Here is a brief description of each group family in the periodic table:

- ***Group 1*** **(**or alkali metal family): contains the elements lithium, sodium, potassium, rubidium, cesium and francium. These elements have an electronic valence of +1, are highly reactive and react easily with water.
- ***Group 2*** (or alkaline earth metal family): contains the elements beryllium, magnesium, calcium, strontium, barium and radium. These elements have an electronic valence of +2, are equally reactive but less so than alkali metals, and are often used in construction and alloy production.
- ***Group 3*** (or scandium family): contains the element scandium and the rare earth elements (lanthanides and actinides). These elements have properties similar to scandium.
- ***Group 4*** (or titanium family): contains the element titanium and the elements zirconium and hafnium. These elements are transition metals and are often used in the aerospace and defense industries.

Group 5 (***or vanadium family***): contains the element vanadium and the elements niobium and tantalum. These elements are also transition metals and are often used in the alloy industry.

- ***Group 6*** (***or chromium family***): contains the element chromium and the elements molybdenum and tungsten. These elements are transition metals and are also used in the alloy industry.

- ***Group 7*** (***or manganese family***): contains the element manganese and the elements technetium and rhenium. These elements are transition metals and are used in the nuclear and aerospace industries.

- ***Group 8*** (***or iron family***): contains the element iron and the elements ruthenium, rhodium, palladium, osmium, iridium and platinum. These elements are transition metals and are often used in the alloy and jewelry industries.

- ***Group 9*** (***or cobalt family***): contains the element cobalt and the elements rhenium and iridium. These elements are transition metals and are used in the alloy, chemical and electronics industries.

- ***Group 10*** (***or nickel family***): contains the element nickel and the elements palladium and platinum. These elements are transition metals and are often used in the alloy and jewelry industries.

- ***Group 11*** (***or copper family***): contains the element copper and the elements silver and gold. These elements are transition metals and are often used in the jewelry industry.

- ***Group 12*** (***or zinc family***): contains the element zinc and the elements cadmium and mercury. These elements are metals and are used in the galvanizing and chemical industries.

- ***Group 13*** (***or aluminum family***): contains the element aluminum and the elements gallium, indium and thallium. These elements have an electronic valence of +3 and are often used in the semiconductor industry.

- ***Group 14*** (***or carbon family***): contains the element carbon and the elements silicon, germanium, tin and lead. These elements have an electronic valence of +4 and are often used in the semiconductor and construction industries.

- ***Group 15*** (***or nitrogen family***): contains the element nitrogen and the elements phosphorus, arsenic, antimony and bismuth. These elements have an electronic valence of +5 and are widely used in the fertilizer and chemical industries.

- ***Group 16*** (***or oxygen family***): contains the element oxygen and the elements sulfur, selenium, tellurium and polonium. These elements have an electronic valence of -2 and are widely used in the chemical and battery industries.

- ***Group 17*** (***or halogen family***): contains the elements fluorine, chlorine, bromine, iodine and astatine. These elements have an electronic valence of -1 and are often used in the chemical and battery industries. chimique et pharmaceutique.

- Group 18 (***or noble gas family***): contains the elements helium, neon, argon, krypton, xenon and radon. These elements have a stable electronic configuration and are often used in the lamp and laser industries.

Each group has unique properties and uses, making them important in many areas of industry and science.

III-8- Periodic evolution of some properties

The chemical properties of atoms depend essentially on the atom's outermost electrons, known as valence electrons. The valence sublayer of an atom is:

The one with the largest principal quantum number. Eventually, the one that is partially filled. For example, transition metals with properties intermediate between s-block and p-block form cations in several oxidation states. Examples: Cu+ and Cu2+, Fe2+ and Fe3+.

III-8-1- Atomic radius (covalent radius rc)

The radius of an atom can be defined as the distance between the nucleus and the last electron in the valence shell. (Figure III-8-1).

III-8-2- Ionic Radius

The ionic radius characterizes, like any radius, the volume occupied by the electrons in the electron cloud, except that for ions, the number of electrons differs from the neutral form, which explains two inverse phenomena: for cations, this radius will be smaller the greater the positive charge (with fewer electrons), and will be smaller than the atomic radius of the atom. Conversely, for anions (negatively charged, with more electrons), the ionic radius will be greater than the atomic radius, and the greater the charge, the greater the ionic radius.

In short, the atomic radius is expressed in picometers. The measurement of the atomic radius is based on experience. The atomic radius of an atom is equal to the half-distance separating the two nuclei of a homonuclear diatomic molecule linked by a simple covalent bond.

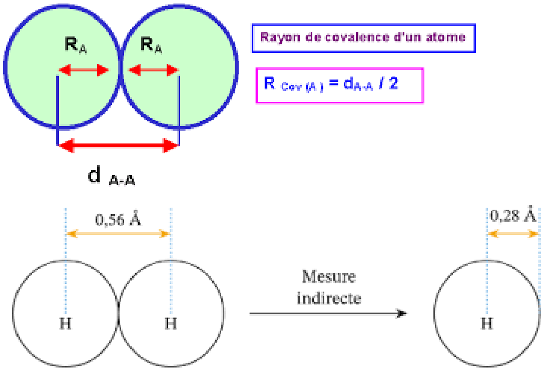


__Figure III-8-1: Atomic radius__

The calculation of the radius in the Slater approximation is given by the following formula:

III-8-3- Ionization energy (IE)

Ionization energy (IE) is the minimum energy required to remove an electron from a neutral atom or ion in the gas phase. This energy is usually expressed in electron volts (eV) or joules (J). IE can be used to determine the chemical and physical properties of elements and compounds. For example, a low EI may indicate that the atom is more reactive, as it is easier to remove an electron.

For the first ionization energy of an X atom, also known as its ionization potential, we start with the neutral X atom.

X(g) + IE (1) ……….. X^+ (g) + 1e- **1^{ere} ionization**
X^+ (g) + IE (2) ……….. X^{+2} (g) + 1e- **2^{eme} ionization**
X^+ (g) + IE (n) ……….. X^{+n} (g) + 1e- **n^{eme} ionization**

Avec: $E_{I1} < E_{I2} < E_{I3}$

The ionization potential **PI** is a quantity related to the voltage required for this removal, i.e. the measurement in eV of the ionization energy. It evolves in the same direction as **IE**.

We know from Bohr that

$$\boldsymbol{E_T = E_H \left(\frac{Z^2}{n^2}\right) = -13{,}6 \left(\frac{Z^2}{n^2}\right)}$$

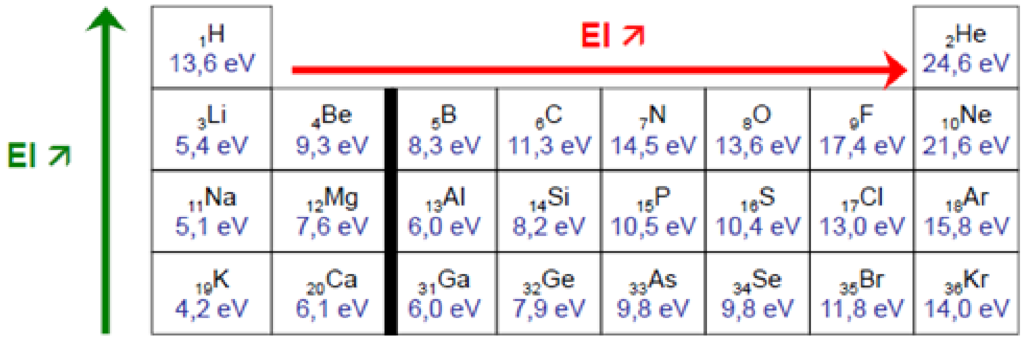
$$\textbf{IE= E(X}^+\textbf{) - E(X) = } \left[-13{,}6\left(\frac{Z_{eff}\,(X^+)^2}{n^2(X^+)}\right)\right] - \left[-13{,}6\left(\frac{Z_{eff}\,(X)^2}{n^2(X)}\right)\right]$$

It is therefore sufficient to calculate the Z eff of the atom and its cation to obtain the ionization energy.

In summary, only elements with low ionization energies, such as those in the s, d and f blocks, as well as the lower left-hand part of the p block, can form metallic solids, as they tend to lose their electrons easily. Elements in the upper right-hand part of the periodic table have high ionization energies, which means they do not lose their electrons easily and are therefore not metals.

The second ionization energy, which is the energy required to remove a second electron from the positive ion formed after the first ionization, is generally higher than the first ionization energy for the same element. This energy is much higher if the electron has to be removed from a complete layer.

Within the same period of the periodic table, ionization energy increases from left to right, as the effective charge of the nucleus increases. This means that electrons are more tightly bound to the nucleus and more difficult to remove as you move to the right in the period. **(Figure III-8-4) :**



$_1$H 13,6 eV							$_2$He 24,6 eV
$_3$Li 5,4 eV	$_4$Be 9,3 eV	$_5$B 8,3 eV	$_6$C 11,3 eV	$_7$N 14,5 eV	$_8$O 13,6 eV	$_9$F 17,4 eV	$_{10}$Ne 21,6 eV
$_{11}$Na 5,1 eV	$_{12}$Mg 7,6 eV	$_{13}$Al 6,0 eV	$_{14}$Si 8,2 eV	$_{15}$P 10,5 eV	$_{16}$S 10,4 eV	$_{17}$Cl 13,0 eV	$_{18}$Ar 15,8 eV
$_{19}$K 4,2 eV	$_{20}$Ca 6,1 eV	$_{31}$Ga 6,0 eV	$_{32}$Ge 7,9 eV	$_{33}$As 9,8 eV	$_{34}$Se 9,8 eV	$_{35}$Br 11,8 eV	$_{36}$Kr 14,0 eV

III-8-4 : The evolution of the ionization energy EI(in eV) in the periodic table

Example :

$_3$Li : $1s^2\,2s^1$; E_I = 520 Kj/mol

$_9$F: $1s^2 2s^1\,2p^5$; E_I = 1681 Kj/mol

In the same column, the effective charge increases from top to bottom, and the ionization energy decreases.

$_3$Li : $1s^2\,2s^1$; E_I = 520 Kj/mol = 5,4eV

$_{37}$Rb : $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}$ ……..$6p^6\,6s^1$; E_I = 402 Kj/mol = 4,2eV

III-8- 4-Electronic affinity (E.A.) :

When a gaseous atom captures an electron to form an anion, the energy released is called the electron binding energy **(E.A.) 0**It is expressed in Kj/mol. The greater the electron affinity, the more energy is released when an atom captures an electron, and the more stable it is. This energy can be positive or negative.

$X_{(g)}$+ 1e- …………$X^-_{(g)}$ + A.E

Examples :

O(g) +1e- ………………$O^-_{(g)}$ $1^{ére}$ electronic affinity AE(1)= -142Kj/mol

O-(g) +1e- ………………$O^{2-}_{(g)}$ 2^{eme} electronic affinity AE(2)= +744 Kj/mol

Similarly, calculating affinity is like calculating Z_{eff}

$$\mathbf{EI= E(X) - E(X^-) =} \left[-13{,}6\left(\frac{Z_{eff}(X)^2}{n^2(X)}\right)\right] - \left[-13{,}6\left(\frac{Z_{eff}(X^-)^2}{n^2(X^-)}\right)\right]$$

It's difficult to draw generalized periodic trends for electron affinity, as there are many irregularities. However, electron affinity is generally greater in absolute terms for smaller atoms, as the electrons are closer to the nucleus and therefore the attraction to it is stronger.

In general, it's harder to remove an electron from an atom than it is to acquire one, so electron affinity values are generally greater in absolute terms than the corresponding ionization energies.

III-8-5- Electronegativity (E.N) :

Electronegativity (E.N) is a measure of an atom's ability to attract electrons to itself when forming a chemical bond with another atom. This property is often used to predict the polarity of chemical bonds and the reactivity of molecules.

In general, elements in the upper right-hand part of the periodic table have a higher electronegativity, as they have a higher effective nuclear charge and an electron distribution closer to the nearest noble gas. Elements on the lower left of the periodic table have a lower electronegativity, as they have a lower effective nuclear charge and an electronic distribution further away from the noble gases. Electronegativity is an important property for understanding chemical bonds and the properties of molecules. Bonds between atoms with a large difference in electronegativity are often polar, while bonds between atoms with similar electronegativity values are often non-polar.

Note

Electronegativity (EN) measures an element's ability to attract electrons within a bond, resulting in partial charges ð- and ð+: $A^{\delta+} \rightarrow B^{\delta-}$; B is more electronegative.

Electronegativity is not defined for an isolated atom, as it corresponds to the tendency of a bonded (non-isolated) atom to attract electrons from other atoms in the molecule or ion in which it is involved. There are several definitions of electronegativity (Mulliken, Pauling, Allred and Rochow), which have led to the construction of several scales.

III-8-5-1- Mulliken's scale

The Mulliken scale is a method for measuring the electronegativity of an atom. It was proposed by the American chemist Robert Mulliken in 1934. The scale is based on the values of an atom's ionization energy and electron affinity. Electronegativity χ is then defined as the product of the average of these two quantities with an alpha coefficient of 0.317eV-1. The higher an atom's electronegativity, the more electrons it tends to attract when forming chemical bonds with other atoms.

According to the MILLIKAN scale, electronegativity is calculated by the following formula:

$$\chi_M = K\left(\frac{AE+EI}{2}\right) = 0,317\left(\frac{AE+EI}{2}\right)$$ avec: K = 0,317 ; (A_E et E_I) en eV

Example : alculate the electronegativity of fluorine F :

Data: AE and EI of the fluorine atom are respectively: 3.40 eV and 17.40 eV

$$\chi_F = K\left(\frac{AE+EI}{2}\right) = 0{,}317\left(\frac{3.40+17.40}{2}\right) = 3.3\ eV$$

III-8-5-2- PAULING's scale

This scale uses single bond energy values to determine the difference in electronegativity between two atoms. In a molecule of type AB, the binding energy EAB is not equal to the average of the binding energies of molecules EA-A and EB-B respectively. This difference is attributed to the difference in electronegativity between atoms A and B. This difference in electronegativity is determined by the formula:

$$\left[\Delta\chi_{AB} = 0.317\left(E_{AB} - (E_{AA} * E_{BB})\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}$$

The coefficient 0.102 comes from the unit used for energy values (initially in eV) which, in this formula, must be expressed in kJ. mol-1.This definition only gives the difference between two electronegativities. We therefore need an origin that has been arbitrarily fixed by giving the value of 4 to the electronegativity of fluorine (the most electronegative element in the classification): $\chi_F = 4$

Note:

The advantage of the Mulliken scale over Pauling's is that it uses atomic quantities, independent of the chemical environment. This makes it possible to determine the electronegativity of noble gases, which Pauling was unable to do.

III-9 -5- 3- The ALLRED-ROCHOW scale

This scale is based on the effective attraction of the atom's peripheral electrons. It uses the effective charges Zeff of the outer layer.

Electronegativity using the d'ALLRED-ROCHOW scale is calculated by the following law:

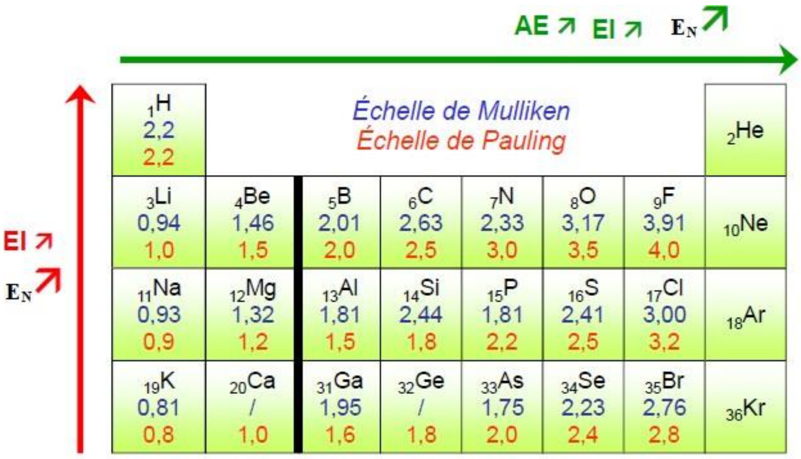
$$\chi = \frac{(Z_{eff})}{r_{cov}^2}\, e^2 \quad \textbf{With;}$$

Z_{eff} is the effective charge of the nucleus.

r_{cov} is the atom's covalent radius expressed in Angström (A°).

(e) the elementary charge.

In summary, electronegativity increases from left to right in a row of the periodic table, while electronegativity decreases from top to bottom in the same column **(Figure III-8-4).**



$_{1}$H 2,2 2,2	Échelle de Mulliken Échelle de Pauling						$_{2}$He
$_{3}$Li 0,94 1,0	$_{4}$Be 1,46 1,5	$_{5}$B 2,01 2,0	$_{6}$C 2,63 2,5	$_{7}$N 2,33 3,0	$_{8}$O 3,17 3,5	$_{9}$F 3,91 4,0	$_{10}$Ne
$_{11}$Na 0,93 0,9	$_{12}$Mg 1,32 1,2	$_{13}$Al 1,81 1,5	$_{14}$Si 2,44 1,8	$_{15}$P 1,81 2,2	$_{16}$S 2,41 2,5	$_{17}$Cl 3,00 3,2	$_{18}$Ar
$_{19}$K 0,81 0,8	$_{20}$Ca / 1,0	$_{31}$Ga 1,95 1,6	$_{32}$Ge / 1,8	$_{33}$As 1,75 2,0	$_{34}$Se 2,23 2,4	$_{35}$Br 2,76 2,8	$_{36}$Kr

Figure III-8-5: The evolution of EN, AE and EI in the periodic table

III-9- Calculation of polyelectron energies using the Slater rule

III-9- 1- General information on Slater's method

Bohr's model cannot be used for atoms other than hydrogenoids, i.e. atoms with a single electron, due to inter-electronic repulsion. To overcome this limitation, various methods have been developed. We present here the method proposed by J.S. Slater in 1930.

In this method, the effective charge is calculated on the assumption that the complex electrostatic interactions in an atom can be simplified to a small number of simple interactions.

The attraction between the Z protons in the nucleus and any E electron in the atom is taken into account. However, this attraction is disturbed by the other electrons between the nucleus and the electron E, which form a screen.

A shielding constant is therefore introduced, which depends on the position of the electrons relative to electron E. The charge Z of the atom's nucleus is thus replaced by an effective charge Z* relative to the electron E:

Bohr's model gives the expression for the radius of allowed orbits for atoms:

$$E = a_0 \frac{n^2}{Z} \quad ; a_0 = 0{,}53 \text{ A}^0$$

For polyelectronic atoms, we use the effective value of Z, denoted Z*, and assume that the radius of the atom is proportional to the Bohr orbit corresponding to the valence shell of the atom in question.

$$E = a_0 \frac{n^2}{Z^*}$$

The total energy of the atom will simply be evaluated by the sum of the following energies of all its individual electrons.

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

With , $Z^* = Z - \sum \delta_i$ = Z - S **où** δ is called the screen constant.

III-9-2- Calculated of The effective nuclear charge

To calculate the effective charge, follow these steps:

* Write the electronic configuration of the element and order it according to :

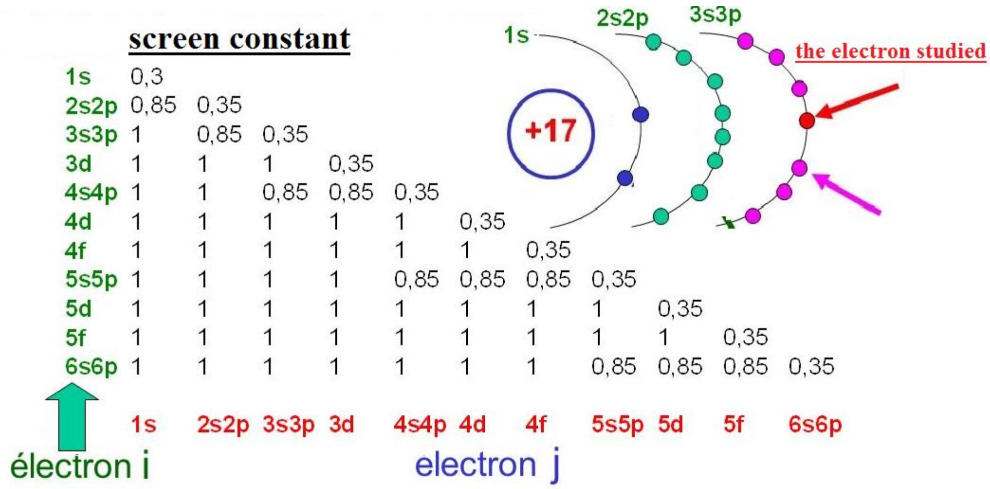
(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) (5d) (5f)...

- ➢ Choose the electron for which you want to find the effective charge.
- ➢ All other electrons make a partial contribution δ_i to total screen constant $\delta = \sum \delta_i$.

This contribution depends :

- the type of orbital (s, p), (d) or (f) of the electron

- ➢ the electron's electronic layer n.
- ➢ The value of δ_i is summarized in the following table **(III-10-1)**



screen constant

électron i \ electron j	1s	2s2p	3s3p	3d	4s4p	4d	4f	5s5p	5d	5f	6s6p
1s	0,3										
2s2p	0,85	0,35									
3s3p	1	0,85	0,35								
3d	1	1	1	0,35							
4s4p	1	1	0,85	0,85	0,35						
4d	1	1	1	1	1	0,35					
4f	1	1	1	1	1	1	0,35				
5s5p	1	1	1	1	0,85	0,85	0,85	0,35			
5d	1	1	1	1	1	1	1	1	0,35		
5f	1	1	1	1	1	1	1	1	1	0,35	
6s6p	1	1	1	1	1	1	1	0,85	0,85	0,85	0,35

Table III-9-1: Screen constants for n layers and sublayers(s, p ,d, f)

,

III-9-2-1- Examples of calculated of The effective nuclear charge

L'azote $_7$**N** has the following electronic configuration: 1s2 $2s^2\ 2p^3$.

This can be written as $(1s)^2\ (2s, 2p)^5$ (by Group).

An electron on the outer layer (2s, 2p) therefore has the following screen electrons:

4 electrons (s, p) of layer **n** : δ_i= **0,35,**

2 electrons s of layer **n**-1 : δ_i= **0,85.**

Electron origenal	Contribution from other electrons					
	n-2	n-1	n			n+1, n+2
			s, p	d	f	0
s, p	1	0,85	0,35	0	0	0
d	1	1	1	0,35	0	0
f	1	1	1	1	0,35	0

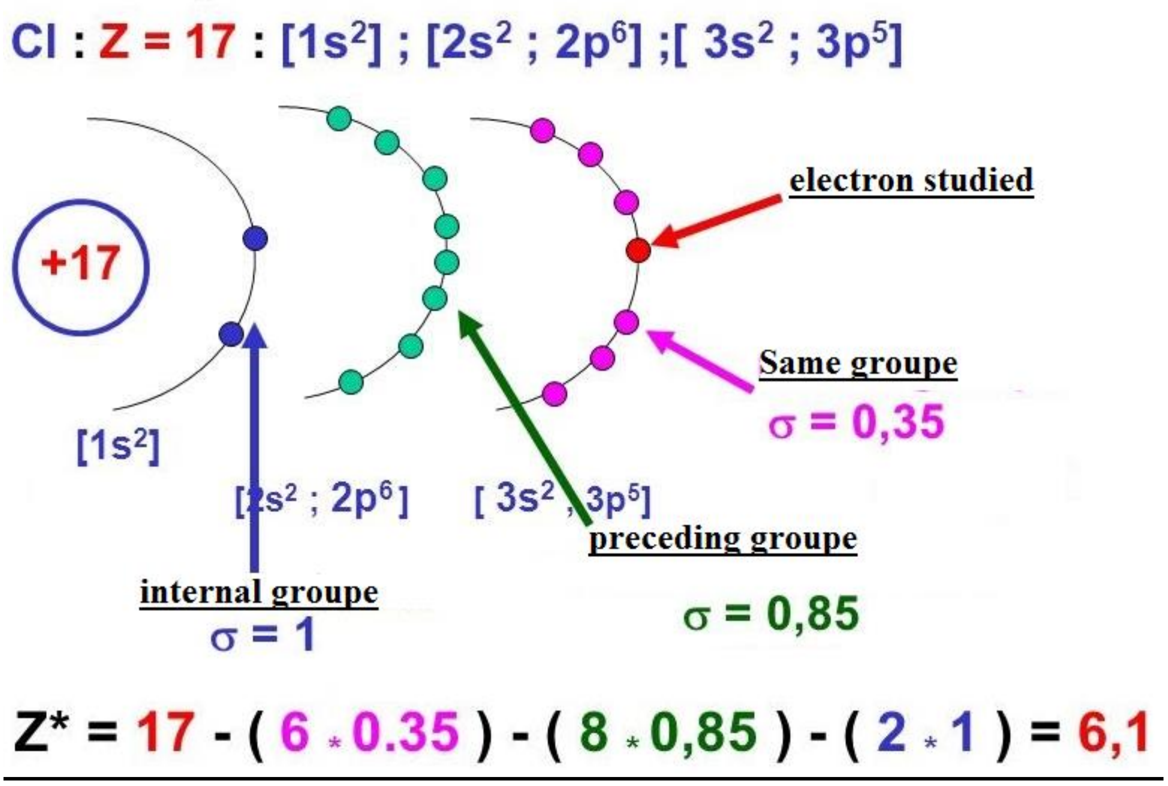
We deduce : $\boldsymbol{\delta}$ = (2 x 0,85) + (4 x 0,35) = 3,10

So the charge effective : $\boldsymbol{Z^* = Z - \delta = 7 - 3,10 = 3,9}$

Chlore $_{17}$Cl: Charge effective of electron 3s du zinc

The configuration du $_{17}$Cl est : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ which we rewrite as:

$$\mathbf{(1s)^{2}\ (2s, 2p)^{8}\ (3s, 3p)^{7}\ .}$$



Zinc $_{30}$Zn: Charge effective of electron 4s du zinc

The configuration du $_{30}$Zn est : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$ which we rewrite as:

$$\mathbf{(1s)^{2}\ (2s, 2p)^{8}\ (3s, 3p)^{8}\ (3d)^{10}\ (4s)^{2}.}$$

For the electron 4s, the screen is:

1 electron s for layer n : $\boldsymbol{\delta_i}$= 0,35,

10 electrons d of layer n-1 : δ_i= 0,85,

8 electrons (s, p) of layer n-1 : δ_i= 0,85,

8 electrons (s, p) of layer n-2 : δ_i= 1,

2 electrons s of layer n-3 : δ_i = 1.

We calculate : δ = (1 x 0,35) + (18 x 0,85) + (10 x 1) = 25,65

Sothe charge effective : $Z^* = Z - \delta = 30 - 25{,}65 = 4{,}35$

Zinc $_{30}$Zn: Charge effective for the electron 3d du zinc

the configuration du $_{30}$Zn est : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$ which we rewrite as

$$\mathbf{(1s)^{2}\ (2s, 2p)^{8}\ (3s, 3p)^{8}\ (3d)^{10}\ (4s)^{2}.}$$

For trhe electron 3d, the screen is::

2 electron s for layer n+1: δ_i= 0,

9 electrons d for layer n: δ_i= 0,35,

8 electrons (s, p) for layer n-1: δ_i= 1,

8 electrons (s, p) for layer n-2: δ_i= 1,

2 electrons s for layer n-3: δ_i = 1.

We calculate: δ = (9 x 0,35) + (18 x 1) = 21,15

So the charge effective: $Z^* = Z - \delta = 30 - 21{,}15 = 8{,}85$

III-10-Application to the calculation of the energy of light polyelectronic atoms (non-hydrogenoids)

III-10-1Generalisations

For a hydrogenoid atom with atomic number Z, energy is calculated by;

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

For a non-hydrogenoid atom, each electron contributes an energy of:

$$E_i = -13{,}6\ \frac{{Z_i^*}^2}{{n_i}^2}$$

The total energy of the atom is the sum of the contribution of each electron.

$$E_T = \sum E_i$$

Application example lithium

The lithium $_3$**Li** a for configuration electro electronic $1s^2\ 2s^1$.

electron **2s** for chargeeffective : Z_2^* = 3 - (2 x 0,85) = 1,3

His energy is:

$\boldsymbol{E_i = -13{,}6\ \frac{{Z_i^*}^2}{{n_i}^2} = E_2 = -13{,}6\ \frac{(1{,}3)^2}{2^2}}$ **= -5,75 eV**

<u>One of the electrons **1s**</u> for the charge effective: $Z_1^* = 3 - (1 \times 0{,}30) = 2{,}7$

His energy is: : $\boldsymbol{E_i = -13{,}6\ \frac{{Z_i^*}^2}{{n_i}^2} = E_1 = -13{,}6\ \frac{(2{,}65)^2}{1^2}}$ **= - 99,14 eV**

The total energy is therefore:

$E_T = E_2 + 2\,E_1 = (-2{,}65) - 2 \times (99{,}14) = -\,200{,}94$ eV

III-10-2-Calculation of ionization energies

Ionization energy (IE) is the minimum energy required to remove an electron from a neutral atom or ion in the gas phase. This energy is generally expressed in electron volts (eV) or joules (J).Soit l'atome X qui va subir une première ionisation :

$X \rightarrow X^+ + e^-$

The ionization energy is given by : $E_{I_1} = (E_{X+}) - (E_X)$

The total energy of the atom will simply be evaluated by the sum of the individual energies of all its electrons.

Deducing the energy of first ionization In the reaction: Li → Li+ + e- it's the 2s electron that's ejected. The energy of first ionization E_{I1} is therefore equal to:

$E_{I_1} = (E\ \mathrm{Li}+) - (E_{\mathrm{Li}})$ **; avec** $E_{Li^+} = 2\,E_1$; $E_{Li} = E_2 + 2\,E_1$

$\Rightarrow E_{I_1} = (2\,E_1 - E_2 - 2\,E_1) = -\,E_2 = -(-5{,}75) =$ **+ 5,75eV**.

Introduction

Chemical bonds are the forces that hold atoms together in a molecule or compound. Atoms can form chemical bonds to achieve a stable electronic configuration, i.e. a state in which all valence electrons are optimally distributed between the different atoms. There are several types of chemical bond, including ionic, covalent and metallic bonds. Ionic bonds are formed between positive and negative ions, while covalent bonds are formed when atoms share electrons. Metallic bonds are formed between metal atoms that share valence electrons. The physical and chemical properties of compounds depend largely on the chemical bonds that hold them together. For example, ionic compounds have a rigid crystal structure and a high melting temperature, while covalent compounds tend to be softer and have a lower melting temperature. Understanding chemical bonds is essential to understanding the chemistry and structure of matter.

IV-1- Classical conception of atomic bonding

The classical conception of atomic bonding is based on the octet theory, which states that atoms tend to form chemical bonds to complete their outer electron layer and reach a stable electronic configuration (ns^2 np^6) of 8 outer electrons. This theory was proposed by Lewis and Kossel in the early 20th century. According to this theory, atoms can form covalent bonds by sharing electrons from their outer layer. In a covalent bond, atoms share one or more electrons to form a binding electron pair. These bonding electrons are represented by lines between the atoms in Lewis diagrams.Atoms can also form ionic bonds by transferring electrons from their outer layer. In an ionic bond, one atom gives up electrons to form a positive ion, while another atom accepts these electrons to form a negative ion. Electrostatic forces between the positive and negative ions hold the atoms together in a crystal lattice.

The classical view of atomic bonding can explain many chemical properties of compounds, such as their reactivity and molecular geometry. However, it cannot explain all properties, especially those of complex molecules involving more subtle electronic interactions. More advanced theories of chemical bonding, such as molecular orbital theory, have been developed to explain these more complex properties.

IV-1-1- Valence layer

The valence shell is the outermost electron shell of an atom, containing electrons that are active in chemical reactions. Valence electrons are the electrons located in this valence layer, and they play a crucial role in the formation of chemical bonds between atoms.

The atoms in the s or p block the elements that end in $nsx\ npy$, with $0 \leq x \leq 2$ and

$0 \leq y \leq 6$, the number of valence electrons is equal to : $\sum x + y$.

Example: 5B: $1s^2\ 2s^2\ 2p^1 \Rightarrow$ that 5B has a valence layer: $2s^2\ 2p^1 \Rightarrow$ valence electrons = 2+1=3. Valence electrons are the electrons characterized by the largest n-layer values if (n-1) d^y is not filled (y < 10) d-layer electrons will be considered.

<u>Example:</u> Manganese 25Mn [Ar] $3d^5 4s^2 \Rightarrow$ number of valence electrons: 5+2= 7.

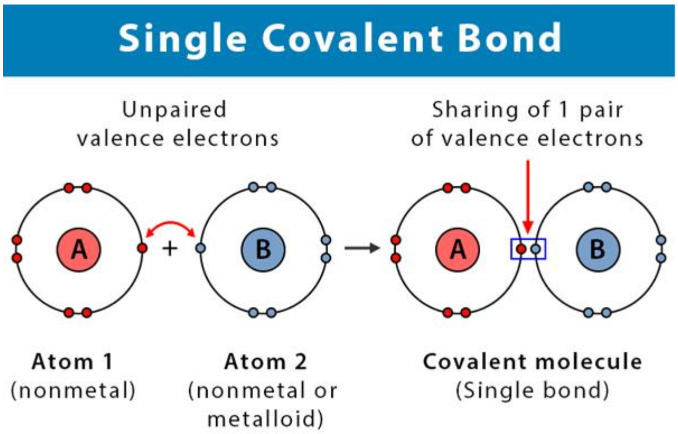
IV-2- The different types Chemical bonds

The valence electrons of atoms are involved in all chemical bonds; however, they interact in different ways, leading to the formation of several types of bond. There are several types of chemical bond, including: The covalent bond, the dative bond, the ionic bond, the metallic bond........

IV-2-1- The covalent bond

Covalent bonding: this occurs when two atoms share valence electrons to form a stable molecule. In other words, the covalent bond between two non-metallic atoms A and B is the pooling of two electrons, with each atom providing a valence electron. **(Figure V-1)**

In this type of bond, there must be a difference in electronegativity of less than 1.7 on the Pauling scale.



<u>Figure V-1 : Single covalent bond</u>

<u>Exemple :</u>

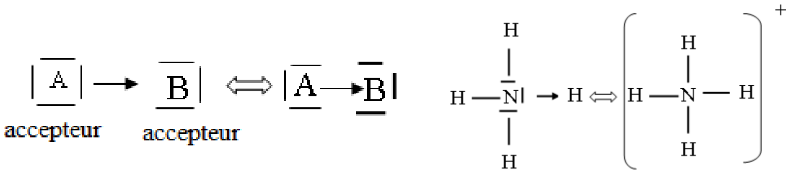
$_1$**H** : $1s^1$; $_1$H : $1s^1$: H• •H ⟶ H•–•H

$_8$O: $1s^2\,2s^2\,2p^4$ (valence layer of O : $2s^2 2p^4$)

IV-2-2- **The dative bond (Coordinate (Dative Covalent) Bonding)**

A dative bond, also known as a dating covalent bond or coordinative covalent bond, is a type of chemical bond in which the two shared electrons come from a single atom, rather than from the two atoms involved in the bond. In this type of bond, the atom providing the two electrons is called the donor (or ligand), while the atom receiving the two electrons is called the acceptor (or central ion). The dative bond is often represented by an arrow (→) pointing from the donor atom to the acceptor atom. Dative bonding is frequently observed in coordination complexes, where a central atom (the metal) is linked to several other atoms (the ligands) by dative bonds. It can also occur in other types of organic and inorganic molecules**.**

Exemple: NH_4^+



IV-2-3-The ionic bond

An ionic bond is a type of chemical bond formed between positive and negative ions. It results from electrostatic attraction between the opposite charges of the ions, which join to form an ionic compound. Positive ions (called cations) are atoms that have lost one or more valence electrons, while negative ions (called anions) are atoms that have gained one or more valence electrons.

Positive and negative ions are generally formed from metallic and non-metallic elements, respectively.

For example, sodium chloride (NaCl) is an ionic compound made up of positive sodium ions and negative chloride ions. In NaCl, each sodium atom donates a valence electron to each chloride atom, forming an ionic bond (Figure V-2).

Consider the NaCl crystal

$_{11}Na$:$1s^2\,2s^2\,2p^6\,3s^2 \Leftrightarrow [Ne]\ 3s^1$

$_{17}Cl$: $1s^2\,2s^2\,2p^6 3\,s^2\,3p^5 \Leftrightarrow [Ne]\ 3s^2 3p^5$

When Na and Cl are in the presence of each other, Na gives up its $3s^1$ electron, acquiring the electronic structure of argon

$Na \rightarrow Na^+ + 1e^-$ suivie de : $Cl + e^- \rightarrow Cl^-$

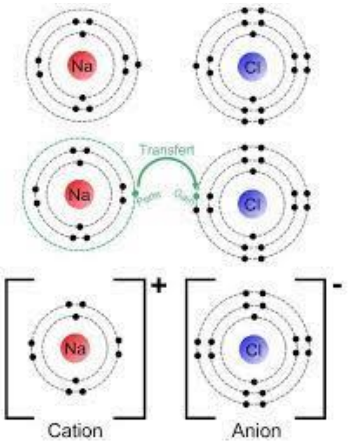


Figure V-2 The ionic bonding of sodium chloride (NaCl)

IV-2-4- The polar bond

A polar bond is a type of covalent bond in which the valence electrons are shared unequally between the two atoms forming the bond. This happens when one of the atoms has a greater electronegativity (ability to attract electrons) than the other. The more electronegative atom attracts valence electrons more strongly than the other atom, creating a partial charge shift across the bond. This means that the more electronegative atom has a negative partial charge and the less electronegative atom has a positive partial charge.

For example, in the HCl bond, chlorine is more electronegative than hydrogen. As a result, it attracts valence electrons more strongly than hydrogen, creating a negative partial charge on chlorine and a positive partial charge on hydrogen. This creates a polar bond.

Note

If an element A with electronegativity EN (A) and an element B with electronegativity EN (B). When these two elements are brought together, if EN (A)-EN (B) = 0, the A-B bond will be pure covalent.

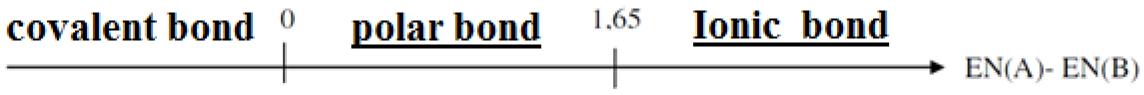
Cl_2 (EN (Cl) = 3, 16)

- ***If EN(A)- EN(B) < 1,65 the bond will be covalent with a certain ionic character or polar bonding***

Example HCl : EN(Cl) = 3,16 ; EN(H) = 2,1□ EN(Cl) - EN(H) = 1,06

- If EN(A)- EN(B) > 1,65 the bond will be ionic

In summary, these three links can be summarized as follows:



IV-2-5- Metallic bonding

Metal bonding is a type of chemical bonding that occurs between metal atoms. In a metallic bond, metal atoms share their valence electrons with neighboring atoms, creating a three-dimensional lattice structure.

In this structure, the valence electrons move freely through the lattice, creating a "sea" of electrons that surrounds the positive metal ions. This sea of electrons is what enables metals to conduct electricity and heat.

IV-2-6- Hydrogen bond

Hydrogen bonding is a type of weak chemical bond that occurs between a hydrogen atom and a more electronegative atom, such as oxygen, fluorine or nitrogen.

In a hydrogen bond, the hydrogen atom is partially positive due to the difference in electronegativity between the hydrogen and the more electronegative atom. The more electronegative atom has a partial negative charge, creating an electrostatic attraction between the two atoms. Although hydrogen bonds are weaker than covalent or ionic bonds, they can play an important role in the stability and structure of molecules..

IV-2-7- Van der Waals bonding

The van der Waals bond is a weak interaction between the molecules or atoms that occurs due to the attraction between opposite partial charges. This interaction is also known as the London dispersion force.

In a molecule, electrons are in constant motion, creating fluctuations in the distribution of electric charges. These fluctuations create temporary electric dipoles, which can interact with the temporary electric dipoles of other neighboring molecules. This weak interaction can create an attraction between molecules, creating a van der Waals bond. There are three types of van der Waals force: the dispersion force, the dipole-dipole force, and the hydrogen bonding force. Dispersion forces are the weakest and are present in all molecules, while dipole-dipole and hydrogen bonding forces are stronger and only occur in molecules with permanent dipoles or hydrogen bonds.

IV-3 LEWIS diagram

The Lewis diagram is a visual representation of an atom's valence electrons and how they are shared or transferred in a chemical bond. The diagram uses symbols to represent atoms and dots or lines to represent valence electrons.To construct a Lewis diagram, start by noting the symbol of the atom in the center, surrounded by the valence electrons represented by dots. The electrons are placed in pairs around the atom, respecting the octet rule, which stipulates that atoms tend to form bonds to reach a stable electronic configuration with 8 valence electrons in their outer layer (with the exception of hydrogen and helium, which have only two valence electrons).

Bonds between atoms are represented by shared electron pairs, which are represented by a line between the two atoms. Non-bonding electrons are represented by dots around the atom. The Lewis diagram is useful for understanding the molecular structure polarity and reactivity of chemical compounds. It can also help predict molecular geometry and the physical and chemical properties of molecules. In general, the Lewis representation schematizes the external electronic structure, also known as the valence layer.

- Paired electrons are represented by **dashes.** —
- Single electrons are represented by pointsb (dots). •
- The number of single electrons gives the atom's valency.

Example:

${}_{7}$N : $1s^2 2s^2 2p^3$: valence layer : $2s^2 2p^3$ 

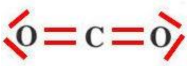
${}_{17}$Cl : $1s^2 2s^2 2p^6\ 3s^2 3p^5$: valence layer : $3s^2 3p^5$ 

IV-3-1-Lewis diagrams of molecules

When two atoms are bonded, each of them tends to have a saturated outer layer analogous to that of rare gases (ns^2np^6), so each atom has eight electrons, the octet rule.

Example : Carbon dioxide molecule (CO2) :

The carbon atom shares two pairs of electrons with each oxygen atom to form two double covalent bonds.



IV-3-2-The octet rule

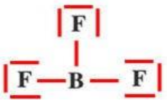
The octet rule is a rule of thumb in chemistry which states that most atoms tend to form chemical bonds in such a way as to have eight valence electrons in their outer layer, or two electrons for hydrogen and helium atoms. This outer layer is also known as the valence layer. When an atom has fewer than eight valence electrons, it can form chemical bonds with other atoms to complete its valence layer and achieve a more stable electronic configuration. Atoms can share electrons to form covalent bonding, or transfer electrons to form ionic bonding.The octet rule is useful for predicting the molecular geometry and properties of chemical compounds. For example, molecules that respect the octet rule have a more symmetrical geometry and are often more stable than molecules that do not. However, there are exceptions to the octet rule, notably for elements in the third period and beyond, such as sulfur, phosphorus, and chlorine, which can form chemical bonds by having more than eight valence electrons in their outer layer.

Note:

Many cases are exceptions to this rule, and are governed not by the octet rule but by the duet rule (This is a rule of thumb in chemistry that applies to atoms in the first period of the periodic table, i.e. hydrogen and helium. This rule stipulates that these atoms tend to form chemical bonds in such a way as to have two valence electrons in their outer layer, rather than eight electrons as for atoms in later periods).

$_1$H : $1s^1$, $_2$H : $1s^2$; $_5$B: $1s^2 2s^2 2p^1$

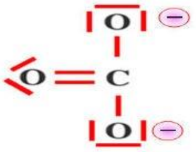
Example: BF_3



IV-4- LEWIS diagram for molecular ions

Lewis diagrams can also be used to represent molecular ions, which are molecules that carry an overall electrical charge.

The carbonate ion CO_3^{2-} :



IV-5- Dipole moment and partial ionic character of the bond

When a heteronuclear molecule AB is partially polarized, a portion of the electric charge (represented by the letter, with $\boldsymbol{\delta} < 1.6 \times 10^{-19}$) is transferred from the less electronegative element to the more electronegative element, which is schematically represented by.

$$A^{\delta-} \xrightarrow{\hspace{6cm}} B^{\delta+} \qquad EN(A) > EN(B)$$

The molecule then becomes an electric dipole, represented by a vector pointing from the negative charge to the positive charge, that is, from the more electronegative element to the less electronegative element. This dipole is characterized by its dipole moment (or electric moment) μAB, which depends on the distance between the two elements (l) and the transferred charge (ð), according to the relation: μAB = ð × l. The dipole moment is expressed in coulombs × meters (C·m) in the International System of Units (SI), but it can also be expressed in a more convenient unit, the Debye (D): *1 D* = 3.33 × 10^{-30} coulomb·meter. In the case of a 100% ionic bond, the dipole moment is equal to the elementary charge (e) multiplied by the internuclear distance (l): μAB = e × l. For a polyatomic molecule, the dipole moment is the geometric sum of the dipole moments of the different bonds in the molecule: $\mu = \sum \mu i$, where μi is the dipole moment of each bond.

Example: H_2O: $\mu_{H_20} = \mu_{0-H} + \mu_{0-H}$

For polar covalent bonds, the percentage of ionic character of the bond can be calculated using the following formula:

$$\% \boldsymbol{Ionic}\ (\boldsymbol{A-B}) = \mathbf{100}\ \frac{\boldsymbol{\mu_{A-B}}}{\boldsymbol{\mu_{A-B}}}\ \frac{(\boldsymbol{experimental})}{(\boldsymbol{theoretical})} = \mathbf{100}.\frac{\boldsymbol{\delta}}{\boldsymbol{e}}$$

With :

l : Longueur de la liaison A-B ; **e** : Charge de l'électron ; $\boldsymbol{\delta}$: Charge partielle

Example: either to calculate the ionic percentage of the O-H bond in the water molecule. We give:

l(O-H) = 0,98A°

HOH = 105°

μ_{H_20} = 1,84D

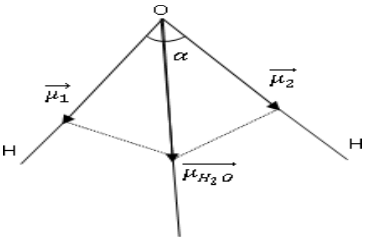


Figure IV-5--1 : Décomposition of the dipole moment H_2O

$$\overrightarrow{\mu H_20} = \overrightarrow{\mu_1} + \overrightarrow{\mu_2}\ , |\overrightarrow{\mu_1}| + |\overrightarrow{\mu_2}| = \mu H_20\ ,\ \mu H_20 = 2\,\mu_{0-H}\,.\cos\frac{\alpha}{2} \Rightarrow$$

$$\frac{\mu H_20}{2\ \cos\frac{\alpha}{2}} = \frac{1{,}84}{2\ \cos\frac{105°}{2}} = \mathbf{1,60}\ \boldsymbol{D}\ (\boldsymbol{exp}\text{é}\boldsymbol{rimental})$$

$$\mu_{0-}(100\%\ ionic) = \text{e}.\,l(O-H) = 1{,}910^{-19}.\,0{,}958.\,10^{-10} = 1{,}53610^{-29}\,Cb.m$$

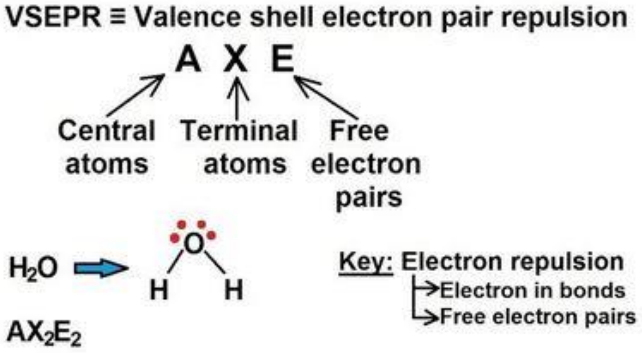
$$1\text{D} = 3{,}33\ x\ 10^{-30}Cb.m \Rightarrow {}_{(0-H)} = 4{,}598D$$

The ionic percentage of the bond O-H is : % $ionic$ (O-H) = $\frac{1{,}6}{4{,}598} = \mathbf{34,8}$ %

IV-6- Géométrie des molécules : théorie de Gillespie ou VSEPR

The Lewis representation of molecules allows for the determination of the arrangement of atoms and covalent bonds between them, but it does not predict the actual geometry of molecules. For this, it is necessary to use a theory that takes into account the repulsion between electron pairs around the central atom to predict the three-dimensional shape of the molecule. The VSEPR (Valence Shell Electron Pair Repulsion) theory is one of the most widely used theories in chemistry to predict the geometry of molecules. It is based on the idea that electron pairs around the central atom repel each other to minimize electron interactions and achieve the most stable electron configuration possible. Depending on the number of valence electron pairs around the central atom, the molecular geometry of the molecule can be predicted. Thus, the VSEPR theory allows for the prediction of the actual three-dimensional shape of molecules by considering the repulsion between electron pairs around the central atom. This helps to better understand the physical and chemical properties of molecules and their behavior during chemical reactions. The VSEPR method allows, after analyzing the Lewis structure, to predict the geometry of simple molecules or ions. It applies to molecules or ions of the type: **AX_nE_p,** where A denotes the central atom that is bonded to **X_n** atoms and has **p** lone pairs of electrons (or **p** non-bonding pairs). **(Figure V-6-1)**

<u>Note:</u> a double bond only counts as 1 bonding doublet



<u>Figure IV-6--1: VSPER representation of molecules</u>

IV-6- 1- Principle of the method

The geometry of a molecule or ion is determined by the total number of electron pairs (also called electron doublets) present in the valence shell of the central atom A. The electron pairs arrange themselves in a way that minimizes their mutual repulsions, meaning they maximize the distances between each other.

IV-6-2. Molecules of Type AX_n with Single Bonds

Molecules of type AXn with single bonds are molecules that have a central atom (A) bonded to n peripheral atoms (X) through single covalent bonds. The molecular geometry of these molecules depends on the number of valence electron pairs around the central atom and the repulsion between these electron pairs, according to the VSEPR theory.

In general, to apply the VSEPR method:

- Count the bonding pairs in the valence shell of the central atom using the Lewis structure.
- Deduce the geometry of the molecule or ion using the reference table. (See Table V-6-1 for examples.)

Example: Determine the geometry of the following molecules: BeCl2, BF3, CH4.

To apply the VSEPR method:

- Count the bonding pairs in the valence shell of the central atom using the Lewis structure.
- Deduce the geometry of the molecule or ion using the reference table.

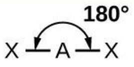
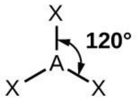
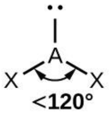
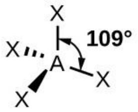
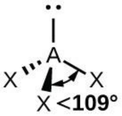
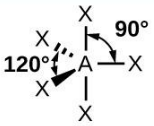
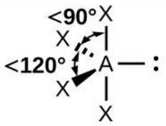
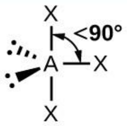
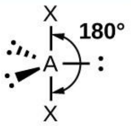
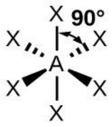
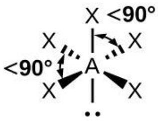
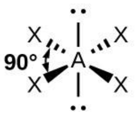
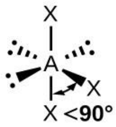
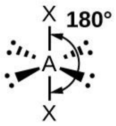
Explanation of Examples:

1. **BeCl2 (Beryllium Chloride):**

    - Central atom: Be (Beryllium)
    - Number of bonding pairs: 2 (Be forms 2 single bonds with Cl atoms)
    - Number of lone pairs: 0
    - **Geometry: Linear**

- ✓ **BF3 (Boron Trifluoride):**
    - Central atom: B (Boron)
    - Number of bonding pairs: 3 (B forms 3 single bonds with F atoms)
    - Number of lone pairs: 0
    - **Geometry: Trigonal planar**
- ✓ **CH4 (Methane):**
    - Central atom: C (Carbon)
    - Number of bonding pairs: 4 (C forms 4 single bonds with H atoms)
    - Number of lone pairs: 0
    - **Geometry ; Tetrahedral**

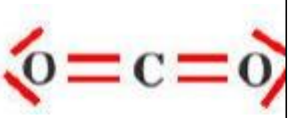
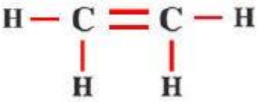
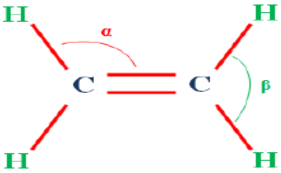
Table IV-6-1: Configuration of AXn-type molecules with single bonds

Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

IV-6- 3- AXn-type molecules with multiple bonds.

- ✓ The number of bonds surrounding the central atom is counted, with each multiple bond counting as a single bond.
- ➢ The geometry of the molecule or ion, conditioned by the minimum repulsion, is deduced. (Table V-6-2).
- ➢ A multiple bond is, however, more repulsive than a single bond.
- ➢ A triple bond is more repulsive than a double bond.
- ➢ The angles formed by double bonds are larger than those formed by single bonds.

Tableau IV-6-2: Exemples de molécules de type AX_n :

Example of moleculs	Diagram Lewis of molecule	Geometry of the molecule	Type of molecule
The carbon dioxide molecule CO_2		 Molécule linéaire	AX_2
The carbon dioxide molecule C_2H_4		 **α** = 117,4°, **β** = 121,3°, ℓ_{C-H} = 109 pm $\ell_{C=C}$ = 134 pm The angles are close to 120° for trigonal atoms.	AX_3

IV-6- 4- AXnEp-type molecules

- **VSEPR method. (Table V-6-3).**
- We count the total number of pairs of bound and free electrons surrounding the central atom without differentiating them.
- We deduce the geometry of the molecule or ion conditioned by the minimal repulsion.
- A pair of free electrons is more repulsive than a pair of bonded electrons.
- The angle between two lone pairs is greater than the angle between two bonding pairs.

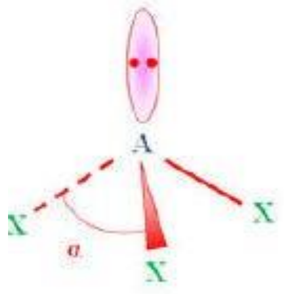
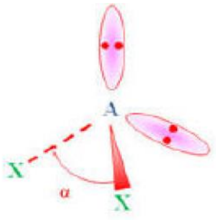
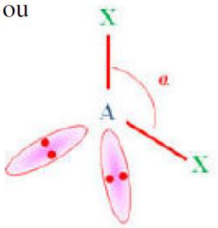
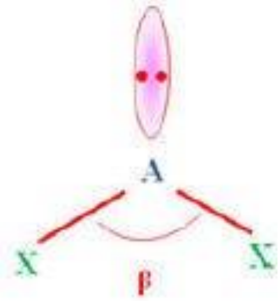
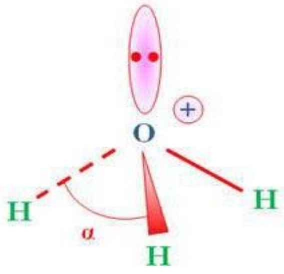
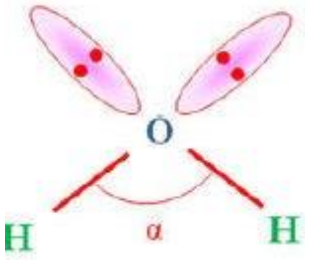
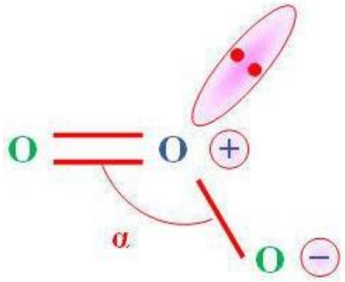
Low pairs p	1	2	3
Type of molecules	AX_3E_1	AX_2E_2	AX_2E_1
Geometry		 ou  ou	
Angle	α < 109,5°	α < 109,5°	β < 120°
Structure	Pyramidal trigonale	Angular or ongled	Structure angular
Example	 ion oxonium **H_3O^+** has a pyramidal structure with a triangular base **α** < 109,5° **α** ≈ 107,5°	 The water molecule H_2O Bent molecule **α** < 109,5°, **α** ≈ 104,5°	 The ozone molecule O_3 α ≈ 120°

***Tableau IV-3:* Configuration of AXnEp-type molecules**

IV-7- Chemical bonding in the quantum model

The chemical bond in the quantum model is one of the most important applications of quantum mechanics in chemistry. It helps us understand how atoms bond together to form molecules. According to the quantum model, atoms consist of a positively charged central nucleus and electrons orbiting around this nucleus. The electrons are described by quantum wave functions, which are solutions to the Schrödinger equation. These wave functions describe the probability of finding an electron at a given location in space. When two atoms come close to each other, their electrons occupy overlapping regions, where the wave functions of the electrons from both atoms overlap. This overlap leads to the formation of molecular orbitals, which are quantum wave functions that describe the probability of finding the electrons within the molecule. The chemical bond is then the result of the stabilization of these molecular orbitals, which have a lower energy than the sum of the energies of the individual atomic orbitals. This stabilization occurs due to a redistribution of electrons in the molecular orbitals, leading to a decrease in the total energy of the system. Thus, the quantum model allows us to understand how atoms bond together to form molecules and how the chemical properties of molecules are determined by the structure of their molecular orbitals.

IV-7-1- Principle

The valence bond theory (VB) explains that when a covalent bond forms between two atoms A and B, only the shared electrons lose their individual character and localize between the two atoms, while the atomic orbitals of the non-bonding electrons remain unchanged. This method examines each bonding pair independently from the rest of the molecule. If A and B each share an electron (1) and (2) respectively, before the bond formation, each electron is described by a distinct wave function, namely $\psi(1)$ for electron (1) and $\psi(2)$ for electron (2), corresponding to two probability domains of presence, namely OA(1) and OA(2). In the bonded molecule AB, electrons (1) and (2) cannot be distinguished and belong to both A and B. They are described by a single wave function, ψAB, which can be expressed as follows: $\boldsymbol{\psi_{AB} = c_1\psi_A(1)\,\psi_B(2) + c_2\psi_A(2)\,\psi_B(1)}$. This single wave function corresponds to a probability domain of presence of the bonding electrons resulting from the interpenetration or overlap of the atomic orbitals OA(1) and OA(2), called a molecular orbital (MO).

IV-7-2- Formation and nature of bonds

Bond formation requires the signs of the ψ wave function to be identical on the overlapping orbitals. Overlap occurs in the direction where the orbital lobes are concentrated, and the strength of the bond depends on the extent of atomic orbital (AO) overlap. The greater the overlap, the stronger the bond..

I **V-7-2-1- Binder σ**

The **σ** (sigma) bond is a covalent bond that forms when two atoms share electrons through the head-on overlap of their atomic orbitals. This bond is characterized by cylindrical symmetry around the bond axis, and the electrons are localized in a plane perpendicular to this axis. In a **σ** bond, the overlap of atomic orbitals occurs through the direct superposition of the orbital lobes of the involved atoms, creating a region of maximum electron density along the bond axis. This electron density is responsible for the stability of the bond and the distance between the two atoms. The **σ** bond is the strongest and most common type of bond in organic and inorganic molecules. It can be single, double, or triple, depending on the number of electron pairs shared between the atoms **(Figure V7-1).**

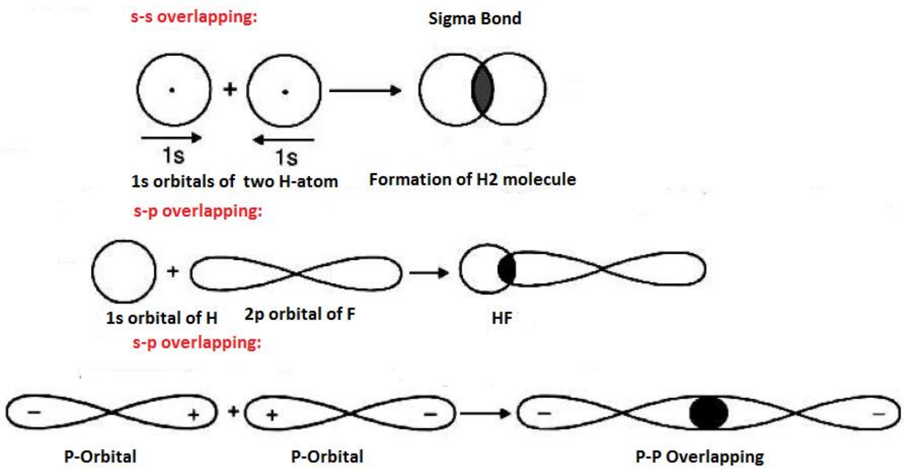


Figure V7-1: The σ bond resulting from the axial overlap of two s orbitals, p

IV-7-2-2- Bond π

A covalent chemical bond is referred to as a π (pronounced "pi") bond when it results from the overlap of two lobes of an atomic orbital occupied by a single electron with two lobes of an orbital occupied by an electron from another atom. The orbital overlap is lateral and occurs in a single nodal plane passing through the internuclear axis where the electron density is zero. π bonds are commonly found in double and triple bonds, but rarely in single bonds. (Figure V7-2).The symbol π refers to the p orbitals due to the symmetry of these bonds along the bond axis. d orbitals can also form π bonds, particularly in multiple bonds between metals.

Note: From an energy point of view, the (π) bond is weaker than the (σ) bond.

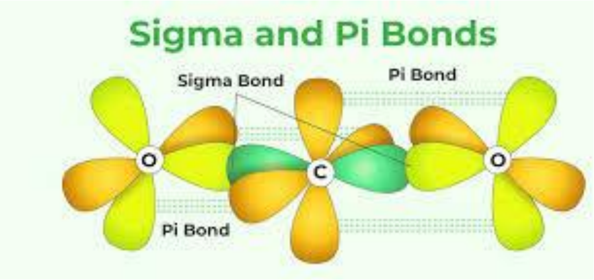


Figure IV-7-2: π-bonding resulting from the lateral overlap of two p, p orbitals

IV-8- Molecular orbital theory (M.O.T.) (LCAO method)

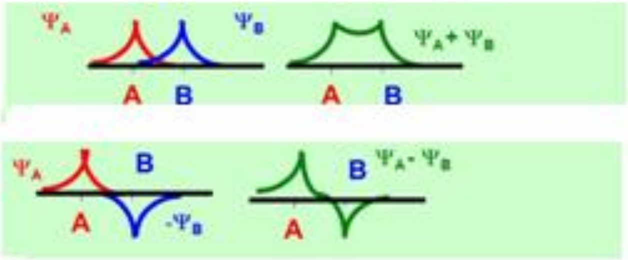
Molecular Orbital Theory (M.O.T.) is a method in quantum chemistry used to describe the electronic structure of molecules. It is based on the concept of molecular orbitals, which are linear combinations of atomic orbitals (A.O.) from the atoms constituting the molecule. The LCAO method (Linear Combination of Atomic Orbitals) involves mathematically combining the wave functions of atomic orbitals to form molecular orbitals. This combination is performed linearly, weighting the A.O. with coefficients known as Slater coefficients.M.O.T. allows for the prediction of electronic properties of molecules, such as their energy, stability, geometry, reactivity, and more. It is particularly useful for studying the interactions between electrons from different atoms in a molecule, as well as the resulting chemical bonds.M.O.T. is a theoretical method that requires complex mathematical calculations to solve the so-called Schrödinger equations. These calculations are typically performed using quantum chemistry software, which enables the simulation of electron behavior in molecules with high precision.

IV-8-1- Principle

Hund and Mulliken developed molecular orbital theory (M.O.T.) around the same time as valence bond theory (V.B.T.). Compared to V.B.T., the molecular orbital method considers that bonded atoms lose their individuality and that the molecule is treated as a whole. Each electron contributes to the formation of molecular bonds, so the molecule can be viewed as a collection of nuclei surrounded by an electron cloud formed by all the electrons of the bonded atoms. This approach can be compared to that of an atom, which consists of a nucleus surrounded by an electron cloud. An electron in atom A is described by a function ψ_A n electron in a molecule AB, in M.O.T., will be described by a function ψABwhich is a linear combination of the wave functions $\psi_A$and ψ_B

$$\Psi_{AB} = C_1\Psi_A \pm C_2\Psi_B$$

Just as any atomic wave function is associated with an atomic orbital (A.O.), any wave function of a molecule corresponds to a molecular orbital (M.O.) (Figure V8-1).The wave function: $\boldsymbol{\Psi^{l}_{AB} = C_1\Psi_A + C_2\Psi_B}$, corresponds to a molecular orbital: **Bonding**, referred to as B.M.O. (Bonding Molecular Orbital) or simply BMO^{L} The wave function: $\boldsymbol{\Psi^{*}_{AB} = C_1\Psi_A + C_2\Psi_B}$, corresponds to a molecular orbital: anti-bonding called O.M.AL or O.M*.

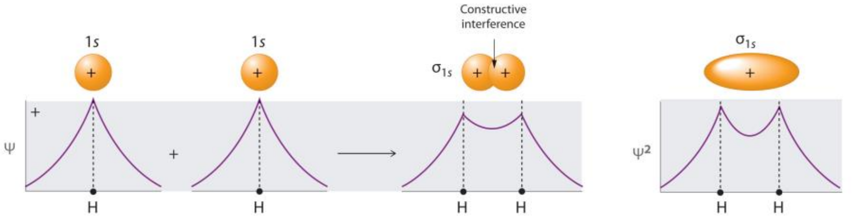


<u>Figure IV8-1: Graphical representation of Molecular Orbitals (M.O.)</u>

<u>Note :</u> Molecular Orbital Theory (M.O.T.) develops a set of molecular orbitals for a molecule, which are occupied by electrons following the same filling rules as those applied to atoms. Each molecular orbital represents the probability region where an electron of a molecule is likely to be found. Just like an atomic orbital, a molecular orbital can hold no more than two electrons with opposite spins.

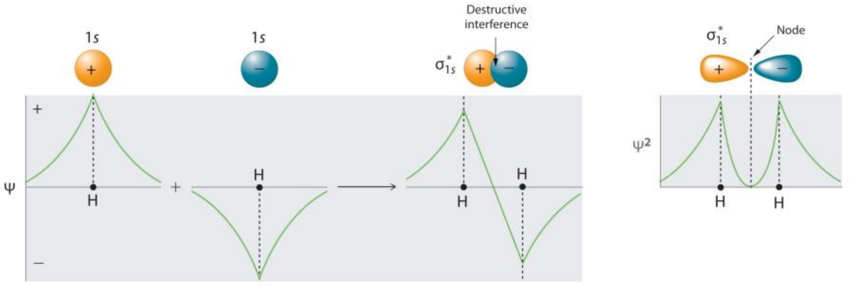
IV-8-2- Energy aspect

By solving the Schrödinger equation in full, we can determine the energies of the two molecular orbitals. It can be seen that the energy of the binding orbital is lower than that of the separate atoms, corresponding to stabilization of the molecule. Conversely, the anti-bonding orbital has a higher energy, corresponding to destabilization of the molecule. **(Figure V8-2)**



(a) Wave functions combined for σ_{1s}

(b) Bonding probability density



(c) Wave functions combined for σ^{*}_{1s}

(d) Antibonding probability density

Figure IV-8-2: Energy aspect of molecular orbital formation

Note:

Combining the two molecular orbitals of the same energy gives rise to two new molecular orbitals of different energies: a stabilized binding orbital and a destabilized antibinding orbital. However, the destabilization of the anti-bonding orbital is more important than the stabilization of the bonding orbital.

IV-8-3- Overlapping atomic orbitals

Atomic orbital overlap is an important concept in quantum chemistry that describes how atomic orbitals overlap when they bond to form a molecule. Overlap is determined by the shape and orientation of the atomic orbitals and can be classified into three types:

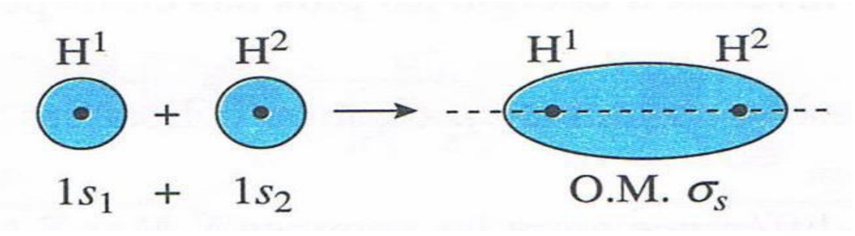
1. ***Axial (or sigma) overlap***: this type of overlap occurs when orbitals overlap directly along the bond axis between the two atoms. Sigma bonds are generally stronger than pi bonds.
2. ***Lateral overlap (or pi):*** this type of overlap occurs when orbitals overlap laterally with respect to the bond axis. Pi bonds are generally weaker than sigma bonds.
3. ***Non-bonding overlap***: this type of overlap occurs when atomic orbitals do not overlap, but are located close to each other. This type of overlap is important for interactions between molecules and for the stability of certain molecular structures.

The overlap of atomic orbitals plays a key role in determining the molecular geometry and chemical properties of molecules. For example, the bond between two hydrogen atoms is a sigma bond, while the bond between two oxygen atoms in an oxygen molecule is a pi bond.

Note

M.O.s are linear combinations of atomic orbitals (C.L.O.A.) which are represented graphically by the overlap of the orbital lobes of the A.O.s which combine

Example: H_2: 1s (1) + 1s (2) = σ^{l}



General rule :

In order to be combined linearly, A.O.s must obey the following three rules:

1. The energies of the combining A.O.s must be of the same order of magnitude.
2. The orbital lobes of the A.O.s must cover each other as much as possible.
3. The overlapping A.O.s must have the same symmetry with respect to the molecule's axis **(Table V8-1).**

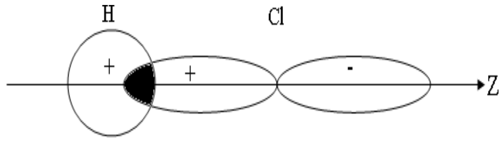
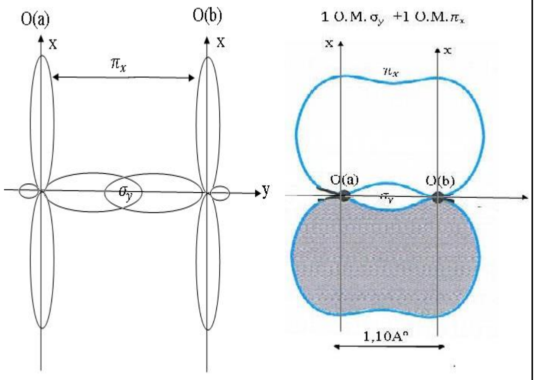
Recovery allowed	Example	Recovery forbidden
s-p p_x-p_x p_y-p_y p_z-p_z	HCl  O_2,  	p_x-p_y p_y-p_z p_x-p_z

Table IV8-1: Permitted and prohibited overlap between different orbitals

The overlap S of two A.O.s is characterized by the overlap integral :

$$S = \iiint \psi_A \psi_B dV \quad \text{avec ;}$$

ψ_A : Wave function associated with the atomic orbital of A

ψ_B Wave function associated with the atomic orbital of B

dV : infinitely small volume = $d_x d_y d_z$

Depending on the sign of the overlap, there are three types of molecular orbital:

If $S > 0 \Rightarrow$ binding molecular orbital (O.M.L. ou O.M^{l}).

If $S < 0 \Rightarrow$ antibonding orbital (O.M.AL. ou O.M*).

If $S = 0 \Rightarrow$ non-bonding molecular orbital (O.M.N.L.).

IV-8-4- binding order

In chemistry, bond order is a measure of the strength of a chemical bond between two atoms in a molecule. Bond order is determined by the number of bonding electrons shared between the two atoms.

Bond order is usually calculated using the following formula:

Bonding order = (number of bonding electrons - number of non-bonding electrons) / 2

$$\mathbf{O.L} = \frac{\sum \mathbf{e^-(O.M.L)} - \sum \mathbf{e^-(O.M.A.L)}}{\mathbf{2}}$$

Bonding electrons are electrons that are shared between the two atoms involved in the bond, while antibonding electrons are electrons that are located in antibonding orbitals and have a repulsive effect on bonding electrons. The total number of bonding and antibonding electrons is equal to the number of electrons in the bond. Bond order can be either integer or fractional. **Single bonds** have a bond order of 1, double **bonds** have a bond order of 2 and Triple **bonds** have a bond order of 3.

Fractional bond orders are possible in certain cases, such as aromatic bonds. Bond order is an important property of molecules, as it correlates with bond length and bond energy. Bonds with a higher bond order are generally shorter and stronger than bonds with a lower bond order.

Note:

- The higher the bond order, the more stable the molecule.

- If the bond order is zero, the molecule cannot exist.

IV-8-5- Magnetic properties

The fundamental electronic configuration of a molecule is established by filling the lowest-energy molecular orbitals with valence electrons, in accordance with Pauling's principle and Hund's rule. If the molecule contains at least one single electron in its electronic configuration, it is considered paramagnetic. If, on the other hand, it contains no single electrons, it is considered diamagnetic.

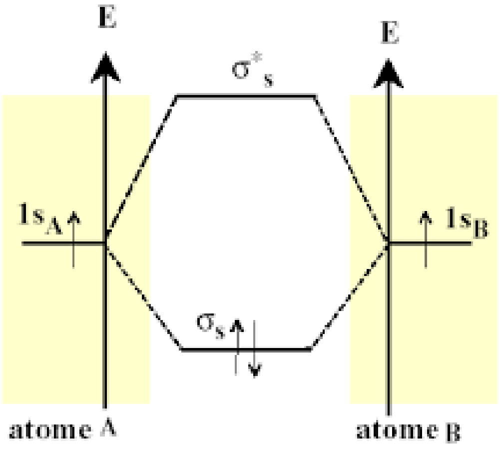
In a nutshell: magnetism

- If all electrons are paired, the molecule is "diamagnetic".

- If there are still single electrons, it is "paramagnetic".

IV-9- Diagramme des niveaux d’énergie

An energy level diagram is a graphical representation of the possible energy levels of a quantum system, such as an atom or molecule. In an energy level diagram, energy levels are represented by horizontal lines, and transitions between these levels are represented by arrows.



In chemistry, energy level diagrams are often used to represent atomic orbitals, molecular orbitals and electronic transitions in molecules. Atomic orbitals are represented by horizontal lines for each energy level, while molecular orbitals are represented by linear combinations of atomic orbitals, also known as bonding or antibonding molecular orbitals. Energy level diagrams are useful for understanding the electronic properties of atoms and molecules, such as their electronic configuration, chemical reactivity and absorption or emission spectrum.

01) Diagram of homonuclear diatomic molecules (A2)

Homonuclear diatomic molecule diagrams are graphical representations of the molecular orbitals and associated energy levels for homonuclear diatomic molecules, i.e. those composed of two identical atoms, such as H2, N2 or O2. These diatomic molecules have energy levels that are determined by the combination of the atomic orbitals of the two atoms. The resulting molecular orbitals can be binding or antibinding, and their energy depends on the distance between the two atoms in the molecule. In a diagram of homonuclear diatomic molecules, binding molecular orbitals are represented by horizontal lines below the horizontal axis, while antibinding molecular orbitals are represented by horizontal lines above the horizontal axis. The energy levels of the molecular orbitals increase as you move up and down the diagram. Electrons are placed in molecular orbitals according to Pauli's filling principle and Hund's rule. Electrons fill the lowest-energy molecular orbitals first, also respecting the limit of two electrons per orbital.

Diagrams of homonuclear diatomic molecules are useful for understanding the properties of diatomic molecules, such as their stability, binding energy, dipole moment and absorption or emission spectrum. **(Figure V9-1).**

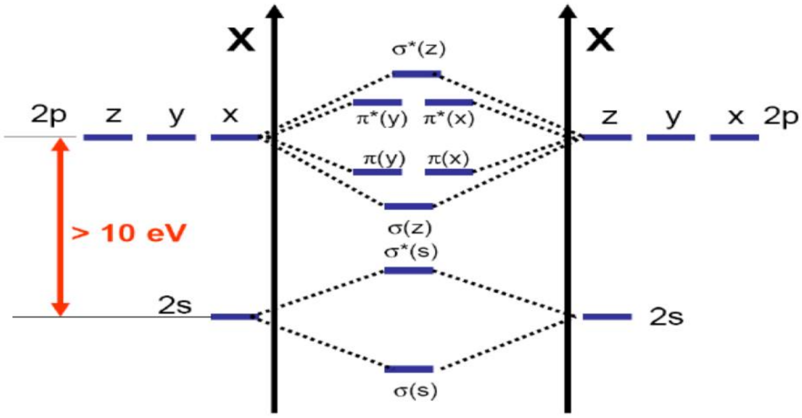


__Figure IV9-1: Diagram of A2 homonuclear diatomic molecules__

02) Diagram of homonuclear diatomic molecules (A2) SP interaction

SP interaction: occurs when a bond between 1 s orbital and 1 p orbital occurs at a distance of less than 10 eV. A pz/pz and s/s overlap is required. The proximity of the 2 bonds creates a kind of energetic "disorder". The consequence of this SP interaction is that the σ overlap rises above the π(y) and ((x) overlaps. **(Figure V9-2).**

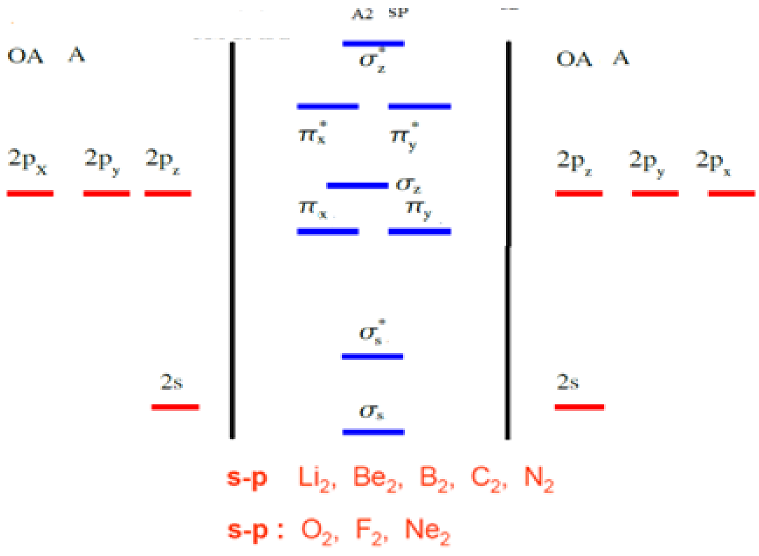


Figure IV9-2: Diagram of diatomic molecules (A2) SP interaction

03) Heteronuclear diatomic molecules (AB)

Heteronuclear diatomic molecules, type AB, are distinguished from A2 molecules by the fact that their ns and np atomic levels are no longer at the same energy. The OMs are no longer symmetrical, and are polarized on the most electronegative atom when they are bonded, and on the least electronegative when they are antillated. Studies show that the energy diagram of AB molecules has the same shape as A2 molecules, but don't forget that we have two atoms with different electronegativities. Figure V9-3:

Note

By convention, the A.O. of the most electronegative atom is always shown on the right.

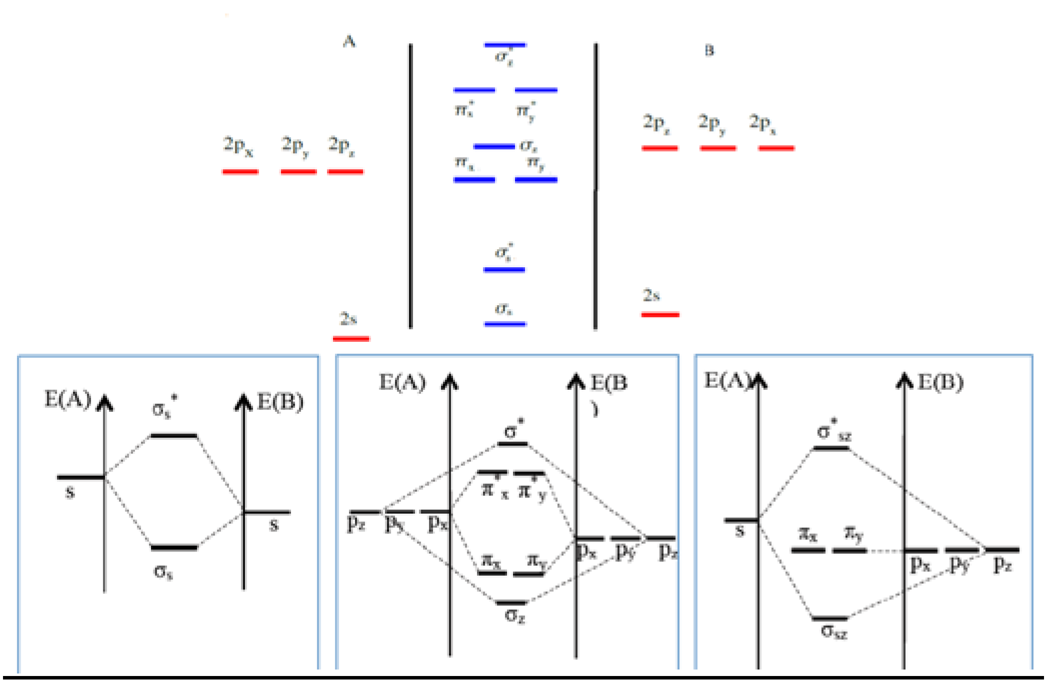


Figure IV9-3 : Les molécules diatomiques hétéronucléaires (AB)

IV-10- Hybridization theory of atomic orbitals

Hybridization theory, or valence bond theory, is a theory in chemistry that describes how an atom's atomic orbitals combine to form hybrid orbitals for the purpose of forming covalent bonds with other atoms. This theory was developed in the 1930s, notably by the American chemist Linus PAULING, who was awarded the **Nobel Prize** for Chemistry in 1954. It's a descriptive theory of chemical bonding that has had, and still has, great success in organic chemistry, as it gives a fairly good account of experimental facts, absolutely incomprehensible by LEWIS' theory, such as the existence of s and p bonds. It's also a theory that has its limits, limits that will be overcome, at least in part, by the theory of molecular orbitals. Atomic orbital hybridization theory is widely used in organic chemistry to explain the molecular structure and physical and chemical properties of organic compounds. It is also useful for predicting molecular geometry and bond angles in molecules.

IV-10-1- The hybridization principle

The principle of atomic orbital hybridization is based on the idea that an atom's atomic orbitals can combine to form hybrid orbitals with properties intermediate between the original atomic orbitals. Hybridization occurs when an atom's atomic orbitals are modified to form hybrid orbitals that have different energies and shapes to the original atomic orbitals. This usually occurs when the atom forms covalent bonds with other atoms. Hybridization enables atoms to form stronger, more stable covalent bonds with other atoms, making compounds more stable and resistant to chemical reactions. When atomic orbitals combine to form hybrid orbitals, electrons are distributed more evenly between the atoms involved in the bond, reducing the polarity of the bond. The theory of hybridization, or valence bond theory, has helped to interpret certain molecular structures for which theoretical calculations did not agree with experimental measurements. Thanks to hybridization, it is possible to justify :

- Equivalent bonding of certain compounds: $BeCl2$, $BCl3$, $CH4$ $PCl5$....
- Bond angles in certain compounds: $H2O$, $NH3$....
- Hybridization is the reorganization of an atom's O.A to give identical hybrid orbitals (O.H) of the same energy and shape, oriented according to a well-defined symmetry, which is that of the molecule.
- H.O.s are linear combinations of A.O.s that have been hybridized.
- The number of hybridized orbitals is equal to the number of atomic orbitals involved in the hybridization.
- In an AXn molecule, hybridization generally involves the A.O.s of the central atom A ($CH4$: hybridization of the s, px, py and pz A.O.s of carbon, involving 4 H.O.s).
- Very often, before hybridizing the O.A.s of an atom, it is necessary to imagine an excited state of the atom. This excited state makes it possible to recover the element's true valence.

<u>NOTE : Hybridization is a calculation process, and H.O.s have no physical reality.</u>

IV-10-2- The different types of hybridization

In general, hybridization mainly concerns s- and p-type atomic orbitals. Depending on the number and type of atomic orbitals hybridized, there are several types of hybridization.

IV-10-2-1- hybridization sp^3

sp^3 hybridization is a type of atomic orbital hybridization that occurs when one s orbital and three p orbitals combine to form four tetrahedral sp^3 hybrid orbitals. This type of hybridization occurs when the central atom of a molecule is surrounded by four bonding atoms and no other non-bonding electron pairs. The sp^3 hybrid orbitals have a tetrahedral shape and are oriented in such a way as to maximize the distance between them, allowing the bonded atoms to be located at the four corners of a tetrahedron. sp^3 hybridization is common in molecules such as methane ($CH4$) and water ($H2O$). sp^3 hybridization allows atoms to form stronger and more stable covalent bonds with other atoms, making molecules more stable and more resistant to chemical reactions. It is also useful for explaining molecular geometry and bond angles in molecules.

Example : We will illustrate the general method with an example: the methane molecule, $CH4$.

- The electronic structure of the carbon atom in its ground state, with the atomic number Z of carbon being 6, is: **$1s^2\ 2s^2\ 2p^2$**.The presence of two unpaired electrons in the 2p subshell of the carbon atom does not explain the tetravalency of carbon in methane. The theory of atomic orbital hybridization has resolved this problem:Since the 2s and 2p subshells (atomic orbitals) of the carbon atom are very close in energy, in valence bond theory, we "hybridize" them, meaning we "mix" them to "create new entities," which we will call "hybrid atomic orbitals of the central atom." These can be written as follows:

  1 atomic orbital 2s + 3 atomic orbitals 2p → 4 hybrid atomic orbitals "sp^3."
- The four electrons that were in the 2s and 2p subshells are now uniformly distributed in each of the four sp^3 hybrid atomic orbitals. This uniform distribution of the four electrons is justified ("explained") by the equivalence of the four chemical bonds in the methane molecule.
- The four electrons, each contained in an sp^3 hybrid orbital, will position themselves in four directions, with angles of **109°28'** between each pair. This arrangement

minimizes the inter-electron repulsions between four point charges of the same nature in space.

- This aligns with the VSEPR (Gillespie) theory, which classifies molecules like CH4 in the **AX4** category. The imposed geometry for the methane molecule will therefore be the **tetrahedral geometry**.
- Once the four sp^3 hybrid atomic orbitals are constructed, the formation of the methane molecule is completed by combining each sp^3 hybrid atomic orbital with a 1s orbital from a hydrogen atom, which carries a single unpaired electron.
- This will create four molecular orbitals of the "σ" (sigma) type, through the axial fusion of each sp^3 hybrid atomic orbital with a 1s atomic orbital.

(Figure V10-1) summarizes all the steps mentioned above

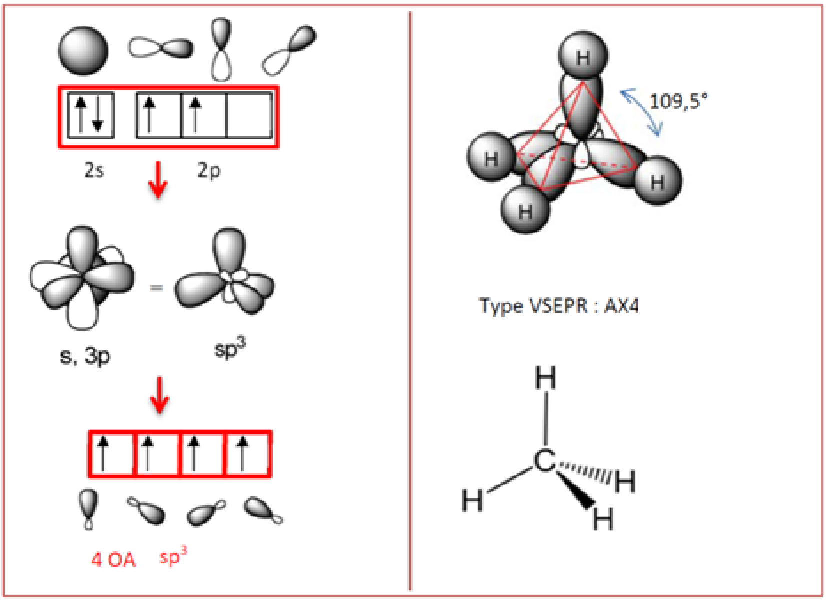


Figure IV10-1: The molecular geometry of methane, CH4.

IV-10-2-2- L'hybridation sp^2

sp^2 hybridization is a type of atomic orbital hybridization that occurs when one s orbital and two p orbitals combine to form three trigonal planar sp^2 hybrid orbitals. This type of hybridization occurs when the central atom of a molecule is surrounded by three bonding atoms and no other non-bonding electron pairs. The sp^2 hybrid orbitals have a **trigonal planar shape** and are oriented in such a way as to maximize the distance between them, allowing the bonded atoms to lie in the same plane. sp^2 hybridization is common in molecules such as **benzene (C_6H_6)** and **ethylene (C_2H_4)**. sp^2 hybridization allows atoms to form stronger and more stable covalent bonds with other atoms, making molecules more stable and more resistant to chemical reactions. It is also useful for explaining **molecular geometry** and **bond angles** in molecules. For example, in sp² hybridized molecules, the bond angles are typically **120°**, which corresponds to the optimal arrangement for minimizing electron repulsion in a trigonal planar geometry.

Example : the ethylene molecule (ethene, officially) C_2H_4.

- The electronic structure $1s^2\ 2s^1\ 2p^3$ for the carbon atom, instead of $1s^2\ 2s^2\ 2p^2$.
- From this point, we hybridize the following atomic orbitals of the carbon atom: 2s, 2px, and 2py.
- We intentionally and arbitrarily leave the 2pz orbital unhybridized.
- We then perform the following combination for the three atomic orbitals of the carbon atom, which have similar energies:
  1 atomic orbital 2s + 2 atomic orbitals 2p → 3 hybrid atomic orbitals "sp²".
  Each of these hybrid orbitals now contains one electron. The way to distribute three electrons in space to minimize inter-electron repulsions follows a planar geometry, with an angle of 120° between each of the chosen directions.
  The 2pz orbital, not affected by the hybridization of the three previous orbitals, occupies a direction perpendicular to the plane where the three sp² hybrid orbitals are located. This orbital also contains one electron.
- We repeat the same operation for the second carbon atom of the future ethylene molecule.
- Between the two hybrid sp² atomic orbitals, each coming from a different carbon atom, undergoing axial fusion, we create what is called a "sigma bond" (σ bond).
- Between the two unhybridized 2pz atomic orbitals, each coming from a different carbon atom and each containing one electron, we create what is called a "pi bond" (π bond). The fusion between these two 2pz atomic orbitals is a lateral fusion.
- We then observe, contrary to what Lewis theory could explain, that the two carbon-carbon bonds in the ethylene molecule are fundamentally different in nature. This is a significant advancement compared to Lewis theory.

To complete the construction of the ethylene molecule, we finally create four bonds, that is, four molecular orbitals of the "sigma" type, between, on one hand, a hybrid sp² atomic orbital and, on the other hand, a 1s atomic orbital from a hydrogen atom. Each time, the Pauli exclusion principle (antiparallel spins) must be respected.

(Figure V10-2) summarizes all the steps mentioned above.

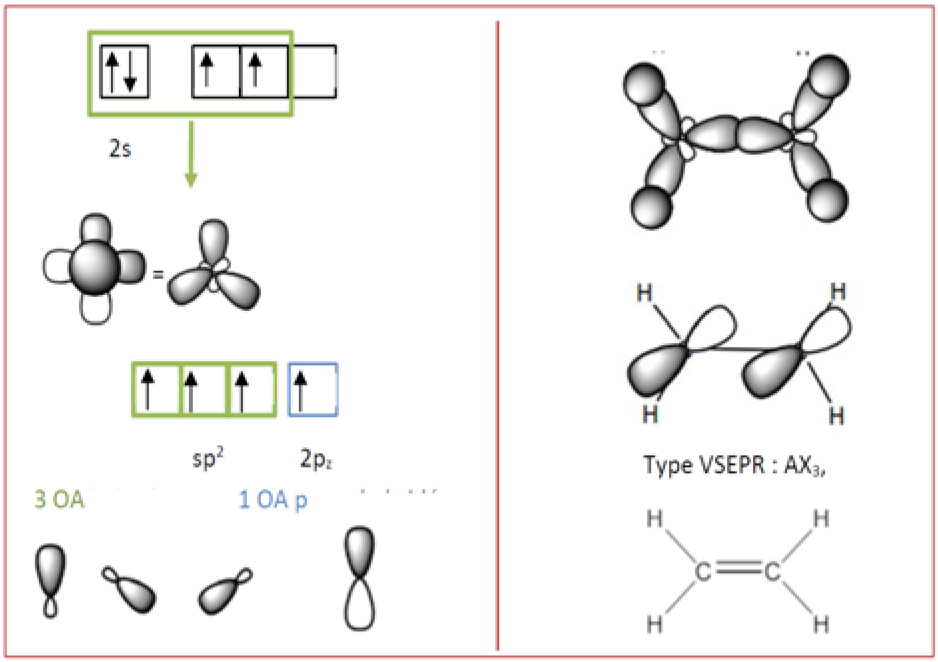


Figure IV10-2: The molecular geometry of ethylene (C2H4).

V-10-2-3- L'hybridation sp

Sp hybridization is a type of atomic orbital hybridization that occurs when an s orbital and a p orbital combine to form two linear sp hybrid orbitals. This type of hybridization occurs when the central atom of a molecule is surrounded by two bonding atoms and no other non-bonding electron pairs.

Sp hybrid orbitals have a linear shape and are oriented 180 degrees to each other, allowing the bonded atoms to lie in a straight line. Sp hybridization is common in molecules such as carbon dioxide (CO_2) and acetylene (C_2H_2).

Sp hybridization allows atoms to form stronger and more stable covalent bonds with other atoms, making molecules more stable and resistant to chemical reactions. It is also useful in explaining molecular geometry and bond angles in molecules.

Example: Let's take the example of the acetylene (ethyne, officially) molecule C2H2. As before, we cannot understand the tetravalence of carbon unless we imagine the following electronic structure for it: 1s22s12p3. From there, we choose, quite arbitrarily, to hybridize, for each carbon atom, a 2s atomic orbital with a 2p atomic orbital.

We therefore leave aside, for each carbon atom, two atomic orbitals, the 2px and 2pz atomic orbitals. We will therefore write:

1 2s atomic orbital + 1 2p atomic orbita l + 2 sp hybrid atomic orbitals. Since each hybrid orbital contains one electron, the only way to minimize inter-electron repulsion is... to align the two hybrid orbitals, forming a 180° angle between them.

From there we construct the acetylene molecule by carrying out:

1. An axial fusion of two "sp" hybrid orbitals, each from a different carbon atom. This results in an "s" type molecular orbital between the two carbon atoms..
2. A lateral fusion of two unhybridized orbitals, 2px, each from two different carbon atoms. This results in a "p" molecular orbital between the two carbon atoms.
3. A second axial fusion between the two unhybridized 2pz atomic orbitals, also coming from two different carbon atoms. This produces a second "p" type molecular orbital between the two carbon atoms. Of course, the Pauli Exclusion Principle will apply each time.

(Figure V10-3) summarizes all the steps mentioned above

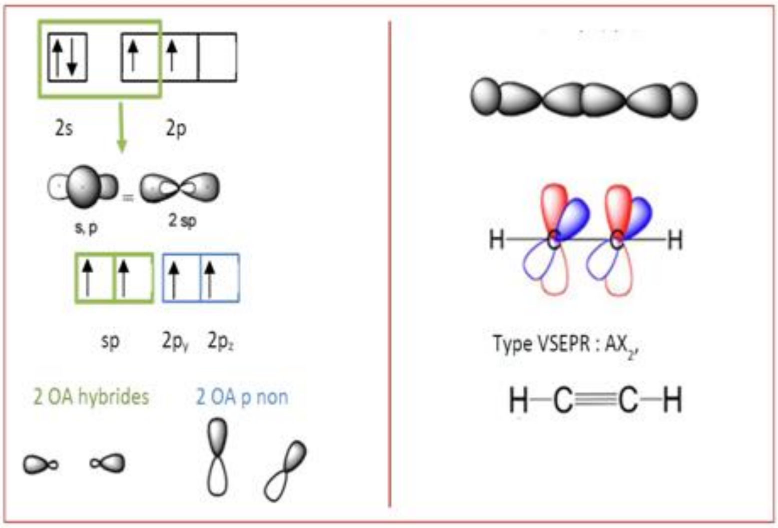
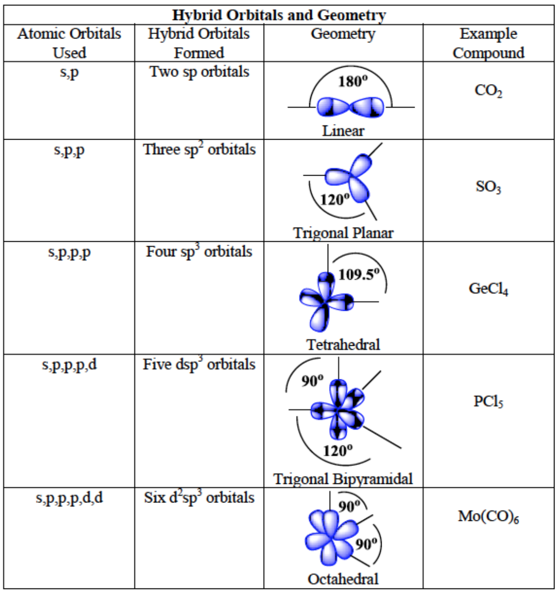


Figure IV10-3: The molecular geometry of ethylene (C2H2).

IV-11- Correspondence between Hybridization and VSEPR

The VSEPR (Valence Shell Electron Pair Repulsion) theory and the atomic orbital hybridization theory are both used to explain the molecular geometry of chemical compounds. VSEPR theory predicts molecular geometry based on the electrostatic repulsion between valence electron pairs around the central atom. On the other hand, the atomic orbital hybridization theory describes how the atomic orbitals of an atom combine to form hybrid orbitals, which enable the atom to form covalent bonds with other atoms. Hybridization determines the number and type of hybrid orbitals formed, as well as their spatial orientation. There is a correspondence between these two theories: the type of atomic orbital hybridization of an atom determines the number and type of electron pairs around the central atom, which allows for the prediction of molecular geometry according to VSEPR theory. For example, sp³ hybridization leads to a tetrahedral geometry, while sp² hybridization results in a trigonal planar geometry (Figure V11-1). Thus, the atomic orbital hybridization theory and the VSEPR theory are complementary and are both necessary for understanding the molecular geometry of chemical compounds.



Hybrid Orbitals and Geometry

Atomic Orbitals Used	Hybrid Orbitals Formed	Geometry	Example Compound
s,p	Two sp orbitals	180° Linear	CO_2
s,p,p	Three sp^2 orbitals	120° Trigonal Planar	SO_3
s,p,p,p	Four sp^3 orbitals	109.5° Tetrahedral	$GeCl_4$
s,p,p,p,d	Five dsp^3 orbitals	90° 120° Trigonal Bipyramidal	PCl_5
s,p,p,p,d,d	Six d^2sp^3 orbitals	90° 90° Octahedral	$Mo(CO)_6$

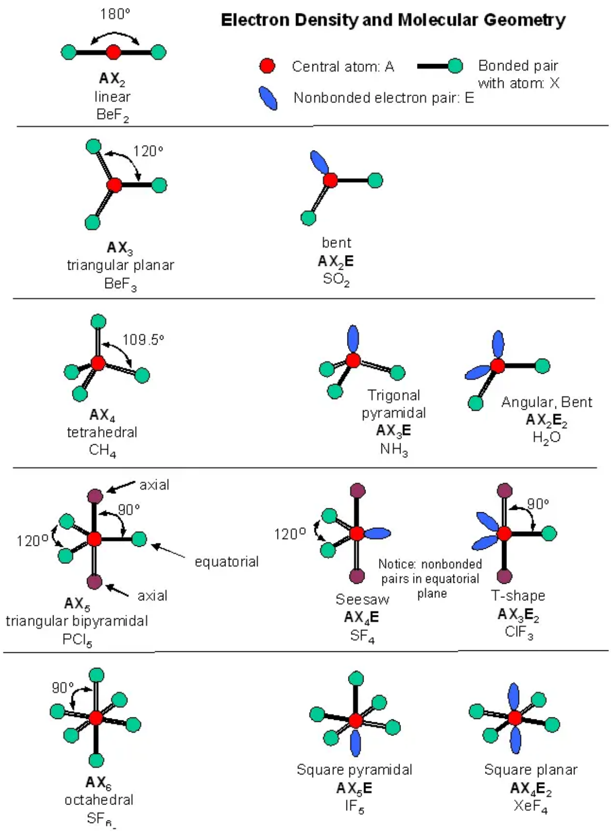


Figure IV11-1: Correspondence between Hybridization and VSEPR

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