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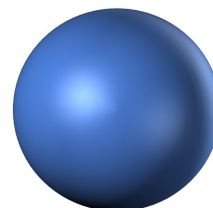
Part I.

Atomistics

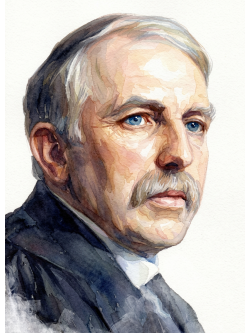
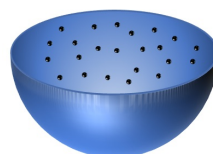
The Advent of Quantum Chemistry: Historical Context



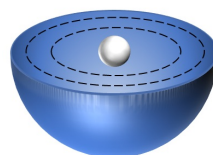
John Dalton's Model (1766-1844) : This British physicist revived Democritus's idea by stating that matter is composed of atoms. He said: "the atom is a simple and indivisible sphere, like a billiard ball." **1803**



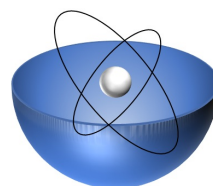
Joseph John Thomson's Model (1858-1940) : An atom contains negative particles that I will call electrons. In my model, the atom consists of a solid sphere filled with a positively charged substance, with electrons embedded in it (**1901**: the discovery of the electron).



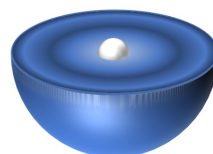
Ernest Rutherford's Model (1871-1937) : By bombarding a gold leaf with positive particles, I noticed that most of these particles passed through the matter without bouncing back. From this, I deduced a new model: the atom consists of a central nucleus, positively charged, around which negative electrons move. Between them, there is empty space (**1911**: discovery of the nucleus).



Niels Henrik David Bohr's Model (1885-1962): In this semi-classical model, the electron orbits the nucleus in a circular path, like a planet around the Sun (**1913**).



Erwin Schrödinger's Model (1887-1961) : It is impossible to know the momentum of electrons located around the nucleus. In other words, it is impossible to know both the position and the velocity of an electron. What might initially be interpreted as a setback is actually a fundamental evolution. The electron cloud becomes a "probability cloud" (**1927**: quantum theory).



Chapter 1.

The Atom

The questioning about the nature of matter dates back as far as Antiquity. The Greek philosopher **Democritus** formulated the hypothesis that all matter was composed of very small particles, which he named "**átomos**" (meaning unbreakable or indivisible). This theory was far from unanimous among his contemporaries. It was rather **Aristotle**'s theory, according to which only four elements (air, earth, water, and fire) formed matter, that prevailed for several centuries. It was not until around the 1600s that scientific experimentation became accessible. Experiments allowed the establishment of certain laws that are at the origin of modern chemistry. Four laws, known as the "weight laws of chemistry," were established towards the end of the 18th century and the beginning of the 19th. According to **Dalton**'s atomic theory, the atom is the smallest part of an element that can combine chemically. However, a series of studies, begun in the 1850s and continued into the 20th century, clearly showed that atoms have an internal structure, meaning they are made of even smaller particles, called subatomic particles. This research led to the discovery of three of these particles: electrons, protons, and neutrons. It should be noted that unlike electrons, protons and neutrons are not elementary particles since they are made up of even smaller particles called "quarks."

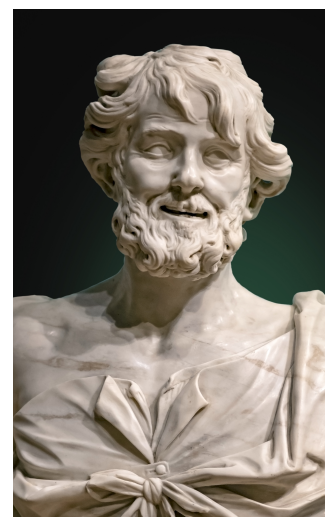


Figure 1.1 Democritus

1.1. Constituents of the Atom

1.1.1. The Nucleus

The nucleus is the center of the atom, composed of protons (Z) and neutrons (N), also called nucleons (A) (with $A = Z + N$). The size of the nucleus is about 100,000 times smaller than that of the atom (10^{-15} m) and contains 99.97% of its mass. Each atom, designated by an element X , is characterized by its number of protons Z and nucleons A . It is written in the form A_ZX .

1.1.2. The Proton

In 1909, **Ernest Rutherford** proposed using α particles (recall that these particles are formed from two protons and two neutrons assembled into a particle analogous to the helium nucleus) as projectiles to test **Thomson**'s atomic model. The experiment, which he conducted with the assistance of his young associate **Hans Geiger** (who later invented a particle counter) and **Ernst Marsden**, yielded completely unexpected results.⁽¹⁾ The goal was to analyze the trajectory of α rays when directed at atoms (see [Figure 1.3](#)). They bombarded a thin gold foil with a beam of α particles, anticipating little deviation given the distribution of mass and charge according to **Thomson**'s model. However, the vast majority of particles passed through the metal foil without deviating from their initial trajectory or with very slight deflection. Yet, a few particles were strongly deflected, some even bouncing back in the opposite direction. This latter phenomenon was the most disconcerting, because according to **Thomson**'s model, the positive charges of the atom were so diffuse that it was expected that the α particles would pass through without their trajectory being significantly altered. Upon learning of these results, **Rutherford** declared: "It is as incredible as firing a 35 cm shell at a sheet of paper and seeing it bounce back towards you." This observation proved decisive, as it invalidated the model proposed by **Thomson**. Indeed, in light of these results, it became impossible to continue assuming that the atom consisted of a positive charge uniformly distributed throughout its volume.

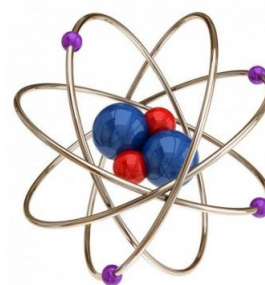


Figure 1.2 The Atom

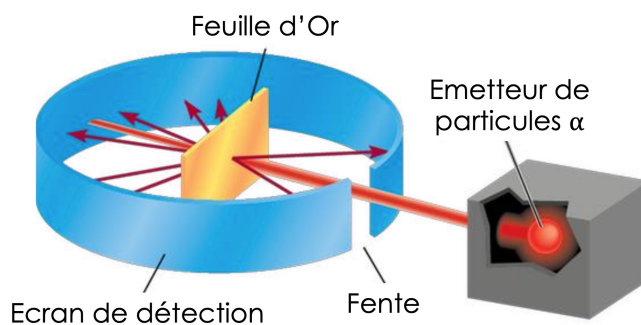


Figure 1.3 Rutherford's experiment on the scattering of α particles by a gold foil⁽²⁾

Rutherford then hypothesized that most of the α particles were not deflected because the atom is essentially empty. As for the positive charges, he suggested that they are concentrated in a nucleus, a dense body located at the center and containing all the positive charge of the atom.⁽³⁾ Since α particles are much heavier and more energetic than electrons, they can easily push them aside, but when passing near the nucleus, they are strongly repelled, hence the observed deflections, which become greater as the particles approach the nucleus.

The experiments of **Rutherford** and his collaborators revealed the density of the atomic nucleus relative to its size. **Rutherford's** atomic model can be imagined as a miniature solar system (as the chemist **Jean Perrin** conceived in 1901), where electrons orbit the nucleus like planets around the Sun, hence its name "planetary model." The existence of protons, these positive particles constituting the atomic nucleus, was demonstrated in 1919 by **Rutherford** himself. In subsequent studies, it was established that the charge of a proton was positive and equal in absolute value to that of an electron, and that its mass was approximately 1800 times greater than that of an electron. While the atom has a radius on the order of 10^{-10} m, that of the nucleus is about 10,000 times smaller, or 10^{-14} m.

1.1.3. The Neutron

However, **Rutherford's** atomic model had a major problem: it was known that hydrogen, the simplest atom, contained only one proton, and that helium contained two. One would therefore expect a helium/hydrogen mass ratio of 2:1 (electrons being negligible), but this ratio was actually 4:1. **Rutherford** then postulated the existence of other particles without electrical charge in the nucleus, which was confirmed in 1932 by the English physicist **James Chadwick**.⁽⁴⁾ By bombarding a thin beryllium foil with α particles, the metal emitted very high-energy radiation similar to γ rays. Subsequent experiments showed that these rays were actually composed of neutral particles with a mass slightly greater than that of protons. **Chadwick** named these particles neutrons. The mystery of the mass ratio was thus explained. In the nucleus of a helium atom there are two protons and two neutrons, whereas hydrogen contains only one proton and no neutrons, hence the 4:1 ratio. [Figure 1.7](#) shows protons and neutrons in the atomic nucleus. Other subatomic particles exist, but the electron, proton, and neutron are the three that matter in chemistry. [Table 1.1](#) presents the masses and charges of these particles.

1.1.4. The Electron

While chemists were determining atomic masses and discovering new elements whose properties they studied, physicists were exploring matter with discharge tubes (cathode ray tubes) and measuring the spectra of elements. This gradually illuminated the internal structure of atoms and helped to make atomic theory accepted while modifying **Dalton's** idea of an indivisible atom. It was while studying cathode rays that Sir **Joseph John Thomson** made a discovery⁽⁵⁾ that transformed the view of the atom. Cathode radiation was first experimented with by **Faraday** in 1838. When a current passes through a gas at low pressure in a glass tube containing two metal plates, the cathode emits an invisible radiation. When this ray, attracted by the perforated anode, strikes a surface coated with a special material, a bright light (fluorescence) is observed, as shown in [Figure 1.4](#) (right). In 1897, **Thomson** modified the classic cathode ray experiment by applying an electric field outside the beam. The cathode ray was immediately deflected toward the positive plate, and the measured deflection proved independent of the nature of the cathode, the anode, and the gas present in the tube (see [Figure 1.4](#) left). **Thomson** deduced that the radiation consisted of negative particles, subsequently named electrons, and that these electrons were components of all matter.

Source de courant électrique

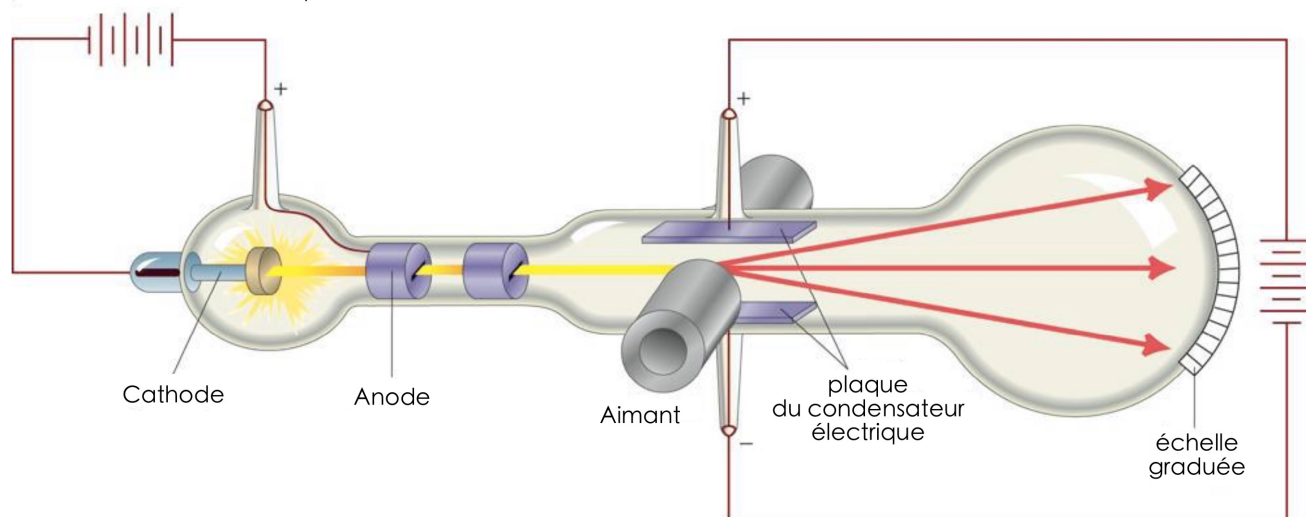


Figure 1.4 Apparatus used by Thomson to determine the ratio between mass and charge.⁽⁶⁾

Moreover, since under an electric field electrons undergo a deflection proportional to their charge (e) and inversely proportional to their mass (m), **Thomson** was able to experimentally measure the charge/mass ratio (e/m) of the electron, namely $-1.76 \times 10^8 \text{ C/g}$, where C is the symbol for the coulomb, the unit of electric charge. **Figure 1.4** shows the effect of a magnet on cathode radiation.

In 1909, the American physicist **Robert Millikan** succeeded in determining the charge of an electron⁽⁷⁾ by studying the effect of an electric field on the trajectory of ionized oil droplets (**Figure 1.5**). The charge of the electron was then established at $-1.6022 \times 10^{-19} \text{ C}$. This charge (in absolute value), combined with the e/m ratio of the electron found by **Thomson**, allowed **Millikan** to calculate the mass of the electron: $9.11 \times 10^{-31} \text{ Kg}$.

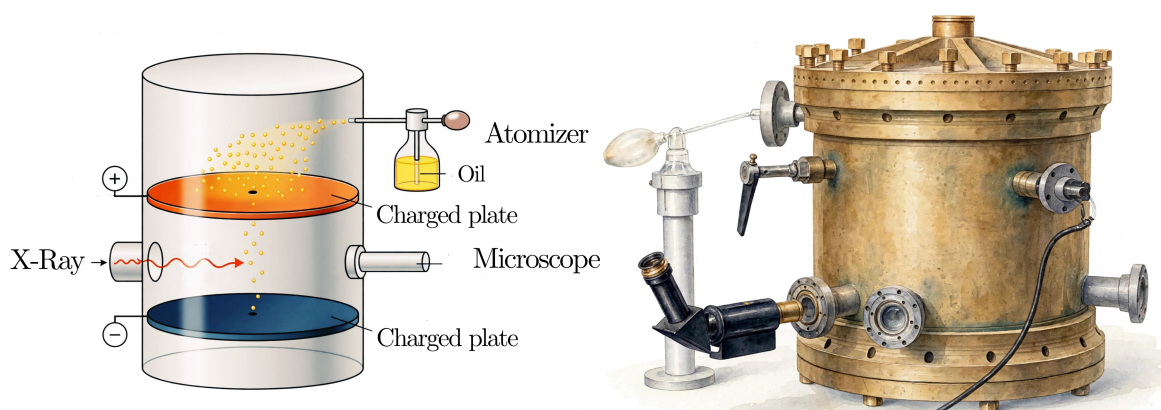


Figure 1.5 Diagram of **Millikan's** experiment⁽²⁾

In this experiment, **Millikan** observed in air the behavior of oil droplets previously charged by static electricity created by ionization of the air. These droplets were suspended in air in the presence of an electric field, and **Millikan** could follow their movement under a microscope.

After demonstrating the existence of electrons, **Thomson** thought that, since electrons could be produced by several metals (used as electrodes), they must be an integral part of the atom. However, he also understood that an atom could not consist solely of negative particles. He therefore imagined the atom as a uniformly positive sphere, in which electrons were dispersed, somewhat like raisins in a cake. **Thomson's** atomic model thus bears the name of the famous British dessert that inspired it: the Plum Pudding.

Table 1.1 Mass and charge of subatomic particles

Particle	Mass (Kg)	Charge (Coulomb)	Discoverer
Proton	1.6726×10^{-27}	$+1.6022 \times 10^{-19}$	E. Rutherford (1910)
Neutron	1.6748×10^{-27}	0	J. Chadwick (1932)
Electron	9.1094×10^{-31}	-1.6022×10^{-19}	J. J. Thomson (1897)

Radioactivity:

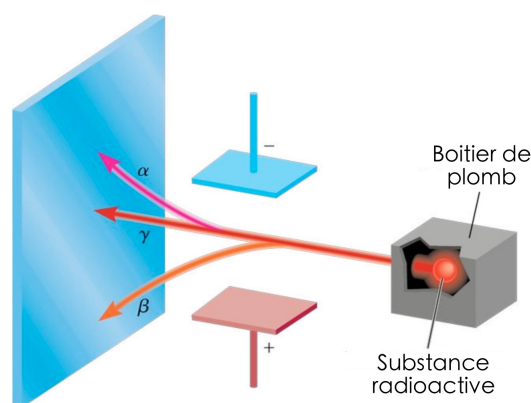
The study of cathode radiation⁽⁸⁾ led to two other major discoveries for modern chemistry. In 1895, **Wilhelm Röntgen** observed the emission of unusual high-energy radiation produced by cathode rays on glass and metal. Ignorant of the nature of these rays, he named them "X-rays".⁽⁹⁾ Almost simultaneously, the French physicist **Antoine Henri Becquerel** discovered by chance that certain elements emitted similar radiation, without requiring the input of cathode rays or any external radiation.

He observed that a piece of uranium, for example, could imprint its own image on a photographic plate, in the absence of any known radiation. **Marie Curie**, who was then studying with **Becquerel**, proposed the term radioactivity to describe the spontaneous emission of particles or radiation. Consequently, any element that spontaneously emits radiation is said to be "radioactive."

Subsequent work by **Becquerel**, **Pierre** and **Marie Curie**, and **Ernest Rutherford** showed that radioactivity is much more complex than the emission of X-rays. It was indeed established that the radiation emitted by the decay of uranium comprised three beams (or three distinct rays): α , β , and γ rays.

Two of these three types of rays are deflected by metal plates of opposite charges (see [Figure 1.6](#)). Alpha (α) rays consist of alpha (α) particles, positively charged particles (which correspond exactly to He^{2+} ions). α rays are therefore repelled by a positively charged plate. Beta (β) rays, or beta (β) particles, are electrons; consequently, they are repelled by a negatively charged plate. It was Ernest Rutherford who identified α and β particles in 1899.

Discovered in 1900 by chemist **Paul Villard**, the third type of radioactive radiation consists of high-energy rays called gamma (γ) rays.⁽¹⁰⁾ Like X-rays, these have no charge, so they are influenced by neither an electric field nor an external magnetic field.

**Figure 1.6** The three types of rays emitted by radioactive elements.⁽²⁾

During the years following the identification of α , β , and γ rays, several radioactive elements were discovered, most by **Pierre** and **Marie Curie**.

Research conducted at **McGill University** by **Ernest Rutherford** and **Frederick Soddy** showed that radioactivity involves fundamental transformations at the subatomic level, meaning that chemical elements transmute into other elements.⁽¹¹⁾ Such transformations are called radioactive decays.

This work earned **Rutherford** the Nobel Prize in Chemistry in 1908.⁽¹²⁾ Interestingly, he always remained slightly disappointed by this, as he considered himself above all a physicist.⁽¹³⁾

As for **Soddy**, he in turn became a Nobel Prize laureate in Chemistry a few years later (in 1921), for his contributions to the chemistry of radioactive substances and to isotopes.⁽¹⁴⁾

1.1.5. Atomic Number, Mass Number, Isotopes, and Ions

All atoms can be identified by their number of protons and neutrons. The number of protons contained in the nucleus of each atom of an element is called the atomic number (Z). The nature of a chemical element can be determined solely by its atomic number. For example, the atomic number of nitrogen **N** is 7, which means that every nitrogen atom has seven protons. In other words, every atom in the universe that has seven protons is nitrogen. A change in atomic number causes a change in the nature of the element. For example, if a nitrogen atom were to lose a proton through spontaneous decay, it would no longer be nitrogen; it would become carbon **C**, since all elements containing 6 protons are carbon. For the same element, the number of protons therefore never changes. In an electrically neutral atom, the number of protons and the number of electrons are equal. An oxygen atom **O** ($Z = 8$) therefore contains eight protons and eight electrons. Unlike the number of protons, the number of electrons can change for the same element.

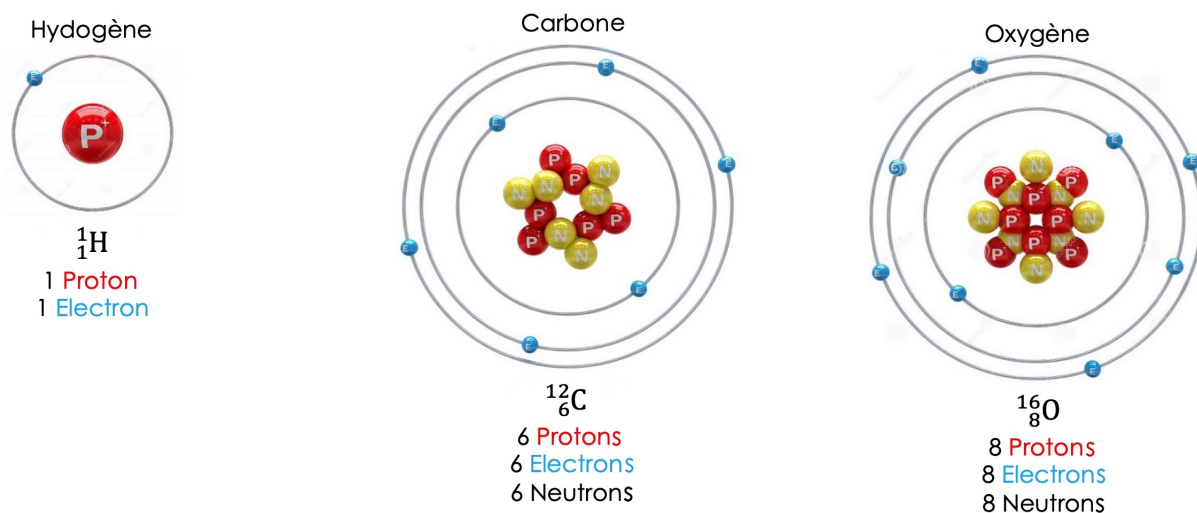


Figure 1.7 Position of particles in Hydrogen, Carbon, and Oxygen.

Atoms can therefore gain or lose electrons, depending on their properties and the experiment performed. Obviously, the number of protons remains intact. When the number of protons and electrons differs, the atom is no longer electrically neutral; these are ions.

These are elements having the same mass number A , but differing in their number of electrons. We have two possibilities: cations and anions (gain and loss of electrons, respectively). In both cases, the element retains the same name.

Example: ${}^A_{Z'}X$ the atom X with Z' electrons (Z' independent of Z).

Since electrons are negative particles, an atom that loses electrons will have a residual positive charge, as it will have an electron deficit: this will be a cation. For example, a sodium atom (Na) can easily lose one electron and become a sodium cation, represented by Na^+ : **Cation:** ${}^A_{Z'-i}X^{i+}$ loss of one or more electrons (i : number of electrons), Na^+ , Pb^{2+} .

Conversely, an atom that gains electrons will have a residual negative charge (an excess of electrons): this will be an anion. A chlorine atom (Cl) can gain one electron and become a chloride ion Cl^- . **Anion:** ${}^A_{Z'+i}X^{i-}$ gain of one or more electrons (i number of electrons), O^{2-} , Cl^- .

While electrons occupy virtually all atomic space and weigh almost nothing, protons and neutrons occupy very little space and confer almost all the mass to the atom. The mass number (A) therefore corresponds to the sum of the number of protons and the number of neutrons contained in the nucleus of an atom. The set of protons and neutrons in the nucleus is also called nucleons. The mass number of an atom is therefore equal to its number of nucleons.

It is therefore possible to know the number of neutrons contained in an atom from its atomic number and its mass number. For example, an oxygen atom ($Z = 8$) with mass number 16 contains 8 neutrons ($16 - 8 = 8$). All atoms of the same element have the same number of protons, but they do not all have the same mass. This means they do not all have the same number of neutrons. Indeed, although most hydrogen atoms found in nature have no neutrons, some have one or two; these are respectively deuterium and tritium.

Atoms of the same element that differ in their number of neutrons are called **isotopes**. Hydrogen therefore has three natural isotopes, all bearing atomic number 1, but with mass numbers of 1, 2, and 3 respectively

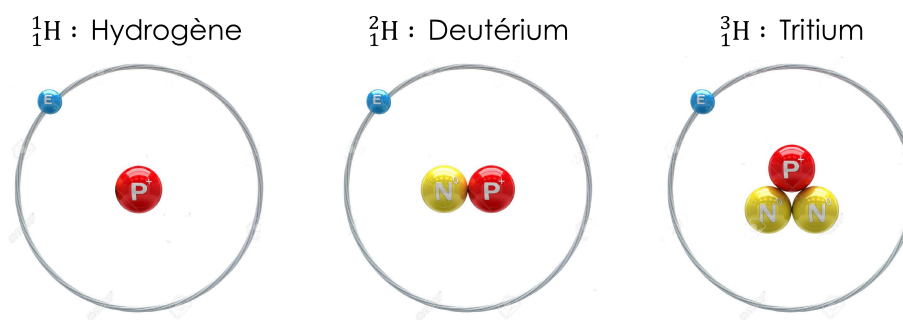


Figure 1.8 Isotopes of hydrogen

(Figure 1.8).

The two common isotopes of uranium have mass numbers 235 and 238, respectively. The first of these isotopes is used in nuclear reactors and atomic bombs. Isotopes of elements are identified by their mass number. The two isotopes mentioned above are generally called "Uranium-235" and "Uranium-238." Unlike hydrogen, where each isotope has its own name (Figure 1.8).

The chemical properties of an element are determined primarily by the protons and electrons contained in its atoms; neutrons do not participate in chemical reactions under normal conditions. This is why isotopes of the same element have identical chemical properties: they form the same types of compounds and react in the same way.

1.1.6. Atomic Mass (m)

Atomic mass (or atomic weight) is the mass of a specific atom or of a chemical element in general. Indeed, the mass of an atom is proportional, as a first approximation, to its number of nucleons, known as the mass number. In other words, the mass of an atom is the sum of the masses of its various constituents (expressed in Kg or in atomic mass units, amu).

$$m_{\text{atom}} = \Sigma m_{\text{proton}} + \Sigma m_{\text{neutron}} + \Sigma m_{\text{electron}}$$

Since the mass of atoms is very small, it is preferable to use a suitable mass scale. The reference of this relative scale is the $^{12}_6\text{C}$ atom, for which the atomic mass is exactly 12 amu (with $1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$). All atomic masses are then defined relative to this value.

The elementary reference mass, called the atomic mass unit, has been defined since the 1960s as one twelfth of the mass of the carbon-12 atom (reference atom).

$$m = 6 \times (9.1094 \times 10^{-31} + 1.6726 \times 10^{-27} + 1.6749 \times 10^{-27}) = 1.99625 \times 10^{-26} \text{ Kg}$$

This corresponds to 12 amu, so $1 \text{ amu} = 1.99625 \times 10^{-26} / 12 = 1.66 \times 10^{-27} \text{ Kg}$.

1.1.7. Avogadro's Number (N_A)

Avogadro's number is the number of elementary entities (atoms, ions, or molecules) contained in one mole of these same entities. In other words, it corresponds to the number of carbon atoms contained in 12 grams of ^{12}C carbon, approximately 6.022×10^{23} units (atoms or molecules).

If one mole of Carbon weighs 0.012 Kg, and one atom weighs $1.99625 \times 10^{-26} \text{ Kg}$, then how many atoms are there per mole?

$$N_A = 0.012 \text{ (Kg/mole)} / 1.99625 \times 10^{-26} \text{ (Kg)} = 6.022 \times 10^{23}$$

Note: The mole is the quantity that allows us to quantify matter. Since atoms and molecules are very small and therefore very light, the idea is to make a "package" of them in order to work with masses between 1 and a few tens of grams.

1.1.8. Molar Mass (M)

The molar mass of a chemical species (atomic, molecular, or ionic) is the mass of one mole of that species, or in other words, it is the mass of 6.022×10^{23} atoms, expressed in g/mole (in the cgs system) or Kg/mole (in the mKs system).

- a) In the case of atoms, it is given by the mass number A of the element appearing on the periodic table.

In general: The atomic molar mass of an element is determined by taking into account the natural abundance of the isotopes of that element (definition of isotopes – see [Page 10](#)).

$$M = \frac{\sum(x_i M_i)}{100}$$

Where: x_i denotes the natural abundance of isotope i with molar mass M_i .

Example: The classic example is that of the element Magnesium, which occurs naturally in three isotopes: 78.6% as $^{24}_{12}\text{Mg}$, 10.1% as $^{25}_{12}\text{Mg}$, and 11.3% as $^{26}_{12}\text{Mg}$. In this case, what is the average molar mass of Magnesium?

$$M_{\text{Mg}} = \frac{(78.6 \times 24) + (10.1 \times 25) + (11.3 \times 26)}{100} = 24.33 \text{ g/mole}$$

- b) In the case of molecules, it is obtained by adding all the molar masses of the constituent atoms of the molecule.

Example: What is the molar mass of the compound $\text{Mg}(\text{NO}_3)_2$?

$$M = 24.33 + (14 \times 2) + (16 \times 6) = 144.33 \text{ g/mole}$$

Exercise (1):

- a) We weigh 10g of NaCl using a balance. What is the amount in moles of NaCl in the weighed mass?
b) The 10g of NaCl are placed in a 250 mL volumetric flask. What is the molar concentration of the solution? Given: $M_{\text{NaCl}} = 58.5 \text{ g/mole}$

Exercise (2): We wish to prepare 250 mL of a 2.5 mole/L solution of copper sulfate CuSO_4 . Given: $M_{\text{Cu}} = 63.55 \text{ g/mole}$, $M_{\text{S}} = 32 \text{ g/mole}$, and $M_{\text{O}} = 16 \text{ g/mole}$.

- a) What mass of CuSO_4 should be weighed?
b) We pipette 10 mL of this solution and place it in a 250 mL volumetric flask. What is the concentration of the resulting solution?

Exercise (3): We dissolve 5 g of FeCl_3 in a 250 mL volumetric flask. Given: $M_{\text{Fe}} = 55.9 \text{ g/mole}$ and $M_{\text{Cl}} = 35.5 \text{ g/mole}$.

- a) Calculate the molar mass of FeCl_3 .
b) What is the molar concentration of the solution in FeCl_3 ?
c) What is the molar concentration of Cl^- ions?

Solution (1) : a) 0.171 mole. b) 0.684 mole/L

Solution (2): a) $m = 99.72 \text{ g}$. b) $C = 0.1 \text{ mole/L}$

Solution (3) : a) 162.4 g/mole . b) 0.123 mole/L . c) 0.369 mole/L .

The study of microscopic particles is completely different from what is observed at the macroscopic scale, hence the necessity of using quantum physics instead of classical mechanics. It is found that the energy of the electron can only take discrete values. It is then said to be quantized. **Schrödinger's** equation helps us rationalize experimental observations further, although the mathematical treatments associated with solving this equation are often quite complex.

1.2. Niels Bohr's Model

The most easily recognizable image of an atom is that of a miniature solar system in which electrons follow concentric trajectories similar to planetary orbits, with the nucleus at the center like the Sun. **Niels Bohr**⁽¹⁵⁾

suggested that electrons do not move randomly around the nucleus, but rather follow orbits (circular trajectories, or allowed orbits – stationary orbits) at a fixed distance from the nucleus (atomic radius), expressed by the following function:

$$2\pi r = n\lambda$$

n : expresses the level where the electron is located (with $n \in \mathbb{N}$) $n = \{1, 2, 3, \dots\}$

$2\pi r$: expresses the circumference of a circle (the electron's trajectory).

λ : wavelength.

In this model, each orbit is associated with a specific energy, and the electron can change orbit by emitting or absorbing energy in fixed quantities called quanta ΔE (Figure 1.11).

The goal of **Niels Bohr** was to study the behavior and energy governing the hydrogen atom, in order to best match the experimental model. Consequently, he postulated the following hypotheses:

- The electron describes a circular trajectory around the nucleus (orbit) of radius (r) (Figure 1.9).
- The electron is subjected to a Coulomb attraction force (F_1).

$$F_1 = \frac{1}{4\pi\epsilon_0} \cdot \frac{+e \cdot -e}{r^2} = -\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2}$$

Where:

- ϵ_0 : Vacuum permittivity, a measure of the degree to which the material is sensitive to the electric field in which it is placed ($\epsilon_0 = 8.85 \times 10^{-12} C^2.N^{-1}.m^{-2}$).
- e : Electron charge ($-1.602 \times 10^{-19} C$).
- The electron is subjected to a centrifugal force (F_2).

$$F_2 = \frac{mv^2}{r}$$

Where:

- v : Electron velocity.
- m : Electron mass ($9.1094 \times 10^{-31} \text{ Kg}$).

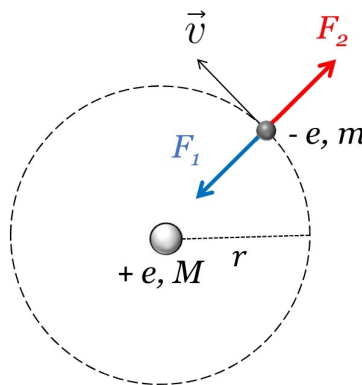


Figure 1.9 Schematic representation of **Bohr's** model

The total energy of any system (macroscopic or microscopic) obeys the following equation:

$$E_{total} = E_{kinetic} + E_{potential}$$

In the case of the hydrogen atom, consider an electron in uniform circular motion around the nucleus, assumed fixed and taken as the origin of the reference frame (a solid point with three orthogonal axes).

The total energy E_{total} of this electron is the sum of the kinetic energy and the potential energy. It is constant over time. The stability of the atom obviously depends on it. The kinetic energy is related to velocity and the potential energy is of the Coulomb type. Thus:

$$E_{potential} = \int_r^{\infty} F_1 dr = \int_r^{\infty} -\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2} dr = -\frac{1}{4\pi\epsilon_0} \cdot e^2 \int_r^{\infty} \frac{1}{r^2} dr = -\frac{1}{4\pi\epsilon_0} \cdot e^2 \left[-\frac{1}{r} \right]_r^{\infty} = -\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r}$$

Therefore:

$$E_{total} = \frac{1}{2} \cdot mv^2 + \left(-\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r} \right)$$

Since the electron, during its motion, is in equilibrium on a stable orbit, there is equality between the centripetal force (related to the radial acceleration that the electron undergoes during uniformly accelerated motion on its circular orbit) and the attractive force related to the opposite charges between electrons and proton.

$$|\vec{F}_1| = |\vec{F}_2| \Leftrightarrow \frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2} \Leftrightarrow mv^2 = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r}$$

Hence:

$$E_{total} = \left(\frac{1}{2} \cdot \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r} \right) + \left(-\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r} \right)$$

$$E_{total} = -\frac{1}{2} \cdot \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r}$$

To find the total energy, we must first know the value of the radius (r). To find the latter, we must satisfy the condition that the attractive force equals the centrifugal force ($|F_1| = |F_2|$).

$$|\vec{F}_1| = |\vec{F}_2| \Leftrightarrow \frac{mv^2}{r} = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2} \Rightarrow r = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{mv^2}$$

We notice that the radius equation is a function of velocity – a new parameter that must also be determined. **Louis Victor De Broglie's** equation will be very useful. It states that for any particle of mass (m) moving at velocity (v), we associate a wavelength (λ).

Where: (h) is a scalar quantity expressing the amount of energy (the quantum ΔE) related to its frequency (ν), given as $h = 6.626 \times 10^{-34} \text{ Joule.s}$.

$$\lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda}$$

$$r = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2 m}{h^2} \cdot \lambda^2 = \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2 m}{h^2} \left(\frac{2\pi r}{n} \right)^2 \Rightarrow r = \frac{h^2 \epsilon_0}{\pi m e^2} \left(\frac{n^2}{1} \right)$$

We notice that the radius depends on the level n . In the ground state, the electron in the hydrogen atom is at level $n=1$, therefore:

$$r = \frac{(6.626 \cdot 10^{-34})^2 \cdot 8.85 \cdot 10^{-12}}{3.14 \cdot 9.1094 \cdot 10^{-31} \cdot (1.602 \cdot 10^{-19})^2} \cdot 1^2 = 0.53 \cdot 10^{-10} m$$

In **Bohr's** model, which focuses on the simplest element, the distance between the nucleus and the single electron is 53 pm (picometers). If we assume that the hydrogen nucleus (the proton) has a diameter of 1 cm, then the distance separating it from the electron would be 1 km (of empty space or void between them). The atom has a lacunar character (there is empty space between the nucleus and the electron).

Since the system's energy is a function of the radius:

$$E_{total} = -\frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{r} = -\frac{1}{2} \cdot \frac{e^2}{4\pi\epsilon_0} \left(\frac{\pi m e^2}{h^2 \epsilon_0} \cdot \frac{1}{n^2} \right) \Leftrightarrow E_{total} = -\frac{m e^4}{8 \epsilon_0^2 h^2} \left(\frac{1}{n^2} \right)$$

We notice here also that the energy depends on the level $n = 1$. The hydrogen electron at level $n = 1$ possesses energy equal to:

$$E_{total} = -\frac{m e^4}{8 \epsilon_0^2 h^2} \left(\frac{1}{n^2} \right) = -\frac{9.1 \cdot 10^{-31} \cdot (1.602 \cdot 10^{-19})^4}{8 \cdot (8.85 \cdot 10^{-12})^2 \cdot (6.626 \cdot 10^{-34})^2} \cdot \left(\frac{1}{1^2} \right) = -2.18 \cdot 10^{-18} J = -13.6 \left(\frac{1}{n^2} \right) eV$$

Note: We know that energy can be expressed in *Joules*, but in the case of electrons, the values are very small

in this unit. It is preferable to use a similar unit, namely eV (electron-Volt – a value defined as the kinetic energy acquired by an electron accelerated from rest through a potential difference of one volt), knowing that $1\text{ eV} = 1.602 \times 10^{-19}\text{ Joule}$.

$$E_{total} = -2.18 \cdot 10^{-18} \left(\frac{1}{n^2} \right) \text{Joule} = -13.6 \left(\frac{1}{n^2} \right) eV$$

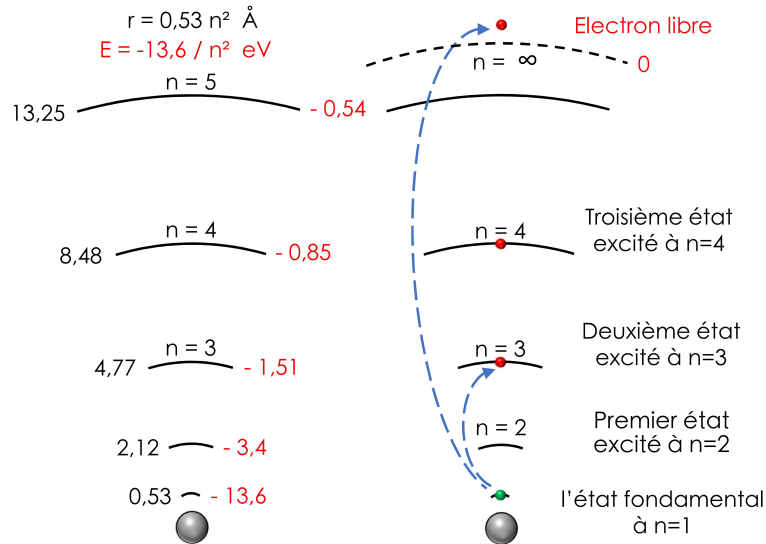


Figure 1.10 Electron excitation

- The electron at the first level ($n = 1$) is in its ground state or stable state, with an energy value of -13.6 eV at a distance from the nucleus of 0.53 Å (the proton in our case).
- If the electron changes level, for example to level three ($n = 3$), we have:
 - An electron that has absorbed energy; it is in an excited (unstable) state.
 - A bound electron, still within the nucleus's attractive field.
 - An electron that still has negative energy.
 - The electron is in the fourth excited state.
- If the electron changes level, this time to the infinite level ($n = \infty$), we have:
 - An electron that has absorbed the greatest amount of energy; we say it is in an ionized state (ionized atom).
 - A free electron, no longer dependent on the nucleus; no interaction between the two.
 - An electron with positive energy.

1.2.1. Electronic Transition

An electronic transition describes the passage of an electron from one energy level to another. In the simplest case, that of the hydrogen atom (one electron and one proton), the electron is trapped in the electric field created by the proton.

Absorption: The electron at energy level E_i , excited by electromagnetic radiation (expressed as ΔE_{f-i} , or λ_{f-i}), passes to a higher energy level E_f . The electron or atom finds itself in an excited state, energetically unstable (very short lifetime); it returns to its initial orbit and emits photons (emission).

Emission: The electron at energy level E_i (higher level), de-excites and returns to a lower energy level E_f . In this case, the electron loses energy in the form of a photon (still expressed as ΔE_{f-i} , or λ_{f-i} , for example ΔE_{1-2} , or λ_{1-2}).

Electronic transitions are expressed as an energy difference. Recall that the passage of an electron from orbit n_i to orbit n_f occurs through an energy exchange ΔE_{f-i} (Bohr's second hypothesis).

$$\Delta E_{f-i} = E_f - E_i = -\frac{me^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{me^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \cdot 10^{-18} \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \text{Joule}$$

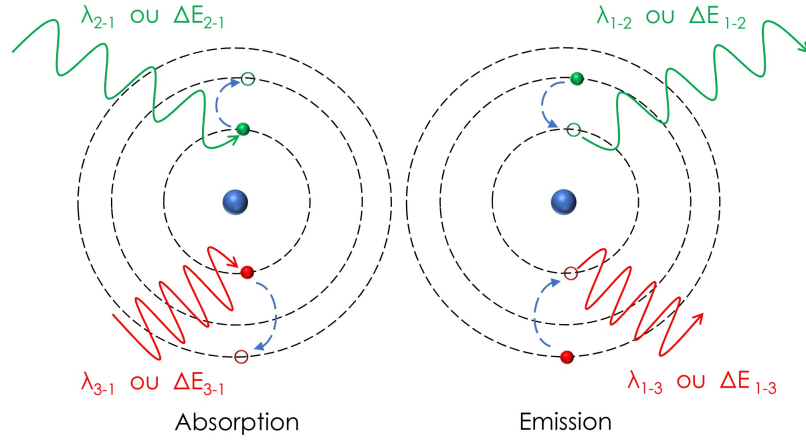


Figure 1.11 Difference between electronic transitions

Note: A photon is absorbed when the electron passes from a lower energy level to a higher energy level, i.e., when $n_i < n_f$. The value of ΔE is then positive (energy is absorbed by the electron). Conversely, a photon is emitted when the electron passes from a higher energy level to a lower energy level, i.e., when $n_i > n_f$. Consequently, the value of ΔE is negative (energy is released into the external environment). Each line in the emission spectrum then corresponds to a particular transition in the hydrogen atom. When studying a large number of hydrogen atoms at once, all possible transitions can be induced, allowing the corresponding spectral lines to be observed. The intensity of a spectral line depends on the number of photons of the same wavelength that are emitted.

Thanks to **Planck's** equation, it is possible to determine the frequency of the corresponding line. Since the energy of a photon is a positive value, we use the absolute value of ΔE in Planck's equation.

$$|\Delta E_{\text{photon}}| = h\nu$$

The results of **Bohr's** work agree perfectly with the empirical laws developed by **Balmer** for the hydrogen emission spectrum.

$$|\Delta E_{(J)}| = h\nu = h \cdot \frac{C}{\lambda} = \frac{6.626 \cdot 10^{-34}_{(J \cdot s)} \cdot 3 \cdot 10^8_{(m \cdot s^{-1})}}{\lambda_{(m)}}$$

$$|\Delta E_{(eV)}| = \frac{6.626 \cdot 10^{-34}_{(J \cdot s)} \cdot 3 \cdot 10^8_{(m \cdot s^{-1})}}{1.6 \cdot 10^{-19} \cdot \lambda_{(m)}} = \frac{6.626 \cdot 10^{-34}_{(J \cdot s)} \cdot 3 \cdot 10^8_{(m \cdot s^{-1})}}{1.6 \cdot 10^{-19} \cdot \lambda_{(m)} \cdot 10^{-10}} = \frac{12400}{\lambda_{(\text{\AA})}}$$

This relationship directly links the energy exchanged during a transition (absorption or emission of a photon) to the corresponding wavelength. It thus makes it possible to convert a spectroscopic measurement (λ) into an energy (ΔE) expressed in joules or electronvolts, and to quantitatively compare electronic transitions (the smaller λ is, the larger ΔE is). The practical form $\Delta E(\text{eV}) = 12400/\lambda(\text{\AA})$ is particularly useful for quickly estimating energy gaps and excitation/ionization energies from UV-Visible spectra.

Note: Electronic transitions, with their two types (absorption or emission) (**Figure 1.11**), are expressed as an energy difference between two energy levels (ΔE between the final and initial levels).

Each electronic transition can also be expressed with a wavelength λ or a frequency ν . It should also be noted that there is a very close relationship between these quantities.

Wavelength λ is a quantity defined for all periodic waves. It represents the distance traveled by the wave during one period T . It also corresponds to the distance over which the elementary wave pattern extends.

The light emitted by atoms is well described by a monochromatic wave. Wave theory describes light phenomena as the propagation of an electromagnetic field, i.e., both an electric field $\vec{E}$ and a magnetic field $\vec{B}$. These waves are, in most cases, progressive waves (time/space coupling) propagating at speed C (speed of light or photon in a vacuum) ($C = 3 \cdot 10^8 \text{ m/s}$).

Frequency ν is the number of times a periodic phenomenon (in our case, a wave) repeats per unit of time. Its unit in the International System of Units is the hertz (Hz).

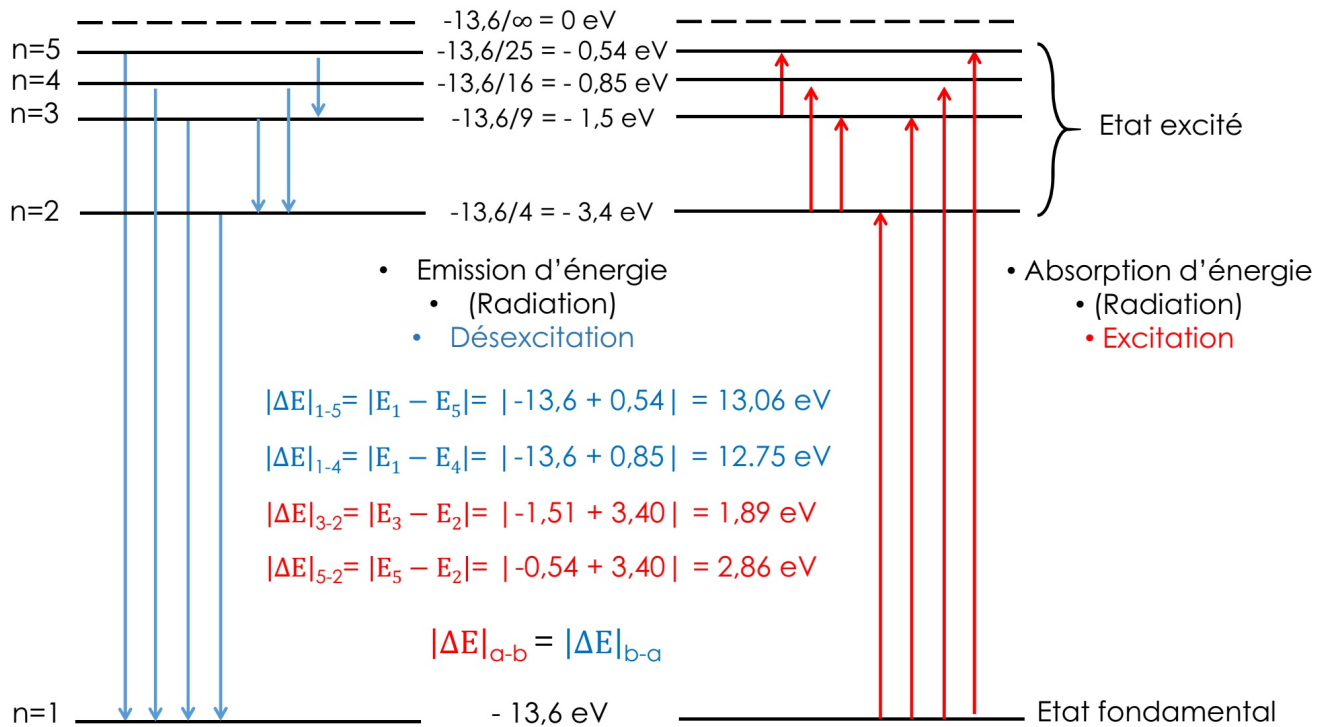


Figure 1.12 Electronic transitions for hydrogen: absorption (Red) and emission (Blue).

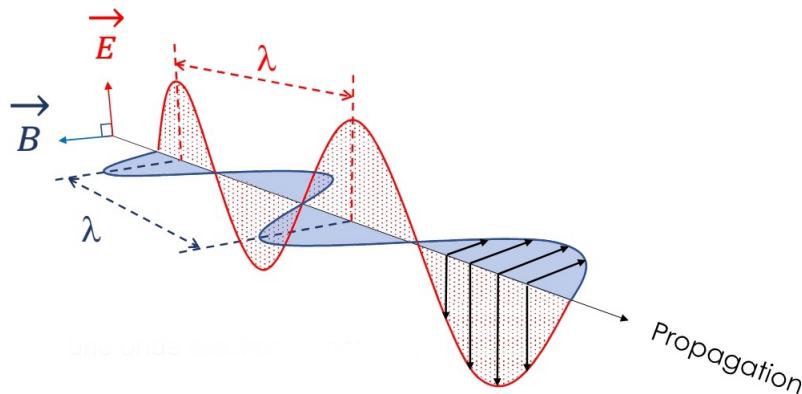


Figure 1.13 An electromagnetic wave

Key points to remember: The energy of an atom varies via electronic transitions. Concretely, this involves (at least) one of its electrons, which undergoes a transition from one energy state to another. In the context of light/matter interaction, these transitions involve light particles (photons).

Absorption: An electron is in an energy state, here called E_i . If a photon provides exactly the energy ΔE corresponding to the energy difference with a state E_f , then the photon is absorbed by the atom, and the electron undergoes a transition $E_i \rightarrow E_f$. The transition can only occur with one photon at a time.

If the photon energy is sufficient, it can ionize the atom, bringing the electron into the continuum of unbound states. Part of the photon energy thus serves to ionize the atom; the remaining energy is carried away by the electron as kinetic energy.

Spontaneous emission: When an electron is in an excited state, in our example, it can undergo a transition to a lower energy state. In the case of a so-called radiative transition, a photon is emitted, carrying away the excess energy, i.e., the difference between the two states. As its name suggests, this emission occurs spontaneously, without external intervention on the atom, randomly. The photon is also emitted in a random direction.

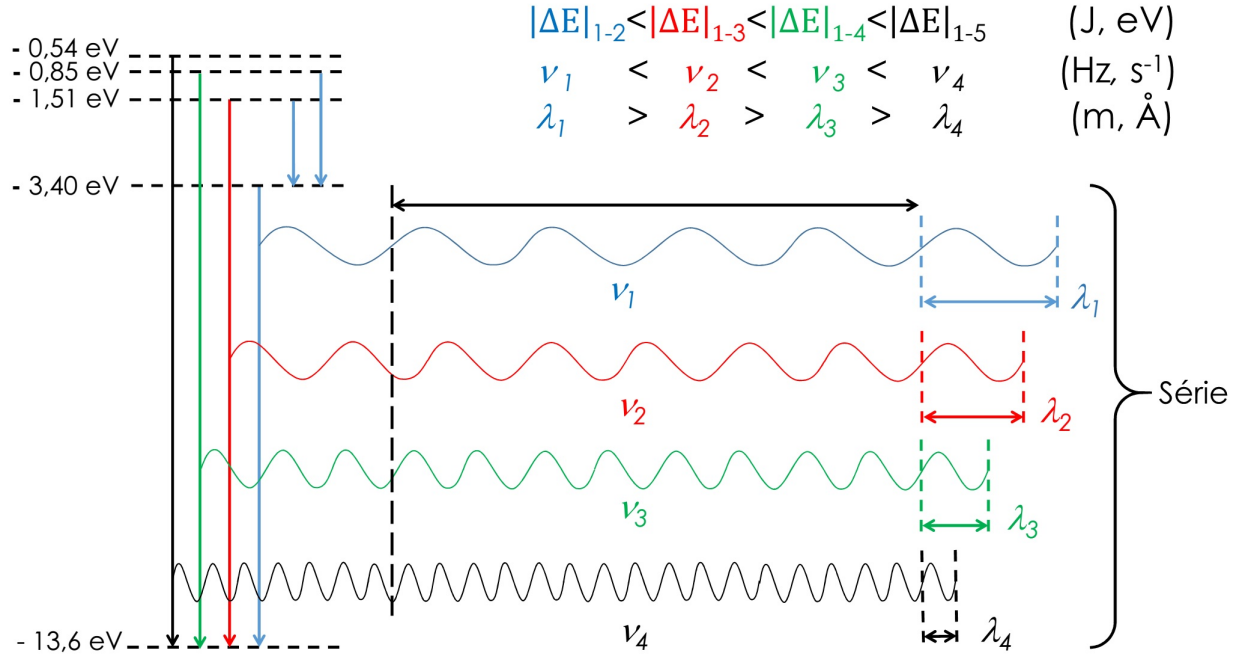


Figure 1.14 Relationship between frequency and wavelength

The emission phenomenon is considered the most important given the amount of information it can provide. Several researchers have studied the spectral lines resulting from the emission phenomenon, among them the physicist **Johann Jakob Balmer**.⁽¹⁶⁾

1.2.2. Emission Radiation

There is a direct correspondence between radiation and its wavelength. Radiation refers to the process of emitting or transmitting energy involving a wave. There are several ways to calculate the wavelength. To obtain the wavelength of radiation, simply divide its propagation speed by its frequency (it is very important to use appropriate units):

$$\nu = \frac{C}{\lambda} \Rightarrow \lambda = \frac{C}{\nu}$$

In this section, we have an electromagnetic wave resulting from an electronic transition, so we will calculate the wavelength as a function of photon energy:

$$\lambda = \frac{hC}{\Delta E}$$

1.2.2.1. Balmer Equation

In quantum mechanics, the energy difference is expressed as a function of energy levels (final and initial levels).

$$|\Delta E_{f-i}| = h\nu = h \frac{C}{\lambda}$$

And

$$|\Delta E_{f-i}| = \frac{me^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 2.18 \cdot 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Therefore:

$$\Rightarrow \frac{1}{\lambda} = \frac{2.18 \cdot 10^{-18}}{hC} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 1.097 \cdot 10^7 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Where R_H is the **Rydberg** constant, which equals $1.097 \cdot 10^7 \text{ m}^{-1}$.

The **Balmer** relation allows us to determine the wavelengths of photons emitted during transitions from

excited levels $n > 2$ of the hydrogen atom to $n = 2$.

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

The Swedish physicist **Johannes Rydberg**⁽¹⁷⁾ was inspired by **Balmer's** relation (discovered in 1885) to generalize it in order to determine the complete spectrum of light emitted by hydrogen (1888). It was later generalized to hydrogen-like ions by the Swiss physicist **Walther Ritz** in 1908.⁽¹⁸⁾

Key takeaways $\frac{1}{\lambda} = R_M \left(\frac{1}{p^2} - \frac{1}{n^2} \right)$ with $R_M = R_H \cdot Z^2$

R_M is the Rydberg constant of a chemical element and Z is its atomic number. $n, p \in \mathbb{N}^2$, n is the line index, and p is the series index. It should be known that a series is a set of lines (see the top part of [Figure 1.16](#)).

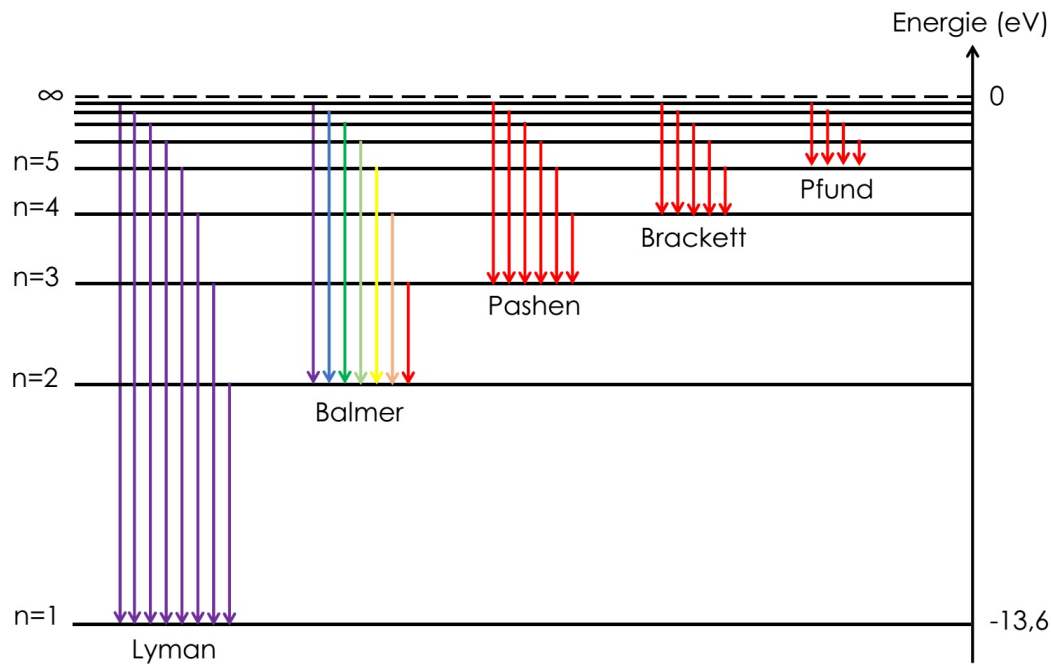


Figure 1.15 Spectral series of the hydrogen atom

Table 1.2 Spectral series of the hydrogen atom

p	n	Series	Domain
1	2,3,4 ...	Lyman (1906)	Ultraviolet
2	3,4,5 ...	Balmer (1885)	Visible Light
3	4,5,6 ...	Paschen (1908)	Near Infrared

p	n	Series	Domain
4	5,6,7 ...	Brackett (1922)	Mid Infrared
5	6,7,8 ...	Pfund (1924)	Far Infrared
6	7,8,9 ...	Humphreys (1953)	Far Infrared

The emission spectrum of the hydrogen atom is the set of electromagnetic waves that can be emitted by an excited hydrogen atom (having received energy). This is obtained experimentally in a tube containing dihydrogen equipped with two metal electrodes. A discharge is operated and partially ionizes the dihydrogen. The generated ions are accelerated by the potential difference between the two electrodes and collide at high speed with the dihydrogen molecules, causing dissociation into hydrogen atoms and excitation of the formed atoms. The atoms retain this excess energy for only a very short time. They release it in the form of light (they are said to de-excite).

The emitted radiation consists of a series of lines of different wavelengths. This is the emission spectrum of the hydrogen atom ([Figure 1.17](#)).

Experimental observations Examining the experimental results, we observe the following facts:

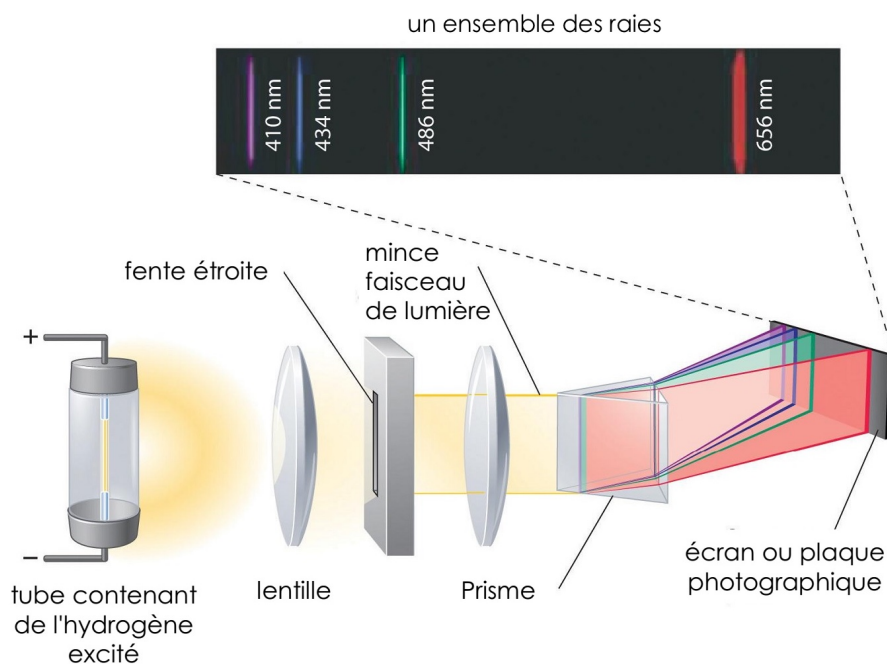


Figure 1.16 Balmer's experiment on spectral lines.

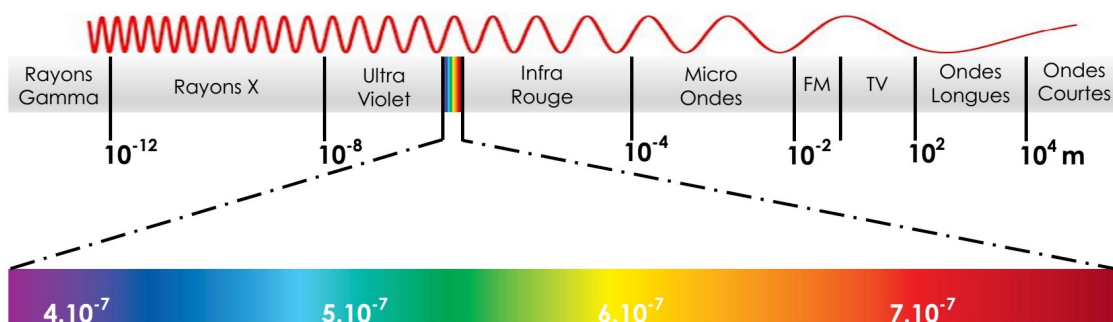


Figure 1.17 Electronic spectroscopy

- Only certain radiations, with very specific energies, are emitted by the hydrogen atom. Represented on a wavelength-graduated axis, the spectrum takes the form of a set of lines (**Figure 1.16**). The emission spectrum of the hydrogen atom is typically described as a line spectrum. The energy of the emitted radiation is quantized (a concept introduced by **Planck** as early as 1900).
- The lines appear in groups: the spectrum is composed of several series of lines. The first series was observed by **Balmer** (series located in the visible domain). **Lyman** discovered a series in the ultraviolet, then **Paschen** located a new series in the infrared domain. After **Bohr's** theories, **Brackett** and **Pfund** identified two new series.
- Within the same series, the lines are not separated by the same wavelength: the lines get closer as the wavelength decreases and seem to tend toward a limit line.

It is possible to observe the absorption spectrum of an atom. To obtain the atomic absorption spectrum, a sample containing atoms of this element in the gaseous state is subjected to incident radiation. The latter consists of a continuous spectrum (it contains all wavelengths). The radiation is analyzed after passing through the sample; it no longer contains the wavelengths that were absorbed (these wavelengths are the same as those revealed by an atomic emission spectrum of the same element). In practice, an absorption spectrum appears as a continuous spectrum in which certain radiations are missing (absorbed). The absorbed radiations appear as thin black lines. Quite empirically, spectroscopists have observed that the frequency or wavenumber σ of the emitted (or absorbed) radiation in the case of the hydrogen atom satisfies the following relation, known as the **Ritz-Rydberg** relation:

Key takeaways

$$\sigma = \frac{1}{\lambda} = R_H \left(\frac{1}{p^2} - \frac{1}{n^2} \right)$$

Note: The constant R_H applies only to the emission spectrum of the hydrogen atom. Furthermore, pay attention to units: if it is in cm^{-1} , the wavenumber sigma will be in cm^{-1} and subsequently λ in cm . If the unit is in meters or nanometers, conversion is necessary.

Key equations to remember:

Relationship between photon energy and its frequency	$E = h\nu$
Relationship between photon energy and its wavelength	$E = h\frac{C}{\lambda}$
Energy of an electron in the nth energy state of a hydrogen atom (eV)	$E_n = \frac{-13.6}{n^2}$
Energy change during an electronic transition from level n_i to level n_f	$\Delta E_{f-i} = -13.6 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$
Relationship between photon energy and energy change during an electronic transition	$E_{\text{photon}} = \Delta E_{f-i} $
Distance between electron in its nth level and the hydrogen nucleus (Å)	$r_n = 0.53 \cdot n^2$
Relationship between electronic transition levels and wavelength (cm)	$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$

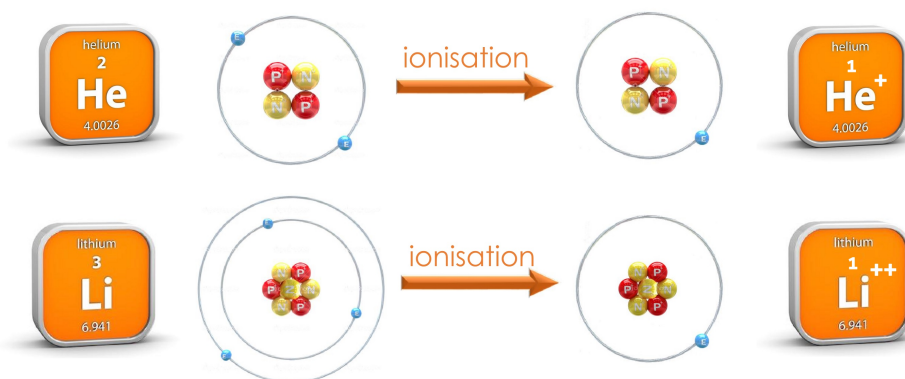
Transition

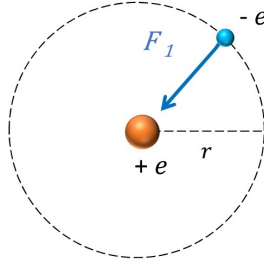
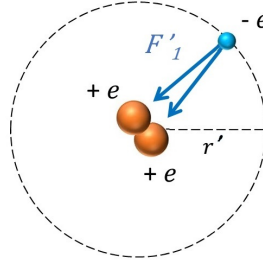
From the Bohr model to the hydrogen-like model.

The Bohr model introduced the essential idea of quantized energy levels for the electron, which accounts for the stability of the hydrogen atom and its spectral lines. However, its domain of validity remains limited and its construction remains semi-classical. The natural generalization consists of retaining the same framework (a single electron bound to the nucleus by Coulomb interaction) by replacing the nuclear charge $+e$ with $+Ze$. This yields the **hydrogen-like** model, applicable to all one-electron species (H, He^+ , Li^{2+} , etc.). In this framework, increasing Z strengthens the nucleus-electron attraction: the energy levels become deeper (stronger binding) and the characteristic dimensions of the atom contract. This transition thus prepares the systematic study of hydrogen-like ions and highlights the central role of Z in electronic structure.

1.2.3. Hydrogen-like Ions

A hydrogen-like ion is a monoatomic cation that possesses only one electron, like hydrogen (it has an electronic structure similar to that of the hydrogen atom: $1s^1$). It is therefore an atom from which ($Z-1$) electrons have been removed, except that the nucleus still contains Z protons, which can influence the attractive force F_1 between the nucleus and the electron (NB: Z is also called the charge number). The following figure illustrates this definition:



Quantity	Hydrogen	Hydrogen-like
Attractive force	$F_1 = -\frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r^2}$ 	$F'_1 = \frac{1}{4\pi\epsilon_0} \cdot \frac{(\mathbf{Z} \cdot +e) - e}{r'^2} = -\frac{1}{4\pi\epsilon_0} \cdot \frac{\mathbf{Z} e^2}{r'^2}$ 
Radius	$r = \frac{h^2\epsilon_0}{\pi m e^2} (n^2)$	$r' = \frac{h^2\epsilon_0}{\pi m \mathbf{Z} e^2} (n^2) = \frac{r}{\mathbf{Z}}$
Energy	$E = -\frac{m e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2} \right) = -13.6 \cdot \left(\frac{1}{n^2} \right)$	$E' = -\frac{m \mathbf{Z}^2 e^4}{8\epsilon_0^2 h^2} \left(\frac{1}{n^2} \right) = -13.6 \cdot \left(\frac{\mathbf{Z}^2}{n^2} \right)$
Energy difference	$\Delta E = -13.6 \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$	$\Delta E' = -13.6 \mathbf{Z}^2 \cdot \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$
Wavelength	$\lambda = \left[R_H \cdot \left(\frac{1}{p^2} - \frac{1}{n^2} \right) \right]^{-1}$	$\lambda' = \left[\mathbf{Z}^2 R_H \cdot \left(\frac{1}{p^2} - \frac{1}{n^2} \right) \right]^{-1}$

1.2.4. Polyelectronic Atoms

In a hydrogen-like (one-electron) atom, the calculation of energy levels is relatively simple because there is no electron-electron interaction. However, in a polyelectronic atom, each electron interacts not only with the nucleus but also with all the other electrons. This complexity makes the exact solution of the Schrödinger equation impossible, forcing us to use approximations.

In a polyelectronic atom, a given electron (especially if it is an outer electron) is separated from the nucleus by other electrons. These form a kind of "barrier" that reduces the attraction the nucleus exerts on it: this is the **screening effect** (or shielding effect).

Consequently, the nuclear attraction force on this electron is weaker than in a one-electron model (where there are no other electrons to screen). This reduction in attraction modifies the energy levels and therefore the observed spectral lines.

To simply model this situation, we consider that a given electron is subject to the action of a nucleus with a reduced charge, called the **effective nuclear charge**, denoted $\mathbf{Z}^*$. We consider that a given electron is subject to the action of a nucleus with an effective charge $\mathbf{Z}^*$ lower than the charge number Z of the atom's nucleus.

$$\mathbf{Z}^* = Z - \sum \sigma_{j-i}$$

where:

- $\mathbf{Z}$ is the atomic number (number of protons in the nucleus).

- is the **screening constant**, which represents the average effect exerted by other electrons on the electron under consideration (the white sphere in our example).
- The sum $\sum \sigma_{j-i}$ is the sum of the screening constants of all other electrons j on electron i .

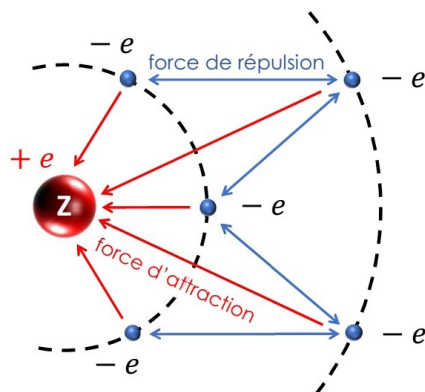


Figure 1.18 Intra-atomic interactions in a polyelectronic atom.

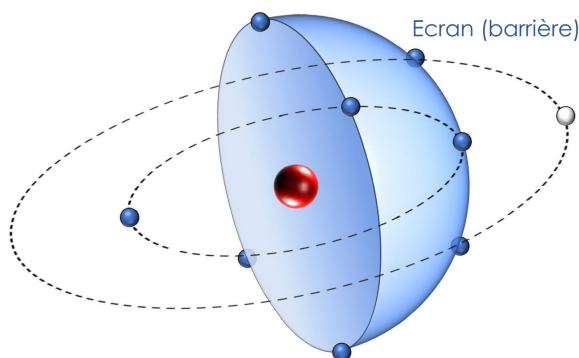


Figure 1.19 Screening effect: $Z_{\text{eff}} = Z - \sigma_j$. Inner electrons mask nuclear charge.

To remember: $\sigma_j = 0.85$ (same shell except target); 0.35 (shell $j - 1$); 0 (inner shells).

What does a screening constant mean?

The screening constant σ depends on the orbital in which the electron is located. In general:

- Electrons in inner shells (closer to the nucleus) screen very well (high σ).
- Electrons in the same shell provide partial screening (moderate σ).
- Electrons in outer shells provide almost no screening on inner electrons ($\sigma \approx 0$).

To calculate these constants, we often use **Slater's rules**,⁽¹⁹⁾ which allow us to estimate σ based on the atom's electronic configuration. These rules establish that:

- Electrons in shells inner to that of the electron under consideration contribute fully to screening ($\sigma = 0.85$ or 1 depending on the shell).
- Electrons in the same shell contribute partially ($\sigma = 0.35$ for valence electrons).
- Electrons in outer shells do not contribute to screening ($\sigma = 0$).

Table 1.3 Screening coefficients σ according to Slater's rules

level j \ level i	1s	2s2p	3s3p	3d	4s4p	4d
1s	0.31	0	0	0	0	0
2s2p	0.85	0.35	0	0	0	0
3s3p	1	0.85	0.35	0	0	0
3d	1	1	1	0.35	0	0
4s4p	1	1	0.85	0.85	0.35	0
4d	1	1	1	1	0.85	0.35

1.2.4.1. Effective Nuclear Charge

In quantum chemistry, the **effective nuclear charge**, usually denoted Z^* , is a fundamental dimensionless quantity that expresses the Coulomb attraction *actually felt* by a valence electron in a polyelectronic atom. This quantity accounts for the attenuation of nuclear attraction due to the presence of other electrons, which exert a *screening effect*.

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

where Z represents the atomic number and σ the screening constant, calculated according to the empirical rules established by Slater in 1930. The value of Z^* is a pure number, generally between 2 and 10 for the valence electrons of p -block elements in the periodic table.

Numerical Illustration Consider the chlorine atom ($Z = 17$) with the electron configuration:

$$1s^2 2s^2 2p^6 3s^2 3p^5$$

For an electron belonging to the $3p$ subshell, the systematic application of **Slater's** rules leads to the following evaluation of the screening constant:

$$\sigma = \underbrace{6 \times 0.35}_{\text{electrons } 3s3p} + \underbrace{8 \times 0.85}_{\text{electrons } 2s2p} + \underbrace{2 \times 1.00}_{\text{electrons } 1s} = 10.9$$

The effective charge equation then immediately gives the effective nuclear charge:

$$Z^* = 17 - 10.9 = 6.1$$

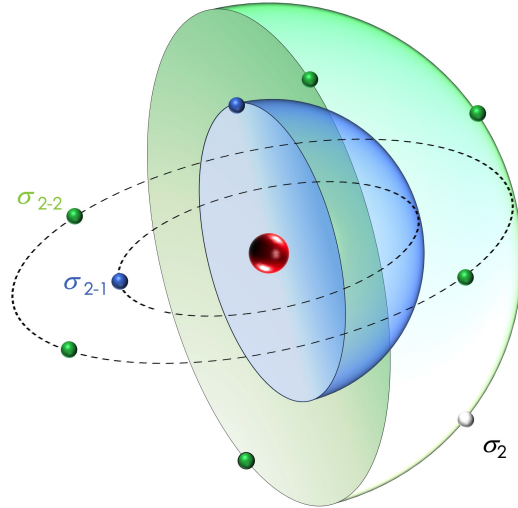
The effective nuclear charge is a determining parameter for all fundamental atomic properties. Within the hydrogen-like model framework, the energy of an atomic orbital is expressed as:

$$E_n \approx -13.6 \frac{Z^{*2}}{n^2} \quad (\text{eV})$$

Visualization of the Screening Effect:

Take an atom X for which we want to calculate the screening constant (σ_2) of one of its peripheral electrons (white sphere, located on the outermost level, in this example $j = 2$). This electron will undergo an influence (repulsion forces) exerted by the electrons i of level j and $j - 1$:

$$\sigma_j = \sum \sigma_{j-i} \Leftrightarrow \sigma_2 = \sigma_{2-1} + \sigma_{2-2} \quad \sigma_2 = 2 \cdot (0.85) + 6 \cdot (0.35) \quad \sigma_2 = 3.8$$



Extension to the Polyelectronic Model: The generalization of the hydrogen-like model to polyelectronic atoms is achieved by systematically substituting the atomic number Z with the effective nuclear charge Z^* in all expressions of physical quantities. This substitution, although approximate, accounts for the shielding of inner electrons and provides remarkably accurate estimates of atomic properties.

Effective Coulomb Force: The attractive force between the nucleus and a valence electron, after taking into account the screening effect, is written:

$$F = -\frac{1}{4\pi\epsilon_0} \cdot \frac{Z^*e^2}{r^2}$$

where the effective nuclear charge Z^* (dimensionless) appears as a multiplicative factor of e the elementary charge .

Effective Orbital Parameters: In this formalism, the orbital radius (mean value of the electron-nucleus distance) and the total electron energy take the following adapted forms:

$$r_n = \frac{h^2\epsilon_0}{\pi m e^2} \cdot \frac{n^2}{Z^*} = a_0 \cdot \frac{n^2}{Z^*}$$

where $a_0 = \frac{h^2 \epsilon_0}{\pi m e^2} \approx 0.529 \text{ \AA}$ denotes the **Bohr** radius.

$$E_n = -\frac{m e^4}{8 \epsilon_0^2 h^2} \cdot \frac{Z^{*2}}{n^2} = -13.6 \cdot \frac{Z^{*2}}{n^2}$$

Electronic Transitions: The energy involved during a transition between two levels n_i and n_f ($n_f > n_i$ for absorption, $n_f < n_i$ for emission) is expressed by:

$$|\Delta E| = 13.6 \cdot Z^{*2} \cdot \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right|$$

The corresponding wavelength of the emitted or absorbed electromagnetic radiation is then given by:

$$\lambda = \left[Z^{*2} \cdot R_H \cdot \left(\frac{1}{p^2} - \frac{1}{n^2} \right) \right]^{-1}$$

where $R_H \approx 1.097 \times 10^7 \text{ m}^{-1}$ represents the Rydberg constant for the hydrogen atom, and where p and n denote the lower and upper principal quantum numbers respectively ($p < n$).

These expressions, although derived from a one-electron model, provide satisfactory quantitative estimates for many polyelectronic atoms, particularly for describing:

- successive ionization energies.
- emission spectra of alkali atoms (where the valence electron is weakly bound to the nucleus).
- periodic trends in atomic and covalent radii.

The main limitation lies in the lack of explicit consideration of interelectronic repulsion and exchange effects, which would require more sophisticated methods (Hartree-Fock, configuration interaction).

Remarks: The evolution of Z^* in the periodic table follows a dual trend:

- **Along a period (row):** Z^* **increases** regularly from left to right, because the increase in atomic number Z is only partially compensated by a nearly stationary screening effect.
- **Down a group (column):** Z^* **decreases** when descending the classification, as the increase in the principal quantum number n is accompanied by a greater screening effect from inner electrons.

Concrete "Biomedical" Example: The relevance of effective nuclear charge extends well beyond theoretical chemistry to find concrete applications in biomedical sciences:

- In hemoglobin, the Fe^{2+} ion has an effective nuclear charge $Z^* \approx 4.8$ for its $3d$ electrons, a value that directly determines its coordination properties and its ability to reversibly bind dioxygen.
- The reactivity of halogens also illustrates the importance of Z^* : fluorine ($Z^* \approx 7.0$) exhibits significantly higher electronegativity than iodine ($Z^* \approx 5.2$), justifying the particular stability of iodinated derivatives used in pharmacy.

Concrete Example on the Sodium Atom ($Z = 11$): Consider the valence electron of sodium, located on the $3s$ shell (electron configuration $1s^2 2s^2 2p^6 3s^1$). This electron is partially shielded from nuclear attraction by the electrons in inner shells.

Let us apply Slater's rules for an ns or np electron (belonging to the $[3s, 3p]$ group):

- Contribution from other electrons in the same $[3s, 3p]$ group: the $3s$ electron being alone in this group, this contribution is zero ($0 \times 0.35 = 0$).
- Contribution from electrons in the $(n - 1)$ shells, i.e., $[2s, 2p]$ (8 electrons): $8 \times 0.85 = 6.80$.
- Contribution from electrons in the $(n - 2)$ and lower shells, i.e., $[1s^2]$ (2 electrons): $2 \times 1.00 = 2.00$.

The total screening constant σ is therefore:

$$\sigma = 0 + 6.80 + 2.00 = 8.80$$

The effective nuclear charge felt by the $3s$ electron is then:

$$Z^* = Z - \sigma = 11 - 8.80 = 2.20$$

Physical Interpretation: The obtained value $Z^* = 2.2$ means that the $3s$ electron of sodium evolves in an effective central potential equivalent to that of a nucleus with charge $+2.2 \times e$. This reflects an incomplete attenuation of nuclear attraction by inner electrons. Within the hydrogen-like model framework, the energy of this electron is written:

$$E_{3s} = -\mathcal{R} \frac{Z^{*2}}{n^2}, \quad \text{with } \mathcal{R} = 13.6 \text{ eV (Rydberg energy), } n = 3$$

The numerical application gives:

$$E_{3s} = -13.6 \times \frac{(2.20)^2}{9} = -13.6 \times 0.538 \approx -7.31 \text{ eV}$$

The experimental ionization energy of sodium is $E_I = 5.14 \text{ eV}$. The difference from our estimate is explained by the approximate nature of Slater's rules, which neglect, among other things, electron correlation and exchange effects.

For comparison, a single electron subjected to a Coulomb potential of charge $+1$ would have energy, at $n = 3$:

$$E_{n=3}^{(Z=1)} = -13.6 \times \frac{1^2}{9} \approx -1.51 \text{ eV}$$

The much lower energy (in algebraic value) obtained with $Z^* = 2.2$ (-7.31 eV instead of -1.51 eV) quantitatively illustrates the influence of effective charge: the $3s$ electron is much more bound than a simple $+1$ charge would suggest, which justifies the measured ionization energy, intermediate between that of a hydrogen-like ion of charge $+1$ and that of a hydrogen-like ion of charge $+2$.

To directly relate the ionization energy to the effective charge, we can write:

$$E_I = -E_{3s} = \mathcal{R} \frac{Z^{*2}}{n^2}$$

This would give with our estimate:

$$E_I \approx 13.6 \times \frac{4.84}{9} \approx 7.31 \text{ eV}$$

The experimental value (5.14 eV) would correspond to a slightly lower effective charge:

$$Z_{\text{exp}}^* = \sqrt{\frac{E_I^{\text{exp}} \times n^2}{\mathcal{R}}} = \sqrt{\frac{5.14 \times 9}{13.6}} = \sqrt{3.40} \approx 1.84$$

This difference between $Z^* = 2.20$ (Slater) and $Z_{\text{exp}}^* \approx 1.84$ illustrates the limitations of the simple Slater model, which slightly overestimates the screening for valence electrons of light elements.

1.3. Limitations of the Bohr Model

The Bohr model successfully reproduces the energy levels of the hydrogen atom and hydrogen-like ions (such as He^+ or Li^{2+}), via the formula:

$$E_n = -\frac{13.6 Z^2}{n^2} \text{ eV}$$

However, it quickly proves incapable of describing atoms with several electrons, for several fundamental reasons:

- It completely neglects electron-electron interactions (Coulomb repulsion), yet essential in polyelectronic atoms.
- It allows calculation of line wavelengths, but not their **intensity**, which depends on transition probabilities.
- It fails to explain phenomena such as the **Zeeman effect** (splitting of spectral lines under a magnetic field), because it ignores the existence of electron spin.
- Finally, the notion of a well-defined electron orbit is incompatible with the wave-particle duality principle proposed by Louis de Broglie in 1924.

The Quantum Mechanics Revolution Schrödinger's equation (1926) marks a profound conceptual break. It abandons the deterministic description of trajectories in favor of a probabilistic approach. The state of the electron is no longer described by an orbit, but by a **wave function** $\psi(\vec{r}, t)$. The square of its modulus, $|\psi|^2$, represents the probability density of finding the electron at a point in space. This is called an **atomic orbital**.

This interpretation is in perfect agreement with Heisenberg's uncertainty principle:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

which states that it is impossible to know both the position and momentum of a particle with precision, rendering the very idea of a trajectory obsolete.

1.3.1. Schrödinger's Equation:

In 1926, **Schrödinger** established the equation of motion associated with the electron of the hydrogen atom.

$$(E_c + E_p)\Psi = (E_t)\Psi \Leftrightarrow -\frac{h^2}{8\pi^2m}\nabla^2\Psi - \frac{1}{4\pi\epsilon_0} \cdot \frac{e^2}{r}\Psi = E_t\Psi$$

or, it is written:

$$-\frac{h^2}{8\pi^2m}\nabla^2\Psi + (E_p - E_t)\Psi = -\frac{h^2}{8\pi^2m}\left(\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right) + (E_p - E_t)\Psi = 0$$

Where:

- Ψ : wave function, depends on three variables x, y, z called spatial variables.
- ∇ : the Laplace operator, kinetic energy associated with the motion of the electron.
- h : Planck's constant.
- E_t : total energy.
- E_p : potential energy.
- m : electron mass.

Note: A new term appears Ψ which we write as $\Psi(x, y, z)$, it is the wave function associated with the electron or wave associated with the electron, according to the postulate of **Louis Victor De Broglie**.⁽²⁰⁾

With this approach, we will replace the classical notion of exact position at an instant t with the notion of elementary probability of presence dP inside a volume dV . This probability is expressed by the following relation.

$$\frac{dP}{dV} = |\Psi(x, y, z)|^2$$

If we want to calculate the probability $P(V)$ of finding the particle inside a finite volume, we must integrate the elementary probability over this volume.

$$P(V) = \int_v |\Psi(x, y, z)|^2 dv$$

To solve this differential equation with three variables, we must replace Cartesian coordinates (x, y, z) with spherical polar coordinates (r, ϑ, φ) .

This figure shows spherical polar coordinates for a particle confined to the surface of a sphere.

Note: The wave function $\Psi(x, y, z)$ has no direct physical meaning.

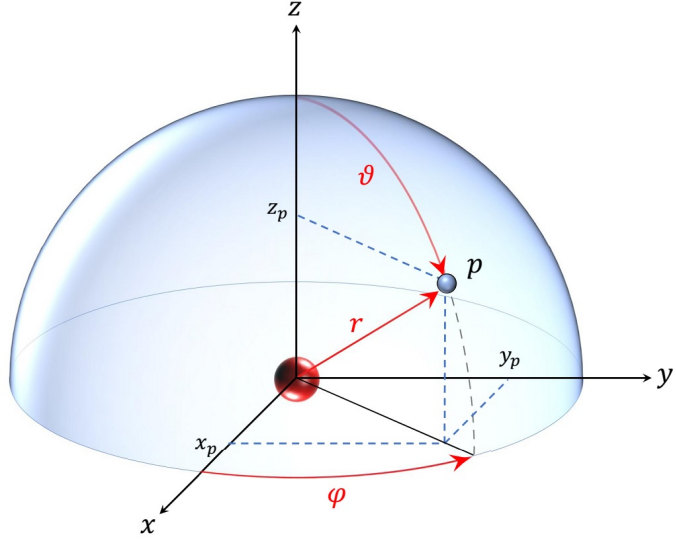
In Cartesian coordinates:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In spherical coordinates:

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{r^2 \sin^2 \vartheta} \frac{\partial^2}{\partial \varphi^2}$$

$$\begin{cases} x = r \sin \vartheta \cos \varphi & 0 \leq r \leq \infty \\ y = r \sin \vartheta \sin \varphi & 0 \leq \vartheta \leq \pi \\ z = r \cos \vartheta & 0 \leq \varphi \leq 2\pi \end{cases}$$



To make the equation simpler to solve, we separate its variables and obtain three differential equations with a single variable, for the hydrogen atom for example.

$$E_t \Psi(r) = E_c + E_p = -\frac{\hbar^2}{2m} \nabla^2 \Psi(r) - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \Psi(r)$$

$$E_t \Psi = -\frac{\hbar^2}{8\pi^2 m} \frac{1}{r^2 \sin \vartheta} \left[\sin \vartheta \frac{\partial}{\partial r} \left(r^2 \frac{\partial \Psi}{\partial r} \right) + \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial \Psi}{\partial \vartheta} \right) + \frac{1}{\sin \vartheta} \frac{\partial^2 \Psi}{\partial \varphi^2} \right] - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \Psi(r)$$

The mathematical expression of the hydrogen wave function is written in two parts: the Radial part $R(r)$ and the Angular part $Y(\vartheta, \varphi)$.

$$\Psi(r, \vartheta, \varphi) = \underbrace{R(r)}_{n, \ell} \overbrace{P(\vartheta) F(\varphi)}^{\ell, m} = R_{n, \ell}(r) Y_{\ell, m}(\vartheta, \varphi)$$

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

$$Y_{\ell, m}(\vartheta, \varphi) = \sqrt{\frac{2\ell+1}{2} \cdot \frac{(\ell-|m|)!}{(\ell+|m|)!}} P_\ell^{|m|}(\cos \vartheta) \cdot \sqrt{\frac{1}{2\pi}} e^{im\varphi}$$

Where:

- a_0 : Bohr radius.
- r : electron-nucleus distance at instant t .
- $L_{n+\ell}^{2\ell+1}$ and P_ℓ^m : Legendre polynomials (particular solutions of the equation).
- n, m, ℓ : quantum numbers.

There exists an infinite number of solutions to this equation, and only those with physical meaning are retained, which imposes precise properties on this probability density in its domain of definition. The solutions of **Schrödinger's** equation: $\Psi_1, \Psi_2, \dots, \Psi_n$, exist only for certain well-defined values of the total electronic energy $E_1, E_2, \dots, E_n$.

At energy level E_1 (ground state) characterized by $n = 1$, the solution of the equation corresponds to the wave function Ψ_1 .

$$a_0 = \frac{\hbar^2 \epsilon_0}{m \pi e^2} \quad E_1 = -\frac{e^2}{8\pi \epsilon_0 a_0} \quad \Psi_1 = \sqrt{\frac{1}{\pi a_0^3}} \cdot e^{-\left(\frac{r}{a_0}\right)}$$

We note that the wave function Ψ_1 depends only on one spatial variable r , since the other two spatial variables ϑ, φ do not appear in its expression. But the other solutions of the Schrödinger equation, associated with energy levels $n = 2, 3 \dots$ etc., are of the form $\Psi_i(r, \vartheta, \varphi)$. This dependence on ϑ, φ introduces, during the resolution of the equation, two other quantum numbers called ℓ and m , associated respectively with each of

these variables.

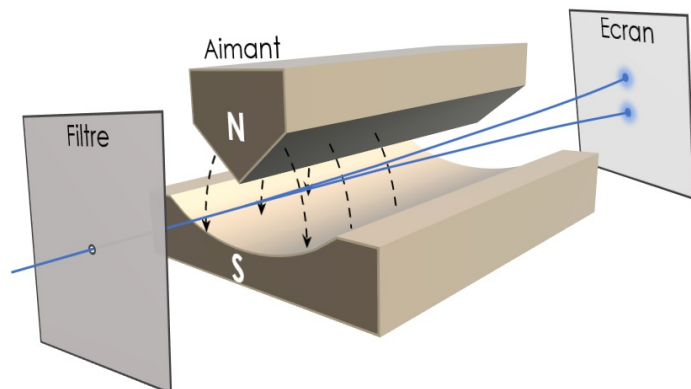
therefore: the function Ψ is the solution of **Schrödinger's** equation; it depends on the three variables n, ℓ and m , named quantum numbers.

1.3.2. Quantum Numbers

The wave function of the electron depends on three spatial coordinates, whether Cartesian (x, y, z) or spherical (r, ϑ, φ) . The latter are used when solving the Schrödinger equation, which naturally leads to the introduction of three quantum numbers. The orbital is defined by the first three quantum numbers:

- **Principal quantum number (n):** an integer that can take non-zero values ($n \in \mathbb{N}^*$ i.e., 1, 2, 3 ...). It defines the level (shell), the orbital size (its radius), and also its energy.
- **Secondary or azimuthal quantum number (ℓ):** also called the orbital angular momentum quantum number. It defines the subshell and the orbital shape ($\ell \in \mathbb{N}$) with: $0 \leq \ell \leq n - 1$.
 - For the first level ($n = 1$), we have $\ell = 0$ (since $0 \leq \ell \leq n - 1$), so we have a single value of spherical geometry called the **s** orbital (from the word **Sharp**). This term comes from the emission spectra of alkali metals (Na, K...) studied by Rydberg (1889). The sharp series designated particularly distinct and narrow spectral lines, corresponding to transitions to the $\ell = 0$ state. Sommerfeld (1916) adopted the notation *s* for the quantum number $\ell = 0$. The spherical shape was discovered later.
 - For the second level ($n = 2$), we have $\ell = 0, 1$: two values, two geometric shapes. The first for $\ell = 0$ has a spherical geometry (**s** orbital). The second for $\ell = 1$ is called **principal** (**p** orbital), with a two-lobe geometry. In alkali metal spectra, the principal series grouped the most intense and characteristic lines (visually more important), also visible in absorption (such as the yellow sodium doublet). Rydberg identified them in 1881 as transitions to $\ell = 1$. Sommerfeld kept *p* for $\ell = 1$.
 - For the third level ($n = 3$), we have $\ell = 0, 1, 2$, therefore three geometric shapes: for $\ell = 0$ a spherical shape (**s** orbital); for $\ell = 1$ a **p** type orbital; for $\ell = 2$ a geometric shape with up to four lobes (Figure 1.29), called **diffuse d**. In alkali spectra, the diffuse series (spread out, blurred) presented visually broadened and fuzzy lines, caused by fine energy splitting of atomic levels (doublets/triplets) of $\ell = 2$ levels. Kayser and Runge (1890) distinguished them from sharp lines. Sommerfeld assigned *d* to $\ell = 2$.
 - For the fourth level ($n = 4$), $\ell = 0, 1, 2, 3$, we have one more orbital compared to the third level, called **fundamental**, with a very specific geometric shape (Figure 1.32), called the **f** orbital type. Origin of *f*: Fourth and final spectral series of alkalis (discovered by Rydberg), called the fundamental series because it completes the scheme of the 4 series (principal, sharp, diffuse, fundamental). Lines with complex fine structure, transitions to $\ell = 3$. Sommerfeld assigned *f* to $\ell = 3$.
- **Tertiary or magnetic quantum number m, m_ℓ :** defines the orientation of orbitals in space, ($m \in \mathbb{Z}$) and $-\ell \leq m \leq +\ell$. Like the previous quantum number, m is a set of values (an interval). For example, at the third level ($n=3$) and on the **d** atomic orbital ($\ell = 2$), and $-2 \leq m \leq +2$, we find $m = \{-2, -1, 0, +1, +2\}$. We see that we have five values corresponding to five orientations in space and consequently five atomic orbitals of type **d** ($d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$)
- **Magnetic spin quantum number s, m_s :** The so-called "intrinsic" quantum numbers express a unique quantum state of an electron in an atom (quantum box to be more precise). It also signifies the intrinsic angular momentum of particles, essential in quantum mechanics.

Stern-Gerlach Experiment: showed that in quantum mechanics, one cannot use only the angular momentum L , a vector operator that has three components, each corresponding to different spatial dimensions.



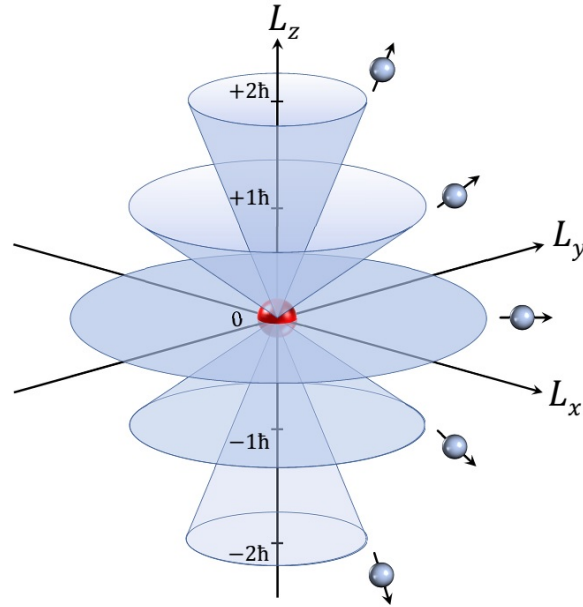


Figure 1.20 Vector model of the number m_ℓ for the azimuthal quantum number $\ell = 2$.

To explain this experiment, one must distinguish between angular (kinetic - orbital) momentum related to the electron's rotation around the nucleus and intrinsic angular momentum or spin s (from the verb to spin) for the particle's rotation about itself. This quantum number can take only two values.

$s = +1/2$ denotes spin up, or an upward-pointing arrow $\uparrow$

$s = -1/2$ denotes spin down, or a downward-pointing arrow $\downarrow$

This means that if a magnetic field is applied to the electron and it is considered as a dipole, it will align either parallel to the field, the most stable position ($s = +1/2$), or antiparallel to the field, the less stable position ($s = -1/2$). These positions correspond to two energy levels.

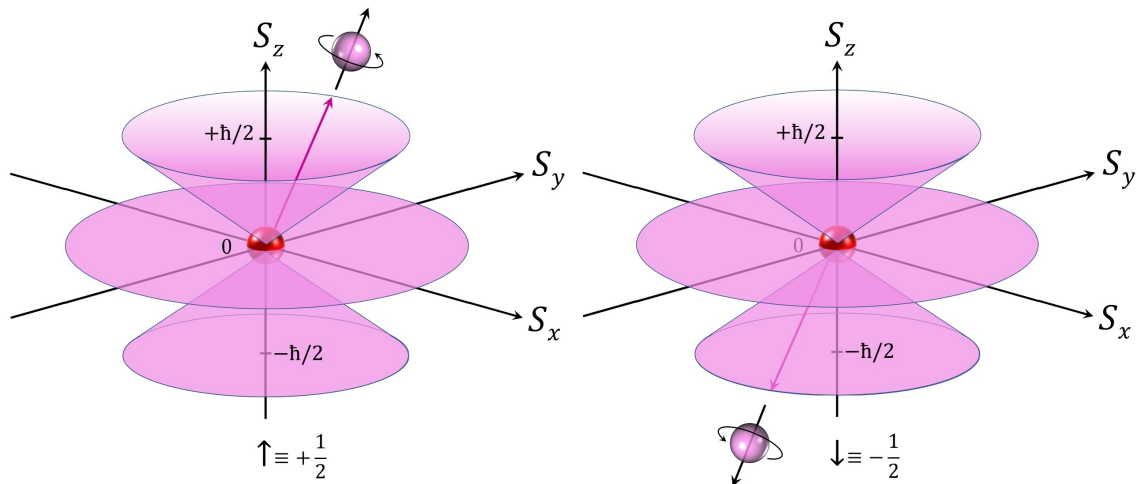


Figure 1.21 Vector model of the magnetic spin quantum number up (left) and down (right).

1.4. Presentation of Atomic Orbitals

Solving **Schrödinger's** equation gives a wave function Ψ , a solution to the equation. This wave function depends on the quantum numbers and allows determining the shape and energy of atomic orbitals.

Example: Take the first four levels and see what subshells they contain.

Table 1.4 Quantum numbers and atomic orbitals

n	$0 \leq \ell \leq n-1$	$-\ell \leq m \leq +\ell$	Remarks
1	0	0	For the first level, $\ell = 0$, a single zero value, therefore a single atomic orbital with spherical symmetry. $m_\ell = 0$ gives a single orientation in space, therefore a single quantum box
2	0	0	2s
	1	-1, 0, +1	For the second level, and the second value $\ell = 1$, presents an atomic orbital of type <i>p</i> . m_ℓ has three values for three orientations in space, therefore three quantum boxes <i>p</i> (p_x, p_y, p_z)
3	0	0	3s
	1	-1, 0, +1	3p
	2	-2, -1, 0, +1, +2	The third level, and for the third value $\ell = 2$, presents an atomic orbital of type <i>d</i> . m_ℓ presents five values for five orientations in space, therefore five quantum boxes <i>d</i> ($d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$)
4	0	0	4s
	1	-1, 0, +1	4p
	2	-2, -1, 0, +1, +2	4d
	3	-3, -2, -1, 0, +1, +2, +3	The fourth level, the fourth value $\ell = 3$, presents an atomic orbital of type <i>f</i> . m_ℓ , seven values therefore seven quantum boxes $f_{z^3}, f_{yz^2}, f_{xz^2}, f_{xyz}, f_{x(x^2-3y^2)}, f_{z(x^2-y^2)}, f_{y(3x^2-y^2)}$

1.4.1. s (sharp) Orbital:

For this orbital, we will take simple cases $n = \{1, 2, 3\}$ for, $\ell = 0$ and $m = 0$ which corresponds to the function $\Psi_{n,0,0}$. We have seen that the wave function is divided into two parts: the radial part $R_{n,\ell}(r)$ (defines the orbital size) and the angular part $Y_{\ell,m}(\theta, \phi)$ (defines the orbital shape).

$$\Psi_{(n,\ell,m)} = R_{n,\ell}(r) \cdot Y_{\ell,m}(\theta, \phi) \iff \Psi_{(n,0,0)} = R_{n,0}(r) \cdot Y_{0,0}(\theta, \phi)$$

Therefore:

$$\Psi_{(1,0,0)} = R_{1,0}(r) \cdot Y_{0,0}(\theta, \phi) = 2\sqrt{\frac{1}{a_0^3}} \cdot e^{-\left(\frac{r}{a_0}\right)} \cdot \sqrt{\frac{1}{4\pi}}$$

$$\Psi_{(2,0,0)} = R_{2,0}(r) \cdot Y_{0,0}(\theta, \phi) = \sqrt{\frac{1}{8a_0^3}} \cdot \left(2 - \frac{r}{a_0}\right) \cdot e^{-\left(\frac{r}{2a_0}\right)} \cdot \sqrt{\frac{1}{4\pi}}$$

$$\Psi_{(3,0,0)} = R_{3,0}(r) \cdot Y_{0,0}(\theta, \phi) = \frac{2}{3} \cdot \sqrt{\frac{1}{3a_0^3}} \cdot \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) \cdot e^{-\left(\frac{r}{3a_0}\right)} \cdot \sqrt{\frac{1}{4\pi}}$$

We notice that $\Psi_{n,0,0}$ depend only on r and have an identical and constant angular part $= (1/4\pi)^{1/2}$, so *s*-type orbitals have a spherical shape. To justify these remarks, we express them by the probability density $|\Psi(r)|^2$ (the notion of finding the particle at r ($0 \leq r \leq \infty$)), and use the probability $Pr_n(r)$ of finding the particle in a volume V around r .

$$Pr_n = |\Psi_{n,0,0}|^2 \cdot 4\pi r^2$$

Where does $4\pi r^2$ come from?

We know that the volume of a sphere of radius r is given by:

$$V = \frac{4}{3}\pi r^3$$

If we increase the radius by an infinitesimal amount dr , the volume increases by an amount dV . This increase corresponds to the volume of a thin **spherical shell** between r and $r + dr$.

Mathematically, this volume dV is obtained by differentiating V with respect to r :

$$\frac{dV}{dr} = \frac{d}{dr} \left(\frac{4}{3} \pi r^3 \right) = 4\pi r^2$$

Thus:

$$dV = 4\pi r^2 dr$$

The term $4\pi r^2$ therefore represents **the surface area of the sphere** of radius r , and multiplied by dr (the thickness), it gives the volume of the spherical shell.

Note: In some works, one can find a simplification applied to these equations:

$$\rho = \frac{r}{a_0} \quad (\text{with } a_0 = 0.53 \text{ \AA} \text{ as atomic unit})$$

We will write the probability equation in the following form:

$$Pr_{ns} = |\Psi_{(n,0,0)}|^2 \cdot 4\pi r^2 = [R_{n,0}(r)]^2 \cdot [Y_{0,0}(\theta, \phi)]^2 \cdot 4\pi r^2$$

$$Pr_{1s} = |\Psi_{1,0,0}|^2 \cdot 4\pi r^2 = \frac{4\rho^2}{a_0} \cdot e^{-\left(\frac{2\rho}{1}\right)}$$

$$Pr_{2s} = |\Psi_{2,0,0}|^2 \cdot 4\pi r^2 = \frac{\rho^2}{8a_0} \cdot (2 - \rho)^2 \cdot e^{-\left(\frac{2\rho}{2}\right)}$$

$$Pr_{3s} = |\Psi_{3,0,0}|^2 \cdot 4\pi r^2 = \frac{\rho^2}{4920.75 \cdot a_0} \cdot (27 - 18\rho + 2\rho^2)^2 \cdot e^{-\left(\frac{2\rho}{3}\right)}$$

We will plot these functions, which essentially amounts to plotting just the radial part. Since the product of the angular part and $4\pi r^2$ produces an r^2 that adds to the radial part, the function becomes primarily a function of r (a radial function). In our example, each function R_n presents the ns orbital (n : level).

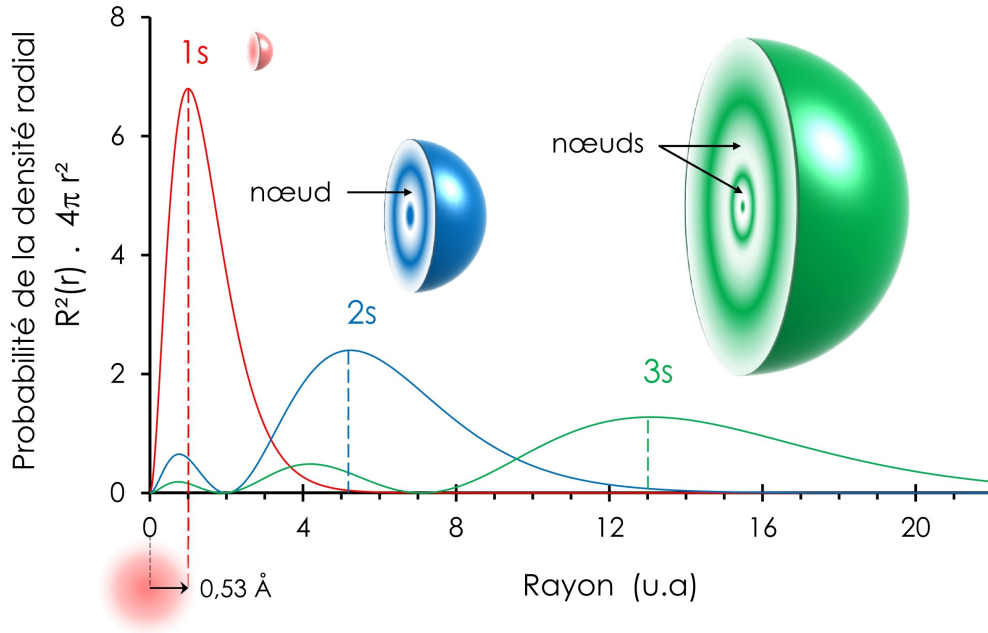


Figure 1.22 Probability of electron presence for atomic orbitals 1s, 2s and 3s.

Note:

1s	1 peak	$r = a_0$	identical to Bohr model
2s	2 peaks	$r = 5 a_0$	$4 a_0$ in Bohr model
3s	3 peaks	$r = 13 a_0$	$9 a_0$ in Bohr model

Take the case of 1s: the distance expressing a significant probability is $a_0 = 0.53 \text{ \AA}$ (the most probable location)

to find the electron). But the average distance $\langle r \rangle$ is given by the following expression.

$$\langle r \rangle = \int_0^{\infty} r \cdot Pr(r) \cdot dr = \frac{3}{2} a_0 = 0.79 \text{ \AA}$$

Equilibrium average distance (attractive force equals centrifugal force).

Note: Due to its physical meaning, the probability density imposes the following properties on the wave function.

- Must be square-integrable; must not tend to infinity in its domain of definition.
- Must be continuous in its domain of definition; must take only one value at a point.
- The first derivative must be continuous in its domain of definition.
- The function must be normalized. This means that the function describes an object that exists somewhere in its domain of definition.

$$Pr(r, \vartheta, \varphi) = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} |\Psi_{n,\ell,m}|^2 r^2 \cdot \sin \vartheta \, dr \, d\vartheta \, d\varphi = 1$$

These two distances, though close in value, reflect distinct physical realities: one is the most probable location, the other the average over all possible positions. This difference illustrates the asymmetry of the radial distribution of the electron in the hydrogen atom. In quantum mechanics, the choice of the relevant quantity therefore depends on the phenomenon under study (instantaneous localization versus effective orbital radius).

1.4.2. p (principal) Orbital:

p orbitals are characterized by a secondary (azimuthal) quantum number $\ell = 1$ and $m_{\ell} = \{-1, 0, +1\}$ valid for levels greater than one ($n > 1$). Take the example of the p orbital of the second level.

$$\Psi_{(2,1,0)} = R_{2,1}(r) \cdot Y_{1,0}(\vartheta, \varphi) = \frac{1}{2} \sqrt{\frac{1}{6}} \sqrt{\frac{1}{a_0^3}} \cdot \rho e^{-\left(\frac{\rho}{2}\right)} \cdot \sqrt{\frac{3}{4\pi}} \cos \vartheta$$

$Y_{1,0}(\vartheta, \varphi)$ is independent of φ , so it is symmetric about the z -axis.

$Y_{1,0}(\vartheta, \varphi) = 0$ if $\vartheta = 90^\circ$ so $\Psi_{2,1,0} = 0$ on the z -plane; the latter is called the nodal plane (plane where the probability density of electron presence is zero).

If $m = -1$ we have symmetry about the x -axis, so the orbital is called $p(x)$ or p_x .

$$\Psi_{(2,1,-1)} = R_{2,1}(r) \cdot Y_{1,-1}(\vartheta, \varphi) = \frac{1}{2} \sqrt{\frac{1}{6}} \sqrt{\frac{1}{a_0^3}} \cdot \rho e^{-\left(\frac{\rho}{2}\right)} \cdot \sqrt{\frac{3}{4\pi}} \sin \vartheta \cos \varphi$$

If $m = +1$ we have symmetry about the y -axis, so it is the $p(y)$ or p_y orbital.

$$\Psi_{(2,1,+1)} = R_{2,1}(r) \cdot Y_{1,+1}(\vartheta, \varphi) = \frac{1}{2} \sqrt{\frac{1}{6}} \sqrt{\frac{1}{a_0^3}} \cdot \rho e^{-\left(\frac{\rho}{2}\right)} \cdot \sqrt{\frac{3}{4\pi}} \sin \vartheta \sin \varphi$$

We will apply the same simplification to obtain information about the size of this orbital (with $\rho = r/(a_0)$, $a_0 = 1$ a.u. as atomic unit, knowing that $a_0 = 0.53 \text{ \AA}$), by plotting the probability curve of radial density $(R_n)^2 4\pi r^2 = fct(r)$.

$$Pr_{2p} = |\Psi_{2,1,0}|^2 \cdot 4\pi r^2 = \frac{\rho^4}{8a_0} \cdot e^{-\left(\frac{2\rho}{2}\right)} \cdot \cos^2 \vartheta$$

$$Pr_{3p} = |\Psi_{3,1,0}|^2 \cdot 4\pi r^2 = \frac{\rho^2}{820.12 \cdot a_0} (6\rho - \rho^2)^2 \cdot e^{-\left(\frac{2\rho}{3}\right)} \cos^2 \vartheta$$

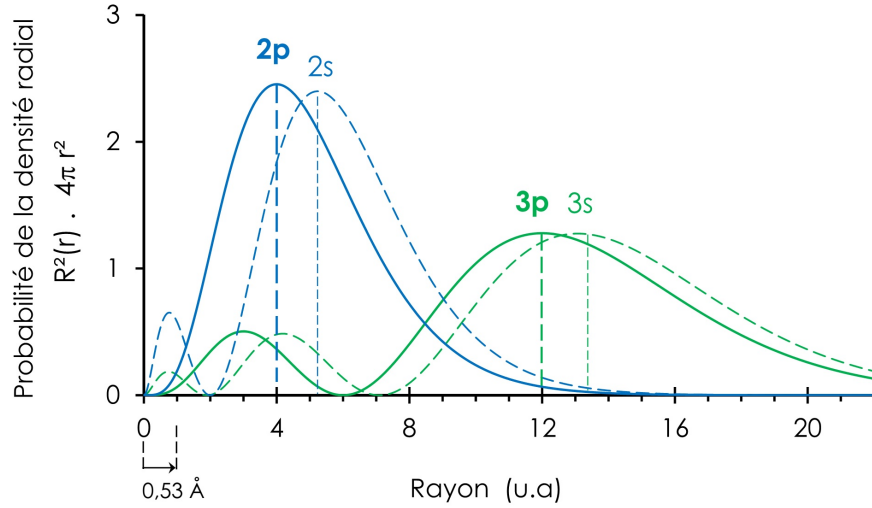


Figure 1.23 Probability of electron presence for atomic orbitals $2s$, $2p$, and $3s$, $3p$.

Note:

Concerning the orbital size (radius to be precise), we notice on the curves that the most probable distance to find the electron on the s or p orbital is approximately identical ($4 a_0$ for $2p$ and $5 a_0$ for $2s$) and ($12 a_0$ for $3p$ and $13 a_0$ for $3s$).

Concerning the geometric shape of the orbital, we will treat the angular part of the wave function, namely $Y_{\ell,m}(\vartheta, \varphi)$, to better visualize it through a polar curve. The unit radius (at $\cos 0^\circ$) is drawn, and from the center, several other radii are drawn at different angles (from 0° to 360°).

Take the simplest case, that of the $2p$ orbital on the z -axis. Its angular function is simple:

$Y_{(1,0)} = \cos \vartheta$ (in this case, $\cos \vartheta$ represents the distance separating the nucleus from the electron).

ϑ	0	30	60	90	...	120	150	210	...	300	360
$\cos \vartheta$	1	0.866	0.500	0.000	...	-0.500	-0.866	-0.866	...	0.500	1

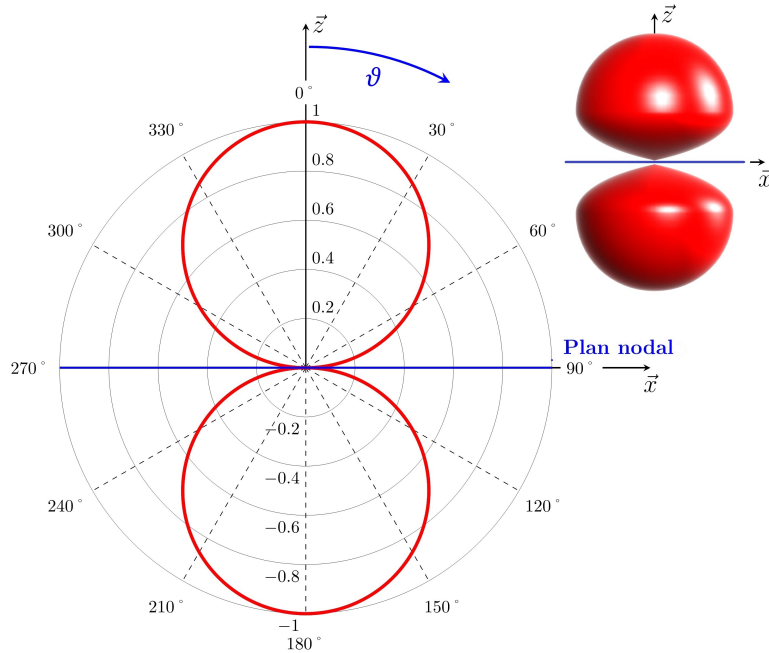


Figure 1.24 Polar or spherical coordinate plots of the p orbital.

We notice that the shape of the p orbital consists of two symmetrical lobes separated by a nodal plane. The upper one (above the nodal plane) has positive values, and the lower one has negative values. Consequently, the sign of the wave function is due to the sign of the angular part.

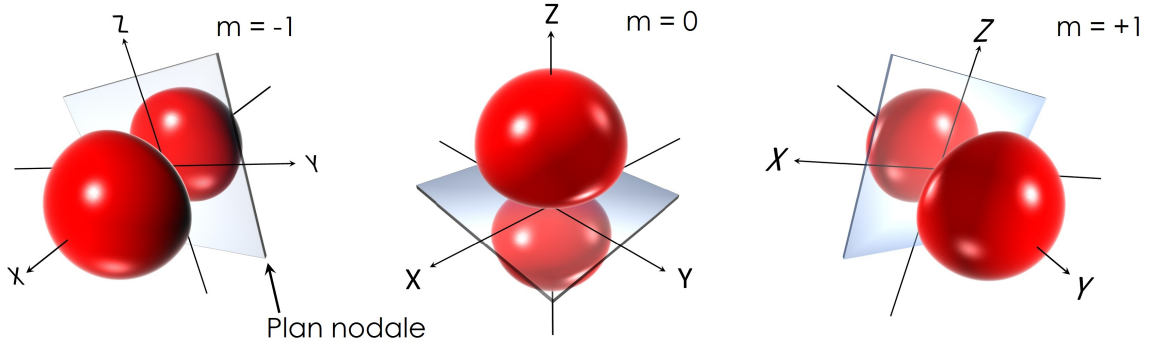


Figure 1.25 Three-dimensional representation of p orbitals.

1.4.3. d (diffuse) Orbital:

d orbitals are characterized by a secondary (azimuthal) quantum number $\ell = 2$ and $m_\ell = \{-2, -1, 0, +1, +2\}$ valid for levels greater than two ($n > 2$). Take the example of the $3d_{z^2}$ orbital to plot the radial probability curve and deduce the size.

$$Pr_{3d} = |\Psi_{3,2,0}|^2 \cdot 4\pi r^2 = \left[\frac{4}{81\sqrt{30}} \sqrt{\frac{1}{a_0^3}} \rho^2 \cdot e^{-\left(\frac{\rho}{3}\right)} \right]^2 \cdot \left(\sqrt{\frac{5}{16\pi}} \cdot (3\cos^2\vartheta - 1) \right)^2 \cdot 4\pi r^2$$

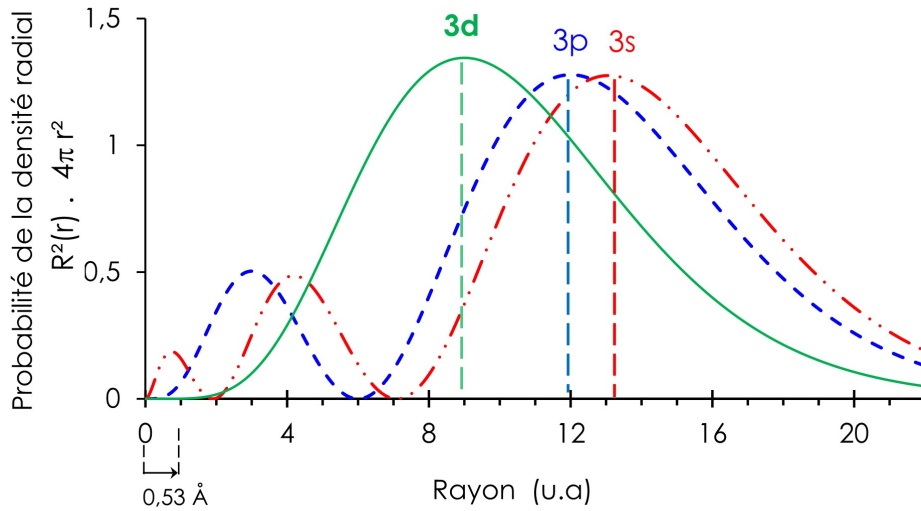


Figure 1.26 Probability of electron presence for atomic orbitals $3s$, $3p$ and $3d$.

We note on the following curve that at level three, the radius of the s orbital is greater than that of p , and the latter is greater than that of the d orbital ($13a_0 > 12a_0 > 9a_0$). For the geometric shape, we use the polar plot in spherical coordinates of the angular part ($Y_{(2,0)}$) of the wave function (NB: just with variation of the angle ϑ).

$$Y_{\ell,m}(\vartheta, \varphi) = P_{\ell,m}(\vartheta)F_m(\varphi)$$

$$F_0(\varphi) = \sqrt{2} \quad F_m(\varphi) = \sqrt{2} \cos(m\varphi) \quad F_{-m}(\varphi) = \sqrt{2} \sin(m\varphi)$$

$$P_{2,0}(\vartheta) = \sqrt{\frac{5}{16\pi}}(3 \cos^2 \vartheta - 1) \quad P_{2,\pm 1}(\vartheta) = \sqrt{\frac{15}{8\pi}}(\cos \vartheta \cdot \sin \vartheta) \quad P_{2,\pm 2}(\vartheta) = \sqrt{\frac{15}{32\pi}}(\sin^2 \vartheta)$$

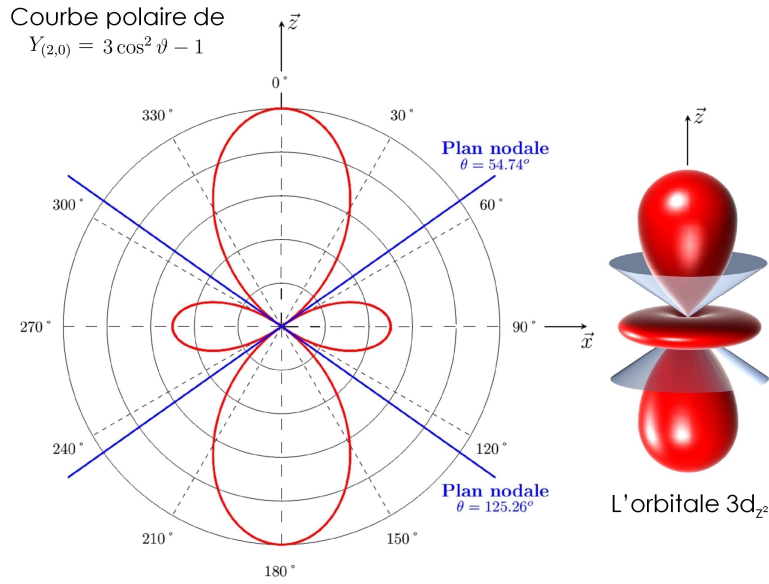


Figure 1.27 Polar or spherical coordinate plots of the $3d_{z^2}$ orbital.

The geometric shape of the $3d_{z^2}$ orbital that occupies the z -axis is very specific: two oval lobes centered by a ring, the two parts separated by two nodal planes of conical shape, with an apex angle of $2 \times 54.74^\circ$. Let us take another example and another equation, namely the $3d_{xz}$ orbital. As in the previous example, we use the angular part without considering the imaginary part.

$$Pr_{3d} = |\Psi_{3,2,1}|^2 \cdot 4\pi r^2 = \left[\frac{4}{81\sqrt{30}} \sqrt{\frac{1}{a_0^3}} \rho^2 \cdot e^{-\left(\frac{\rho}{3}\right)} \right]^2 \cdot \left(\sqrt{\frac{15}{4\pi}} \cdot \sin \vartheta \cos \vartheta \cos \varphi \right)^2 \cdot 4\pi r^2$$

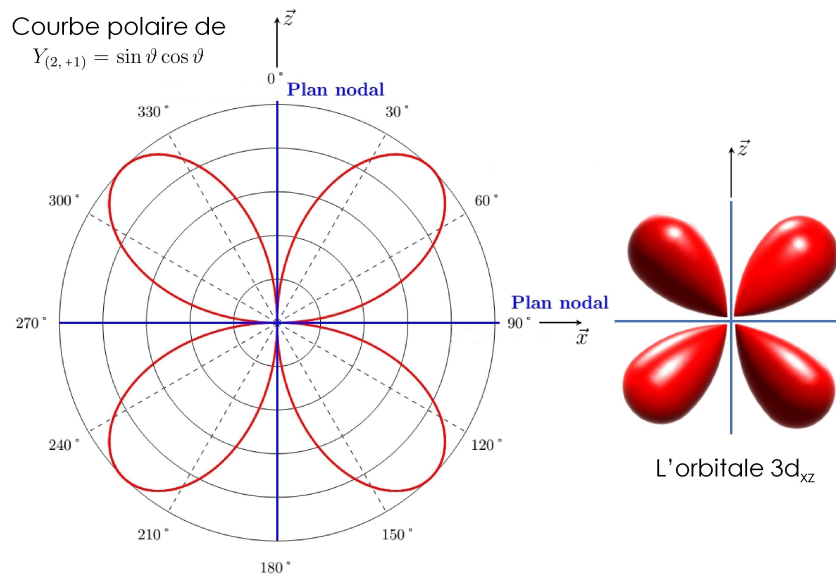


Figure 1.28 Polar or spherical coordinate plots of the $3d_{xz}$ orbital.

Unlike s orbitals or p orbitals which resemble each other (spherical or two oval lobes), d -type atomic orbitals each have their own symmetry dictated by the angular equation that changes as a function of the azimuthal

and magnetic quantum numbers.

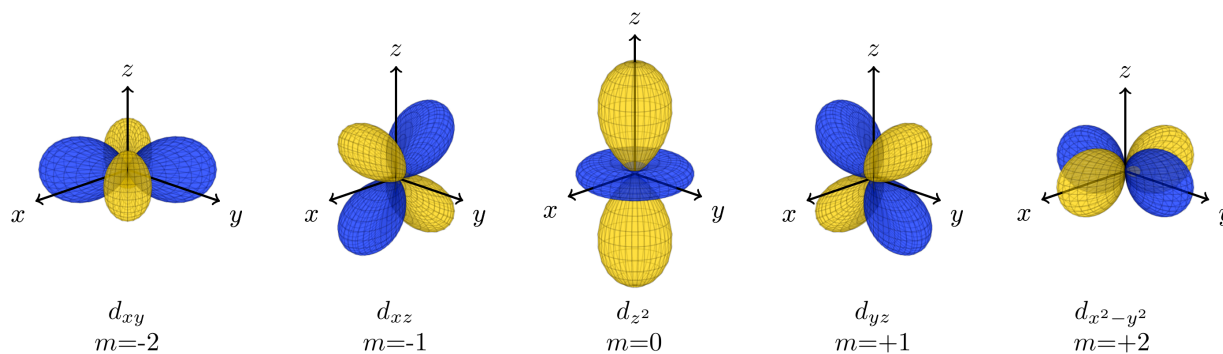


Figure 1.29 Three-dimensional representation of d orbitals.

1.4.4. f (fundamental) Orbital

f orbitals are characterized by a secondary (azimuthal) quantum number $\ell = 3$, which gives the following values $m_\ell = \{-3, -2, -1, 0, +1, +2, +3\}$ valid for levels greater than three ($n > 3$). We take one of the orbitals and plot the radial probability curve to deduce the size of this orbital.

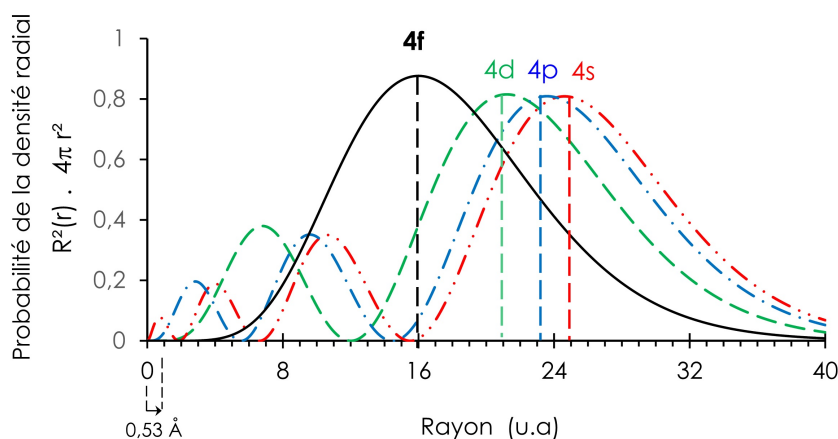


Figure 1.30 Probability of electron presence for atomic orbitals $4s$, $4p$, $4d$ and $4f$.

We note on this curve that at level four ($n = 4$), the radius of the f orbital is the smallest among the four: $s(25a_0) > p(23a_0) > d(21a_0) > f(16a_0)$.

For the geometric shape, we use the polar plot in spherical coordinates of the angular function ($P_{3,m}(\vartheta)$), a part of the wave function (NB: just with variation of the angle ϑ).

We notice a clear difference between f orbitals. To further see this difference, we need to move to a three-dimensional representation of the angular function $V_{3,m}(\vartheta, \varphi)$ as a function of both angles.

1.5. Filling of Atomic Orbitals

Electrons are placed around the nucleus according to several so-called stability rules.

1.5.1. Klechkowski's Rule

Established by **Vsevolod Klechkowski**,⁽²¹⁾ a Russian chemist, it is also called **Madelung's** rule (named after Erwin Madelung, a German physicist). It is an empirical method allowing prediction with fairly good accuracy of the order of electron filling in the subshells of electrically neutral atoms (ground state). Together with **Hund's** rule and **Pauli's** exclusion principle, it constitutes one of the basic tools for predicting the filling of atomic orbitals.

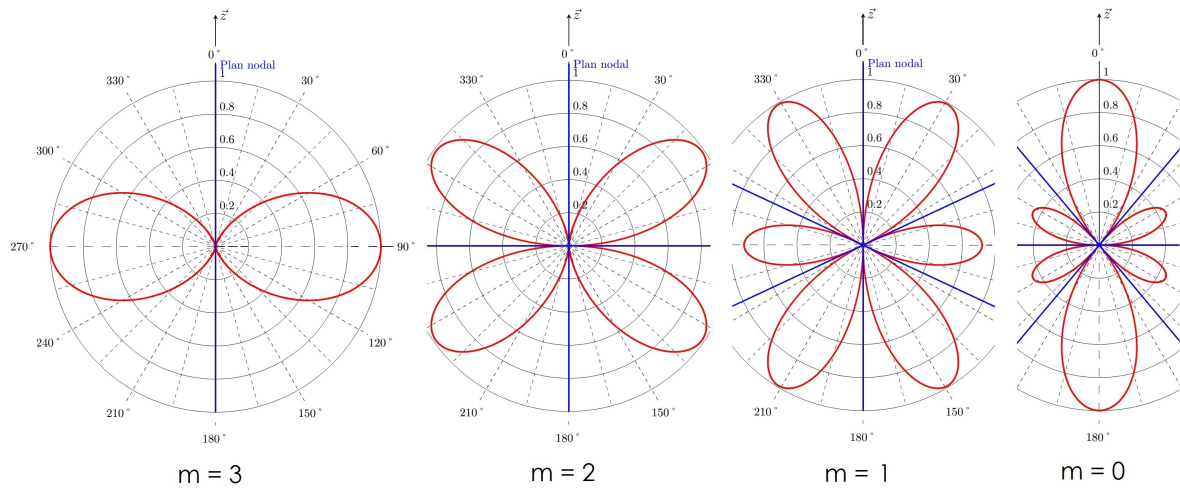


Figure 1.31 Polar or spherical coordinate plots of the f orbital.

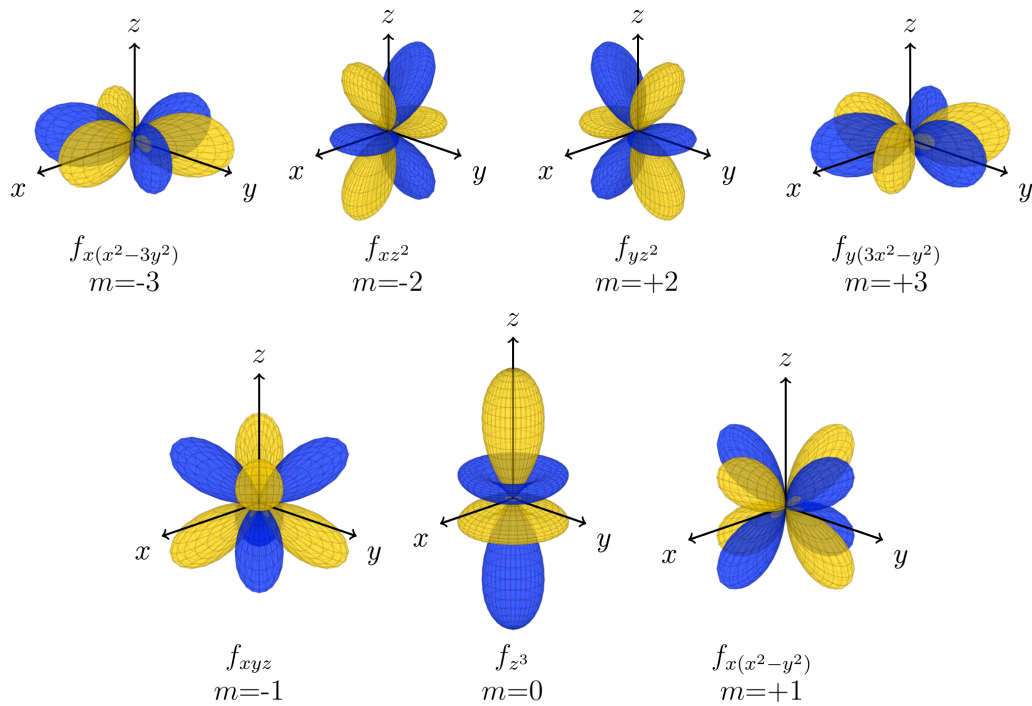
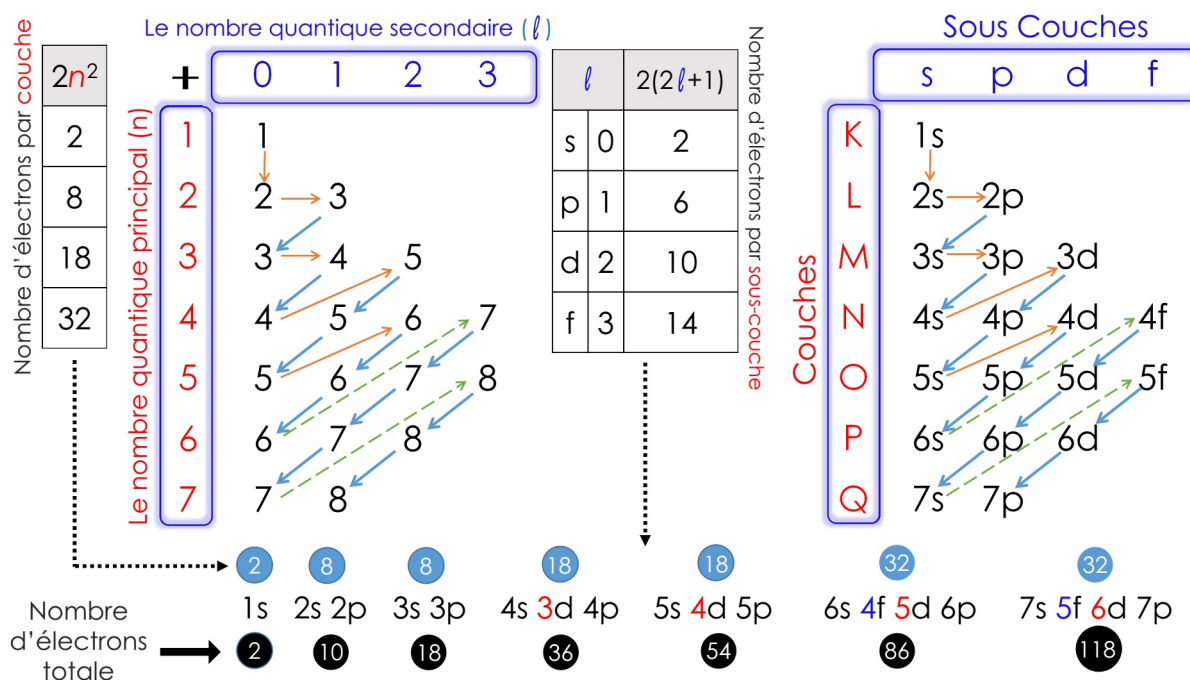


Figure 1.32 Three-dimensional representation of f orbitals.

- **Pauli Exclusion Principle:**⁽²²⁾ in an atom, two electrons cannot have the same quantum numbers (or the same quantum state), knowing that these numbers are like the electron's coordinates in matter.
- **Hund's Rule:**⁽²³⁾ electrons occupy a maximum number of orbitals defined by the azimuthal quantum number ℓ before completing them with a second electron of opposite spin.
- **Klechkowski's Rule:** energy levels are filled in order of increasing energy.
 - This energy is an increasing function of the sum $(n + \ell)$.
 - If two atomic orbitals have the same sum $(n + \ell)$, it is the atomic orbital with the smallest value of n that has the lowest energy.

Klechkowski's rule can be illustrated by a diagram that allows quick and error-free retrieval of the filling order.



filling order: $1s / 2s 2p / 3s 3p / 4s 3d 4p / 5s 4d 5p / 6s 4f 5d 6p / 7s 5f 6d 7p$

- We observe a crossing of levels starting from the third since the $4s$ orbital ($n + \ell = 4$) fills before the $3d$ orbital ($n + \ell = 5$). There are other cases such as $5s$ and $4d$, or $6s$ and $4f$, etc.
- We also observe that the s and p subshells are always at the same level, while d is at $n - 1$ relative to s and p , and the f subshell is at $n - 2$.

Example: For the following elements, using the electron configuration, find the period (row) and group (family) of each element?

3Li	$1s^2 / 2s^1$	$n = 2$ and group 1A or IA
9F	$1s^2 / 2s^2 2p^5$	$n = 2$ and group 7A or VIIA
${}^{22}Ti$	$1s^2 2s^2 2p^6 3s^2 3p^6 / 4s^2 3d^2$	$n = 4$ and group 4B or IVB
${}^{30}Zn$	$1s^2 2s^2 2p^6 3s^2 3p^6 / 4s^2 3d^{10}$	$n = 4$ and group 2B or IIB
${}^{35}Br$	$1s^2 2s^2 2p^6 3s^2 3p^6 / 4s^2 3d^{10} 4p^5$	$n = 4$ and group 7A or VIIA
${}^{54}Xe$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 / 5s^2 4d^{10} 5p^6$	$n = 5$ and group 8A or VIIIA
${}^{61}Pm$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 / 6s^2 4f^5$	$n = 6$ Lanthanide

Additional examples (including exceptions): As shown in Section 1.5.2, some elements do not follow Klechkowski's rule.

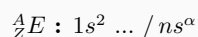
${}^{24}Cr$	$1s^2 2s^2 2p^6 3s^2 3p^6 / 4s^1 3d^5$	$n = 4$ and group 6B or VIB
${}^{29}Cu$	$1s^2 2s^2 2p^6 3s^2 3p^6 / 4s^1 3d^{10}$	$n = 4$ and group 1B or IB
${}^{42}Mo$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 / 5s^1 4d^5$	$n = 5$ and group 6B or VIB
${}^{47}Ag$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 / 5s^1 4d^{10}$	$n = 5$ and group 1B or IB
${}^{79}Au$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 / 6s^1 4f^{14} 5d^{10}$	$n = 6$ and group 1B or IB
${}^{64}Gd$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 / 6s^2 4f^7 5d^1$	$n = 6$ Lanthanide

To easily find the group and period of each element, there are rules to follow:

Let us take the case of element ${}_Z^A E$: $1s^2 \dots / ns^\alpha np^\beta$. For the period (or row), it suffices to find the n_{max} (in our case $= n$); then the element is located in period n . For the group, it is divided into two parts: a capital letter **A** or **B**, and a small number from 1 to 8. For the latter, it suffices to calculate the sum $\alpha + \beta$ (the number of electrons located at n_{max} , called valence electrons). For the letter, we just need to see the last letter written (the last subshell in the electron configuration): if it is s or p , then it is group **A**; if it is d , then it is group **B**.

These rules offer a straightforward method for locating any element on the periodic table, provided its electron configuration is correctly written. However, special attention is required for transition metals (where the last subshell is d) and for lanthanides/actinides, which do not follow the simple $s-p$ group numbering. With practice, this approach becomes an efficient tool for quickly identifying both the period and the family of any element.

The following diagram summarizes all possible cases:

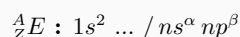


The last subshell is *s*, therefore group **A**.

We have α valence electrons.

* The new IUPAC notation is group (α) .

α **A**

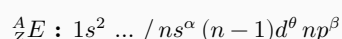


The last subshell is *p*, therefore group **A**.

We have $(\alpha + \beta)$ valence electrons.

* The new IUPAC notation is group $(\alpha + 10 + \beta)$.

$(\alpha + \beta)$ **A**

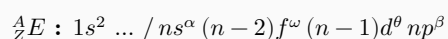


The last subshell is *p*, therefore group **A**.

We have $(\alpha + \beta)$ valence electrons (those at level *n*).

* In the new IUPAC notation, it is group $(\alpha + \theta + \beta)$.

$(\alpha + \beta)$ **A**

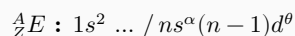


The last subshell is *p*, therefore group **A**.

We have $(\alpha + \beta)$ valence electrons (those at level *n*).

* The new IUPAC notation is group $(\alpha + 10 + \beta)$.

$(\alpha + \beta)$ **A**

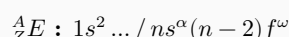


The last subshell is *d*, therefore it is **B**

We have $(\alpha + \theta)$ electrons. Then:

* The new IUPAC notation is group $(\alpha + \theta)$.

$(\alpha + \theta) \leq 8$ $11 \leq (\alpha + \theta) \leq 12$
 $(\alpha + \theta)$ **B** **8B** α **B**
 $8 \leq (\alpha + \theta) \leq 10$



Last subshell *f* $\Rightarrow$ *f* block (inner transition metals).

If $(n-2) = 4$: **La** as **lanthanides** (*4f* filling).

If $(n-2) = 5$: **Ac** as **actinides** (*5f* filling).

* : In this handout, we use the **old A/B notation** (group A = representative elements, group B = transition elements). The **IUPAC** numbering (groups 1 to 18) also exists, but is not used in this chapter (unless otherwise stated).

So far, the **electron configuration** has been mainly used to relate an atom to its position in the periodic table (block, group) via the outer subshell and the number of valence electrons. To move to a finer representation, we no longer simply write $ns^\alpha np^\beta$: we **distribute** these electrons into degenerate **quantum boxes** (orbitals), each capable of containing at most two electrons of opposite spins (Pauli exclusion principle). In this filling, **Hund's rule** imposes that within the same subshell (*p*, *d*, *f*), orbitals of the same energy are filled first **one by one** with parallel spins, before any pairing; this convention allows correct representation of the ground state and anticipation of certain properties (stability of half-filled subshells, paramagnetism).

Example : Concerning **Hund's rule** (maximum spin), we add that for degenerate orbitals (which have the same energy value), the state of maximum stability is obtained when electrons occupy the maximum number of quantum boxes, with their spins parallel. Let us take some examples:

the p subshell with 3 electrons (p^3)

↑↓	↑	
↑	↓	↓
↑	↑	↑
↓	↓	↓

false
false
CORRECT
correct

the p subshell with 4 electrons (p^4)

↑↓	↑	↑
↑	↑↓	↑
↑	↑	↑
↑	↓↓	↑

CORRECT
correct
false
false

the d subshell with 4 electrons (d^4)

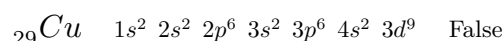
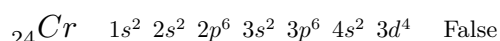
↑	↑		↓	↓
↑↓	↓	↓		
↑	↑	↑		↑
↓	↓	↓	↓	
↑	↑	↓	↓	
↑	↑	↑	↑	

false
false
correct
correct
false
CORRECT

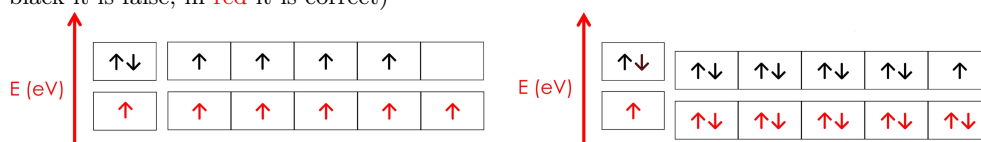
Note: In filling quantum boxes, we must respect **Hund's** rule: we must fill the maximum number of boxes with electrons of the same spin, but by convention we start with positive spins, then complete them with other electrons of opposite spin.

1.5.2. Exceptions to Klechkowski's Rule:

There are elements that do not respect Klechkowski's rule. Let us take some examples.

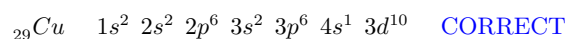
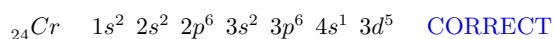


To understand the exception, we present the valence shell with quantum boxes, as well as their energy profile (eV): (in black it is false, in red it is correct)



For Chromium, its valence shell orbitals in the ground state $4s^2 3d^4$ have the same energy level. If we take **Hund's** rule into consideration, we see that one box remains empty. For greater stability, it is necessary to fill the last d box with an electron belonging to the s orbital. The half-filled subshell $3d^5$ has additional stability compared to $3d^4$ in the presence of $4s$.

For Copper, a filled " d " orbital is more stable than d^9 . Therefore, if we take the (theoretical) electron configuration of copper, the electron from $4s$ will be transferred to $3d$ to fill the gap in the latter, thus achieving greater stability. Therefore, the most stable and correct configurations are:



Exceptions to the orbital filling rule affect certain transition metals as well as some lanthanides and actinides. We then observe a transfer from their s subshell (for transition metals) or f subshell (for lanthanides and actinides) to their d subshell. What must be remembered is that the possibility of saturating an orbital sometimes takes precedence over the rule.

1.6. Periodic Classification of Elements:

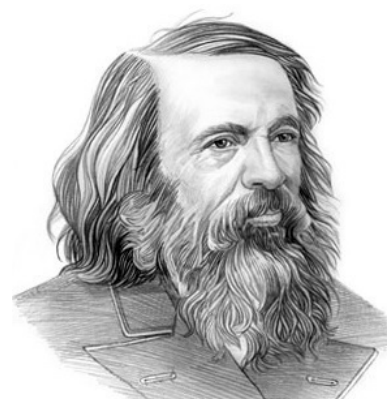
Gathering and classifying all chemical elements is the work of the Russian chemist **Dmitri Mendeleev**.⁽²⁴⁾ He had the idea of using the periodicity of the physicochemical properties of elements.

Initially, in 1869, the classification was based on increasing atomic mass for the sixty or so known elements. He noticed that their properties recurred periodically, thus columns were created to group them. He left some boxes empty and predicted the existence of other elements unknown at the time.

In 1910, with the discovery of the nucleus charge by **Rutherford** and the introduction of the atomic number **Z**, the classification followed a different criterion. The classification of chemical elements is ordered by increasing atomic number and organized according to their electron configuration, which underlies their chemical properties.

Therefore, the great interest of the periodic classification is to organize chemical elements such that their physicochemical properties can be predicted by their position in the table. These properties (radius, ionization energy, electronegativity, etc.) evolve differently depending on whether we move vertically or horizontally in the table.

The periodic table has undergone many adjustments since then until it took the form we know today. It has become a universal reference to which all types of physical and chemical behavior of elements can be related. Since the IUPAC (International Union of Pure and Applied Chemistry) update of November 28,



2016, its standard form contains 118 elements, from hydrogen $Z=1$ to oganesson $Z=118$.⁽²⁵⁾

A period (a row) of the periodic table is defined by the progressive filling of electronic subshells, starting with s and ending with p . The properties of elements vary along a period, but can be quite similar and constitute complete families of chemical elements, particularly in the d block (transition metals) and especially in the f block (lanthanides in the 6th period and actinides in the 7th period).

A group of the periodic table (a column or family) often constitutes a set of elements with properties distinct from neighboring groups, particularly at the left and right ends of the periodic table (i.e., in the s and p blocks), where they have been given names, for example:

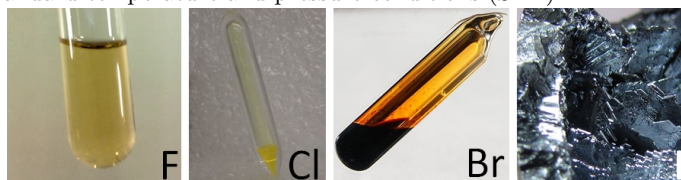
- **Alkali metals** = column 1 (s block) except hydrogen: These are low-density metals (soft at room temperature) with a silvery color, known for their low melting point, forming ionic compounds with halogens. They react violently with water to give hydroxides that are strong bases. They are never found in elemental form in the natural environment.



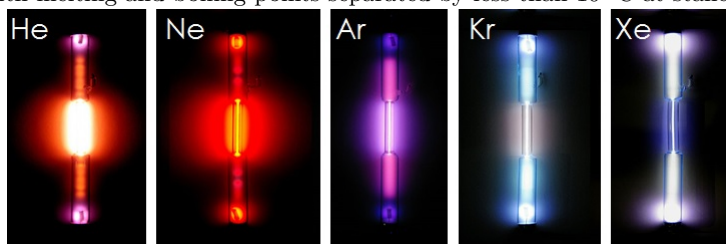
- **Alkaline earth metals** = column 2 (s block): Slightly harder and denser than alkali metals, also form ionic compounds with halogens but do not react with water at room temperature, only with water vapor to form very basic hydroxides.



- **Pnictogens** (term rarely used) = column 15 (p block)
- **Chalcogens** (term rarely used) = column 16 (p block)
- **Halogens** = column 17 (p block): Except astatine and tennessine. They exist in diatomic elemental form and give strong acids with hydrogen. They form ionic compounds with alkali metals and alkaline earth metals. This is the only group in the table whose elements' standard state can be gaseous (fluorine, chlorine), liquid (bromine), or solid (iodine) under standard temperature and pressure conditions (STP).



- **Noble gases** = column 18 (p block) with helium belonging to the s block: Except oganesson, the elements of the 18th group form the noble gas family. At STP, they are colorless, odorless, monatomic gases that are almost non-reactive (inert), with melting and boiling points separated by less than 10 °C at standard pressure.



1.6.1. Laws and Physicochemical Properties of Elements:

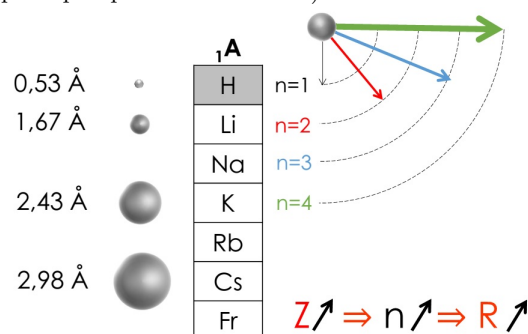
The chemical properties of an element depend essentially on the electron configuration of the valence shell, the latter being the most energetic, and containing the most reactive electrons. Since the periodic classification is constructed by grouping elements having the same electron configuration, it is logical to find in the same group (column) elements with analogous properties. But these properties vary within a period. It is then possible to predict certain properties; these are periodic laws. The use of the periodic table therefore allows the determination of various parameters of an atom, serving the study of chemical reactions. These parameters can be grouped according to the atoms' ability to exchange their electrons and their respective sizes. We will examine some characteristic parameters specific to each atom according to their position in the table.

1.6.1.1. Atomic Radius:

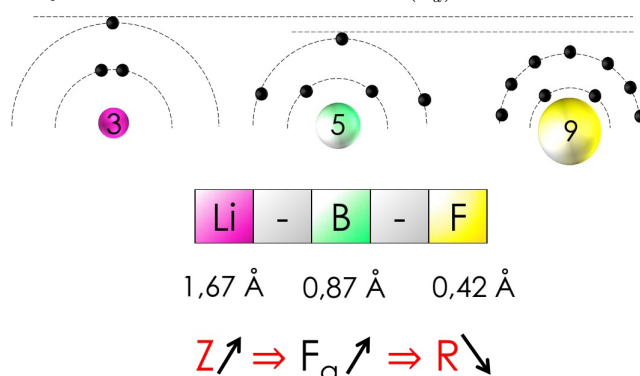
We consider atoms as spherical particles; their size will therefore be their radius. But it is very important to know that when two atoms bond (diatomic molecule), their outer electron shells interpenetrate (overlap), and the internuclear distance becomes less than the sum of their radii. Therefore, the covalent radius of an element is defined as half the distance between the nuclei of two atoms in a molecule of the simple substance.

Experimentally, the radius is determined using an X-ray diffractometer; it is an approximate measurement because electron clouds mix.

- In a column: The atomic radius increases with **Z** in the same column. This is due to the increase in the radial function (increase in the principal quantum number n).

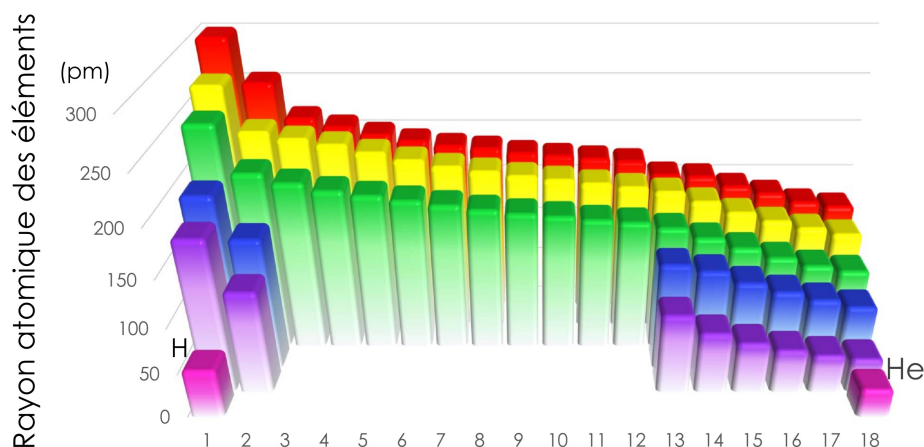


- In a row: For the same number of shells, the atomic radius decreases when crossing a period from left to right. This comes from the fact that the systematic increase in nuclear charge (**Z**) across the period contracts the electron orbitals (caused by the increase in attractive force (F_a) between nucleus and electrons).



Note: Ions do not have the same size as the atoms from which they derive. Anions are larger and cations are smaller, but they follow the same periodic trends. The departure of one or more external electrons decreases the screening effect exerted on those that remain, which are then more strongly attracted to the nucleus. A cation is therefore less bulky than the atom from which it comes. The inverse effect explains the larger volume of anions.

The following figure illustrates the variation of atomic radius in the periodic table.

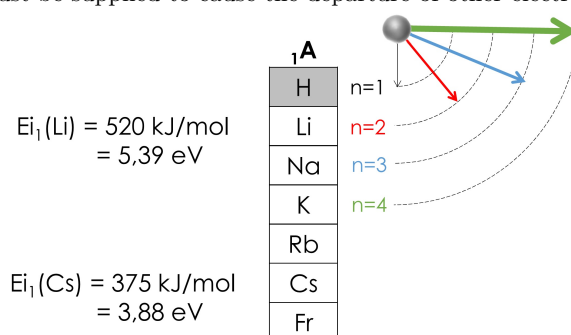


1.6.1.2. Ionization Energy:

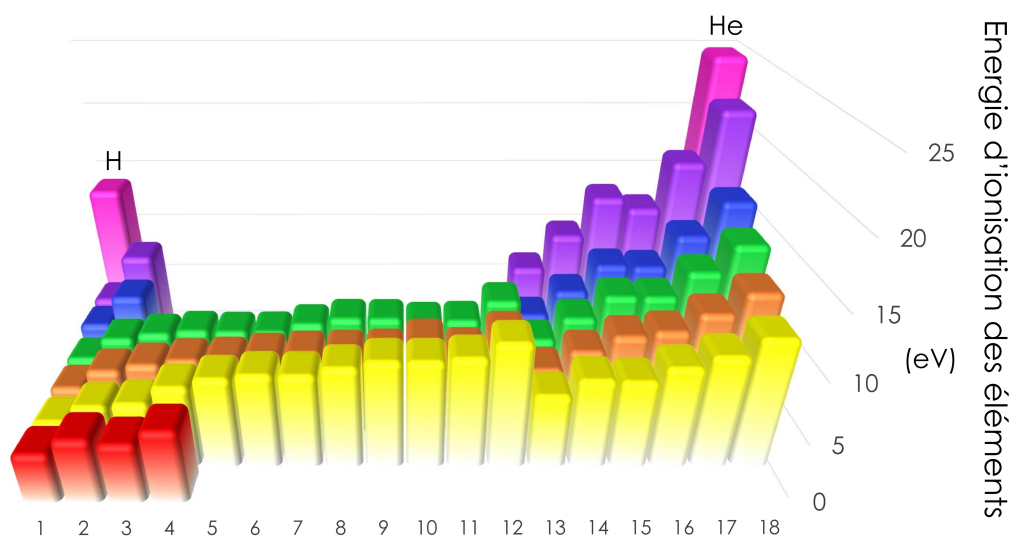
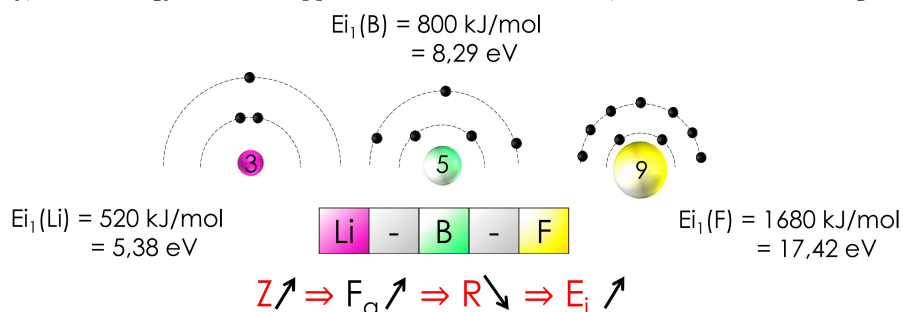
An ion results from the loss or gain of one or more electrons. In the first case, the atom acquires a positive charge and becomes a cation. In the second case, it acquires a negative charge and becomes an anion. But usually, the term ionization is reserved for the case where a loss of electrons transforms an atom into a positive ion. To remove this electron, a certain amount of energy must be supplied. It is necessary to tear it away from the attractive force exerted by the nucleus. This amount of energy is called the first ionization energy (E_i).

Removing an electron from an atom requires energy equal to the difference ΔE between the level at which it is located and the level $n = \infty$ ($\Delta E = E_i - E_\infty$). Generally, the energy required for the first ionization varies greatly depending on the atoms.

- In a column: The higher the energy level of an electron, the smaller the distance between this level and the level $n = \infty$. Consequently, the electron is easier to remove; this is called the distance effect (the greater the distance between the electron (the one susceptible to being removed) and the nucleus, the lower the ionization energy). However, more energy must be supplied to cause the departure of other electrons belonging to lower levels.



- In a row: For an equal number of shells, the nucleus-electron distance decreases when crossing a period from left to right (nuclear charge (Z) increases, therefore attractive force (F_a) between nucleus and electrons increases). Consequently, much energy must be supplied to remove an electron; this is called the charge effect.

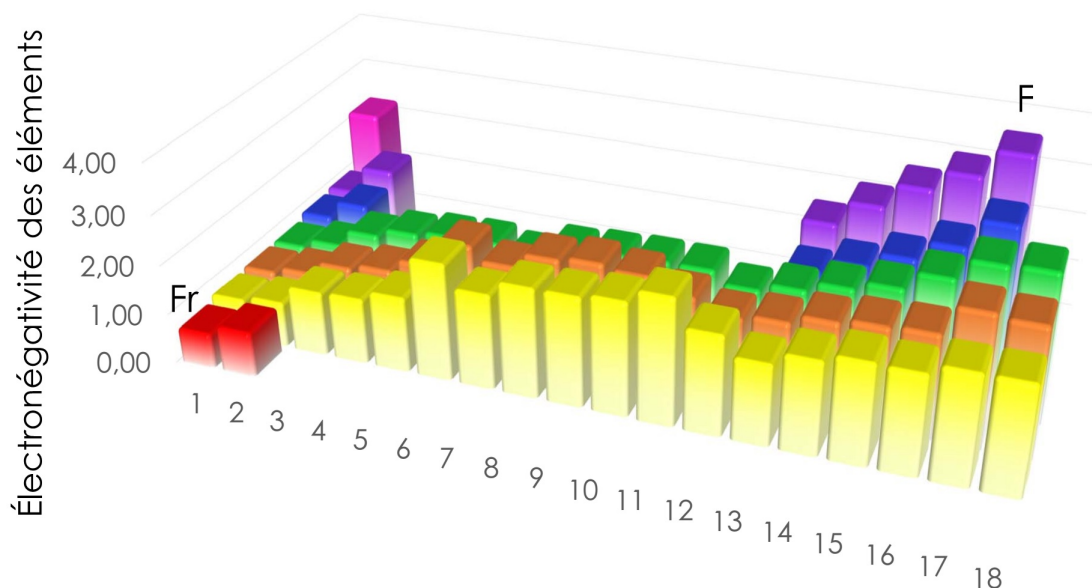


1.6.1.3. Electronegativity:

Electronegativity χ is a quantity that represents the ability of an atom to attract bonding electrons in a molecule. Electronegativity plays a role in the formation of ions, but also in the competition between bonded atoms. We will therefore use the concept of polarity.

Electronegativity is defined empirically, on an arbitrary numerical scale. Several exist, the best known being the **Pauling** scale and the **Mulliken** scale. **Pauling**'s definition, still used today as a reference, is based on the experimental value of bond energies and is between 0.7 and 4.0.

Electronegativity increases with **Z** in a period, with some exceptions for transition elements. It decreases in a group as **Z** increases. Elements located in the lower left of the table are called electropositive (metals) and easily give up valence electrons when forming a chemical bond; while elements located in the upper right are called electronegative (non-metals) and easily capture valence electrons from their partner when forming a chemical bond. The most electronegative element is fluorine. Elements with intermediate electronegativity, separating metals from non-metals, are called semi-metals.



Note: The term electropositivity is used as the opposite of electronegativity. That is, the more electropositive an atom is, the less electronegative it is, and vice versa. Nevertheless, these two terms refer to the same concept of electronegativity, which makes the words "electropositive" or "electropositivity" of very limited utility. An atom is said to be electropositive when it tends to easily lose one or more electrons to transform into a cation. For example, alkali metals are very electropositive compared to other metals.

Tableau périodique des éléments

Groupe																		18/VIIIA																
1/IA																		2	He															
1	¹ H																	4,00260	hélium															
3	³ Li	⁴ Be																10	Ne															
2	6,941 0,98 lithium	9,01218 1,57 béryllium																20,1797	- néon															
3	22,98977 0,93 sodium	24,305 1,31 magnésium																39,948	- argon															

Solved Exercises

Exercise 01:

Emission of electrons extracted from a metal by light radiation. **Einstein** explained it in 1905 by considering that light consists of photons. The photoelectric threshold wavelength of lithium is $\lambda_0 = 5200 \text{ \AA}$.

- Does lithium emit electrons when it receives radiation with wavelengths greater than, or less than, $5200 \text{ \AA}$?
- Calculate the work function W_{ext} for this metal, express it in eV.

Solution

- The photoelectric threshold corresponds to the frequency ν_0 (or wavelength λ_0) of the radiation providing energy E_0 equal to the work function W_{ext} of an electron:

Note:

- if the energy (E) supplied by the light radiation is less than the energy required to overcome the binding energy between the electron and the metal crystal (work function W_{ext}), i.e., $E < W_{\text{ext}}$, nothing happens.
- if $E > W_{\text{ext}}$, photoemission occurs; E is then the sum of W_{ext} and the kinetic energy of the emitted electron (conservation of energy).

It is very important to respect the homogeneity of units. If energy is in Joules (J), wavelength must be in meters.

$$|\Delta E_{(J)}| = h\nu = h \cdot \frac{C}{\lambda} = \frac{19.88 \cdot 10^{-26}}{\lambda_{(m)}} \quad \text{and} \quad |\Delta E_{(\text{eV})}| = \frac{12400}{\lambda_{(\text{\AA})}}$$

There is photoemission under the effect of any light radiation with energy $E > E_0$. If this radiation has wavelength λ : $E = h\nu = h \cdot (C_0/\lambda)$. The photoelectric effect is observed if:

$$h \cdot \frac{C_0}{\lambda} > h \cdot \frac{C_0}{\lambda_0} \quad \text{for Lithium} \quad \lambda < \lambda_0 \iff \lambda < 5200 \text{ \AA}$$

- With numerical application: $\lambda_0 = 5200 \cdot 10^{-10} \text{ m}$

$$W_{\text{ext}}(J) = |\Delta E_{(J)}| = h\nu = h \cdot \frac{C}{\lambda} = \frac{19.88 \cdot 10^{-26}}{5200 \cdot 10^{-10}} = 3.82 \cdot 10^{-19} \text{ J}$$

and to convert to eV:

$$W_{\text{ext}}(\text{eV}) = |\Delta E_{(\text{eV})}| = \frac{W_{\text{ext}}(J)}{1.602 \cdot 10^{-19}} = 2.39 \text{ eV}$$

or:

$$W_{\text{ext}}(\text{eV}) = \frac{12400}{5200} = 2.39 \text{ eV}$$

Exercise

- Calculate the frequency of the radiation that accompanies the transition of an electron in a hydrogen atom from the excited state $n = 6$ to the state $n = 2$. To which series of the hydrogen atom emission spectrum does this radiation belong? Has the atom then returned to its ground state?
- Calculate the wavenumber and wavelength of the radiation causing the ionization of hydrogen initially in the ground state. Knowing that the ionization energy E_i of an atom is the minimum energy required to extract an electron from an atom in its ground state, deduce the ionization energy of hydrogen and express it in eV.

Solution

- The wavenumber σ or $\bar{\nu}$ of the radiation emitted during an electronic transition $n \rightarrow p$ of the hydrogen atom is obtained by applying **Balmer's** formula. The wavenumber σ , the wavelength λ , and the frequency ν are related by:

$$\sigma = \frac{1}{\lambda} = \frac{\nu}{C_0} = R_H \left(\frac{1}{p^2} - \frac{1}{n^2} \right)$$

$$\nu = \sigma \cdot C_0 = R_H \cdot C_0 \left(\frac{1}{p^2} - \frac{1}{n^2} \right)$$

with numerical application:

$$\nu = 1.1 \cdot 10^7 \times 3 \cdot 10^8 \left(\frac{1}{2^2} - \frac{1}{6^2} \right) = 7.33 \cdot 10^{14} \text{ s}^{-1}$$

This line belongs to the **Balmer** series ($p = 2$). After the transition, the atom is not in its ground state, because the final energy level is not 1.

Exercise

A hydrogen-like ion is a cation of atomic number Z , which has only one electron, such as He^+ ; Li^{2+} ; Be^{3+} , etc. Experiment has shown that **Balmer's** formula can be generalized to hydrogen-like ions, with the **Rydberg** constant R_H replaced by the product $R \cdot Z^2$, where R is a new constant. The emission spectrum of the He^+ ion presents, among others, a series of lines with wavenumbers 329,170; 390,120; 411,460; and 421,330 cm^{-1} .

- Show that the generalized **Balmer** formula is verified.
- Calculate R .

Solution

- We will work with the **Balmer** relation:

$$\text{For hydrogen } \frac{1}{\lambda} = R_H \cdot \left(\frac{1}{p^2} - \frac{1}{n^2} \right) \text{ and for hydrogen-like } \frac{1}{\lambda'} = Z^2 R_H \cdot \left(\frac{1}{p^2} - \frac{1}{n^2} \right)$$

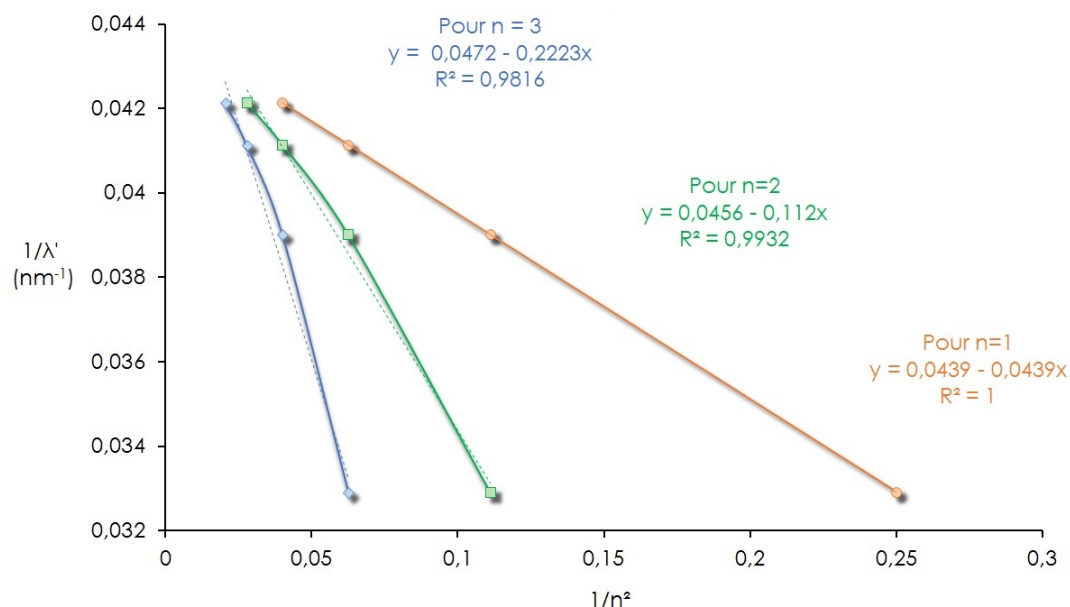
For the same series of lines, p is constant and n varies ($n = p + 1; p + 2, p + 3 \dots$ etc.). Therefore we have a linear variation as a function of $1/n^2$, which gives us the following relation:

$$\frac{1}{\lambda'} = \frac{Z^2 R_H}{p^2} - \frac{Z^2 R_H}{n^2} = A - \frac{B}{n^2} \quad A \text{ and } B \text{ are two constants}$$

To verify **Balmer's** relation, we need to find which value of p corresponds to the series of lines given in the text. We will therefore plot the function $1/\lambda' = f(1/n^2)$ after having calculated, for each possible value of $p(1, 2, 3, \dots)$, the corresponding values of $1/n^2$. Obtaining a straight line with negative slope (B), such that the ratio $B/A = p^2$.

Calculations of $1/n^2$ for $p = 1$ and $p = 2$ and graphical representations:

$1/\lambda' \text{ (cm}^{-1}\text{)}$	$n \text{ (for } p = 1\text{)}$	$1/n^2$	$n \text{ (for } p = 2\text{)}$	$1/n^2$
329,170	2	0.2500	3	0.1111
390,120	3	0.1111	4	0.0625
411,460	4	0.0625	5	0.04
421,330	5	0.0400	6	0.0278



From the graph, we notice that for $n = 1$ we obtain a straight line, unlike for $n = 2$ or 3 . For the orange curve ($n = 1$), the regression coefficient equals 1, which gives us $A = 0.0439$ (y-intercept) and $B = -0.0439$ (slope), so the ratio $B/A = 1$, thus $p = 1$. Therefore, for this series of lines, their electronic transitions have the first level as the final level (final level), and consequently we are facing the **Lyman** series.

- b) Calculation of the **Rydberg** constant (R_H):

$$A = \frac{Z^2 \cdot R_H}{p^2} \Rightarrow R_H = \frac{A \cdot 1^2}{Z^2} = \frac{A}{4} = \frac{0.0439}{4} = 0.010975 \text{ nm}^{-1} = 1.0975 \cdot 10^7 \text{ m}^{-1}$$

Exercise

- a) A photon is associated with the electromagnetic wave of wavelength λ . Express the energy E of this photon as a function of λ , **Planck's** constant h , and the speed of light C .
- b) Calculate the energy of a photon associated with infrared radiation of wavelength $\lambda = 0.1 \text{ mm}$.
- c) At level n , the proper energy of the hydrogen atom is $E = -13.6/n^2 \text{ (eV)}$. To which series of the hydrogen atom emission spectrum does the line corresponding to the transition $3 \rightarrow 2$ belong, and calculate the wavelength corresponding to this transition.

Solution

- a)

$$E = |\Delta E_{f-i}| = h \cdot \frac{C}{\lambda}$$

This relation, which must be memorized, can nevertheless be found by dimensional analysis. The unit of Planck's constant:

$$h \cdot \frac{C}{\lambda} = J \cdot s \cdot \frac{m \cdot s^{-1}}{m} = J$$

- b) The photon energy is calculated using the relation from the previous question:

$$E = h \cdot \frac{C}{\lambda} = 6.626 \cdot 10^{-34}_{(J \cdot s)} \cdot \frac{3 \cdot 10^8_{(m/s)}}{10^{-4}_{(m)}} = 1.99 \cdot 10^{-21} J$$

This energy can also be converted to electron-volt (eV), a unit more appropriate to the order of magnitude of the obtained result. The absolute value of an electron's charge is: $e = 1.6 \cdot 10^{-19} \text{ Coulombs}$.

$$1 \text{ eV} = 1.6 \cdot 10^{-19} (C) \times 1 (Volt) = 1.6 \cdot 10^{-19} J.$$

$$\text{Therefore: } E = 1.99 \cdot 10^{-21} / 1.6 \cdot 10^{-19} = 1.24 \times 10^{-2} \text{ eV}$$

- c) The series presented (tables on page 17) all belong to the emission spectrum of the hydrogen atom, and correspond to transitions of type $n \rightarrow p$, with $n > p$, meaning the atom moves to stabilization, moving from a higher energy state to a lower energy state.
- Therefore, the transition in question is the line due to the transition $3 \rightarrow 2$, which belongs to the **Balmer** series.

Exercise

Theoretical Analysis of the Model:

1. Derivation of Angular Momentum Quantization:

Starting from Bohr's stability condition $\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$ and the quantization condition $mvr = n \frac{h}{2\pi}$, show that the orbital radius is given by:

$$r_n = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2}$$

2. Total Energy:

Express the total energy E_n of an electron in a hydrogen-like ion of atomic number Z as a function of n and Z . Give a physical justification explaining why this energy is negative.

3.) Wavelength and Frequency Calculations:

For the hydrogen atom:

- (a) Calculate the wavelength (in nm) and frequency (in Hz) of the photon emitted during the $n = 4 \rightarrow n = 2$ transition.
- (b) Determine the region of the electromagnetic spectrum corresponding to this radiation.
- (c) Calculate the energy associated with this transition in joules and in electronvolts.

4.) **Absorption and Emission:**

A hydrogen atom in its ground state absorbs a photon of wavelength 97.3 nm.

- (a) Calculate the energy of the absorbed photon.
- (b) To which energy level is the electron excited?
- (c) What are the possible wavelengths of photons that may be emitted when the electron returns to the ground state?

5.) **Series Limit Calculations:**

- (a) Calculate the shortest wavelength of the Balmer series ($n = \infty \rightarrow n = 2$ transition).
- (b) Calculate the longest wavelength of the Paschen series ($n = 4 \rightarrow n = 3$ transition).
- (c) Determine which of these two photons is more energetic.

Solution

Theoretical Analysis of the Model

1) **Derivation of Angular Momentum Quantization:**

Starting from Bohr's stability condition $\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r}$ and the quantization condition $mvr = n\frac{h}{2\pi}$,

demonstrate that the orbital radius is given by: $r_n = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2}$

Express the total energy E_n of an electron in the hydrogen atom as a function of n and Z . Give a physical justification explaining why the energy is negative.

a) We start from the two fundamental equations:

$$\text{Stability condition: } \frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{mv^2}{r} \quad (1)$$

$$\text{Quantization condition: } mvr = n\frac{h}{2\pi} \quad (2)$$

Express v from equation (2)

$$v = \frac{nh}{2\pi mr}$$

Substitute into equation (1)

$$\frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{m}{r} \left(\frac{nh}{2\pi mr} \right)^2 \Rightarrow \frac{Ze^2}{4\pi\epsilon_0 r^2} = \frac{n^2 h^2}{4\pi^2 m r^3}$$

Isolate r

$$r = \frac{n^2 h^2}{4\pi^2 m} \times \frac{4\pi\epsilon_0}{Ze^2} \Rightarrow r_n = \frac{\epsilon_0 h^2 n^2}{\pi m_e e^2 Z} \quad (3)$$

b) Total energy E_n :

$$E_n = E_c + E_p = \frac{mv^2}{2} - \frac{Ze^2}{4\pi\epsilon_0 r_n}$$

With the circular motion condition from eq (1):

$$\frac{Ze^2}{4\pi\epsilon_0 r} = mv^2$$

Therefore:

$$E_n = \frac{Ze^2}{8\pi\epsilon_0 r_n} - \frac{Ze^2}{4\pi\epsilon_0 r_n} = -\frac{Ze^2}{8\pi\epsilon_0 r_n}$$

Substituting the quantized radius from eq (3) into the energy expression:

$$E_n = -\frac{Ze^2}{8\pi\epsilon_0} \cdot \frac{1}{r_n} = -\frac{Ze^2}{8\pi\epsilon_0} \cdot \frac{\pi m_e e^2 Z}{\epsilon_0 h^2 n^2}$$

Final result:

$$E_n = -\frac{m_e Z^2 e^4}{8\epsilon_0^2 h^2 n^2}$$

c) Why is the energy negative?

- **Zero at infinity:** Energy is zero when the electron is very far away.
- **Attraction:** The electron is attracted to the nucleus, so its energy decreases (becomes negative).
- **Binding energy:** $|E_n|$ = energy required to remove the electron.
- **Stability:** $E_n < 0$ means the electron is bound to the nucleus.

The more negative E_n is, the more strongly the electron is bound.

2) Wavelength and Frequency Calculations:

For the hydrogen atom:

- Calculate the wavelength (in nm) and frequency (in Hz) of the photon emitted during the $n = 4 \rightarrow n = 2$ transition.
- Determine the region of the electromagnetic spectrum of this radiation.
- Calculate the energy of this transition in joules and in electronvolts.

2) Wavelength and Frequency Calculations:

For the hydrogen atom:

- Calculation of wavelength and frequency for the $n = 4 \rightarrow n = 2$ transition**

We use the Rydberg formula for the hydrogen atom ($Z = 1$):

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

where $R_H = 1.097 \times 10^7 \text{ m}^{-1}$, $n_1 = 2$, $n_2 = 4$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = 1.097 \times 10^7 \left(\frac{1}{4} - \frac{1}{16} \right)$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times 0.1875 = 2.0569 \times 10^6 \text{ m}^{-1}$$

$$\lambda = \frac{1}{2.0569 \times 10^6} = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$$

Frequency:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8}{4.86 \times 10^{-7}} = 6.17 \times 10^{14} \text{ Hz}$$

$$\lambda = 486 \text{ nm}$$

$$\nu = 6.17 \times 10^{14} \text{ Hz}$$

- Region of the electromagnetic spectrum**

The wavelength of 486 nm lies in the:

Visible (blue-green)

More precisely in the Balmer series.

- Energy of the transition**

In joules:

$$E = h\nu = (6.626 \times 10^{-34}) \times (6.17 \times 10^{14}) = 4.09 \times 10^{-19} \text{ J}$$

In electronvolts:

$$E = \frac{4.09 \times 10^{-19}}{1.602 \times 10^{-19}} = 2.55 \text{ eV}$$

Verification using the energy level formula:

$$E = E_2 - E_4 = \left(-\frac{13.6}{4} \right) - \left(-\frac{13.6}{16} \right) = -3.4 - (-0.85) = -2.55 \text{ eV}$$

The absolute value confirms our result.

$$E = 4.09 \times 10^{-19} \text{ J}$$

$$E = 2.55 \text{ eV}$$

3) **Absorption and Emission:** A hydrogen atom in its ground state absorbs a photon of wavelength 97.3 nm.

- Calculate the energy of the absorbed photon.
 - To which energy level is the electron excited?
 - What are the possible wavelengths of photons that may be emitted when the electron returns to the ground state?
- (a) **Energy of the absorbed photon**

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}) \times (3.00 \times 10^8)}{97.3 \times 10^{-9}} = \frac{1.9878 \times 10^{-25}}{9.73 \times 10^{-8}} = 2.042 \times 10^{-18} \text{ J}$$

In electronvolts:

$$E = \frac{2.042 \times 10^{-18}}{1.602 \times 10^{-19}} = 12.75 \text{ eV}$$

(b) **Excitation energy level**

The energy levels of hydrogen are given by:

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

The electron starts from the ground state $n = 1$ ($E_1 = -13.6 \text{ eV}$) and absorbs 12.75 eV:

$$E_{\text{final}} = E_1 + E_{\text{photon}} = -13.6 + 12.75 = -0.85 \text{ eV}$$

We look for n such that:

$$-\frac{13.6}{n^2} = -0.85 \Rightarrow n^2 = \frac{13.6}{0.85} = 16 \Rightarrow n = 4$$

The electron is excited to the $n = 4$ level.

(c) **Possible wavelengths when returning to the ground state**

The electron is excited to the $n = 4$ level. It can return to the ground state ($n = 1$) through different transitions:

Direct transition: $4 \rightarrow 1$

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{4^2} \right) = 1.097 \times 10^7 \left(1 - \frac{1}{16} \right) = 1.028 \times 10^7 \text{ m}^{-1} \Rightarrow \lambda = 97.3 \text{ nm}$$

Indirect transitions:

- $4 \rightarrow 2 \rightarrow 1$:

$$4 \rightarrow 2 : \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{16} \right) = 1.097 \times 10^7 \times \frac{3}{16} \Rightarrow \lambda = 486 \text{ nm}$$

$$2 \rightarrow 1 : \frac{1}{\lambda} = R_H \left(1 - \frac{1}{4} \right) = 1.097 \times 10^7 \times \frac{3}{4} \Rightarrow \lambda = 121.6 \text{ nm}$$

- $4 \rightarrow 3 \rightarrow 1$:

$$4 \rightarrow 3 : \frac{1}{\lambda} = R_H \left(\frac{1}{9} - \frac{1}{16} \right) = 1.097 \times 10^7 \times \frac{7}{144} \Rightarrow \lambda = 1875 \text{ nm}$$

$$3 \rightarrow 1 : \frac{1}{\lambda} = R_H \left(1 - \frac{1}{9} \right) = 1.097 \times 10^7 \times \frac{8}{9} \Rightarrow \lambda = 102.6 \text{ nm}$$

- $4 \rightarrow 3 \rightarrow 2 \rightarrow 1$:

$$4 \rightarrow 3 : \lambda = 1875 \text{ nm} \quad (\text{already calculated})$$

$$3 \rightarrow 2 : \frac{1}{\lambda} = R_H \left(\frac{1}{4} - \frac{1}{9} \right) = 1.097 \times 10^7 \times \frac{5}{36} \Rightarrow \lambda = 656 \text{ nm}$$

$$2 \rightarrow 1 : \lambda = 121.6 \text{ nm} \quad (\text{already calculated})$$

Possible wavelengths (no duplicates):

$$\boxed{97.3 \text{ nm}, 102.6 \text{ nm}, 121.6 \text{ nm}, 486 \text{ nm}, 656 \text{ nm}, 1875 \text{ nm}}$$

Spectral series:

- Lyman series (to $n = 1$): 97.3, 102.6, 121.6 nm
- Balmer series (to $n = 2$): 486, 656 nm

- Paschen series (to $n = 3$): 1875 nm

4) **Series Limit Calculations:**

- Calculate the shortest wavelength in the Balmer series ($n = \infty \rightarrow n = 2$ transition).
- Calculate the longest wavelength in the Paschen series ($n = 4 \rightarrow n = 3$ transition).
- Determine which of these two photons is more energetic.

Series Limit Calculations:

- Shortest wavelength in the Balmer series** ($n = \infty \rightarrow n = 2$)

Rydberg formula:

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

For $n_1 = 2$, $n_2 = \infty$:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{2^2} - \frac{1}{\infty} \right) = R_H \left(\frac{1}{4} - 0 \right) = \frac{R_H}{4} \Rightarrow \lambda = \frac{4}{1.097 \times 10^7} = 3.645 \times 10^{-7} \text{ m} = 364.5 \text{ nm}$$

- Longest wavelength in the Paschen series** ($n = 4 \rightarrow n = 3$)

For the Paschen series, $n_f = 3$. The least energetic transition is $n = 4 \rightarrow n = 3$:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{3^2} - \frac{1}{4^2} \right) = R_H \left(\frac{1}{9} - \frac{1}{16} \right) = 5.332 \times 10^5 \text{ m}^{-1} \Rightarrow \lambda = \frac{1}{5.332 \times 10^5} = 1875 \text{ nm}$$

- Comparison of photon energies**

The energy of a photon is inversely proportional to its wavelength:

$$E = \frac{hc}{\lambda}$$

Balmer photon: $\lambda = 364.5 \text{ nm}$

$$E_B = \frac{1240}{\lambda(\text{nm})} = \frac{1240}{364.5} = 3.40 \text{ eV}$$

Paschen photon: $\lambda = 1875 \text{ nm}$

$$E_P = \frac{1240}{1875} = 0.661 \text{ eV}$$

Direct comparison:

$$\frac{E_B}{E_P} = \frac{3.40}{0.661} \approx 5.14$$

Conclusion: The Balmer limit photon (3.40 eV) is about 5 times more energetic than the longest Paschen transition photon (0.661 eV).

Exercise

Application to Hydrogen-like Ions:

The He^+ ($Z=2$) and Li^{2+} ($Z=3$) ions are important hydrogen-like systems in medical physics.

1. **Energy transitions:**

Compare the energies of photons emitted during the $n = 3 \rightarrow n = 2$ transition for:

- the hydrogen atom ($Z=1$);
- the He^+ ion ($Z=2$);
- the Li^{2+} ion ($Z=3$).

What pattern (trend) do you observe? Generalize for a hydrogen-like ion of charge Z .

2. **Limit wavelength:**

For the He^+ ion, calculate the wavelength of the photon emitted during the $n = \infty \rightarrow n = 2$ transition. In which region of the electromagnetic spectrum is it located?

Solution

1. **Energy Transitions:** $n = 3 \rightarrow n = 2$

For a hydrogen-like ion, the energy levels are:

$$E_n = -\frac{Z^2 \cdot 13.6}{n^2} \text{ eV}$$

The energy of the $n = 3 \rightarrow n = 2$ transition is:

$$\begin{aligned}\Delta E &= E_2 - E_3 = -Z^2 \cdot 13.6 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) \\ \Delta E &= -Z^2 \cdot 13.6 \left(\frac{1}{4} - \frac{1}{9} \right) = -Z^2 \cdot 13.6 \cdot \frac{5}{36} \\ \Delta E &= Z^2 \cdot 1.889 \text{ eV}\end{aligned}$$

Calculations for each ion:

- **Hydrogen (Z=1):**

$$\begin{aligned}\Delta E &= (1)^2 \cdot 1.889 = 1.889 \text{ eV} \\ \lambda &= \frac{1240}{1.889} = 656 \text{ nm}\end{aligned}$$

- **He⁺ (Z=2):**

$$\begin{aligned}\Delta E &= (2)^2 \cdot 1.889 = 4 \cdot 1.889 = 7.556 \text{ eV} \\ \lambda &= \frac{1240}{7.556} = 164 \text{ nm}\end{aligned}$$

- **Li²⁺ (Z=3):**

$$\begin{aligned}\Delta E &= (3)^2 \cdot 1.889 = 9 \cdot 1.889 = 17.00 \text{ eV} \\ \lambda &= \frac{1240}{17.00} = 72.9 \text{ nm}\end{aligned}$$

Summary:

H: 1.89 eV (656 nm)

He⁺: 7.56 eV (164 nm)

Li²⁺: 17.0 eV (72.9 nm)

Observed pattern: The transition energy is proportional to Z^2

$$\Delta E \propto Z^2$$

Generalization: For a hydrogen-like ion of charge Z :

$$\Delta E_{n_1 \rightarrow n_2} = Z^2 \cdot 13.6 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ eV}$$

2. Limit Wavelength:

For the He⁺ ion, calculate the wavelength of the photon emitted during the $n = \infty \rightarrow n = 2$ transition. In which region of the electromagnetic spectrum is it located?

- a) **Limit Wavelength for He⁺ ($n = \infty \rightarrow n = 2$)**

For He⁺ (Z=2), the $n = \infty \rightarrow n = 2$ transition:

$$\begin{aligned}\frac{1}{\lambda} &= Z^2 R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \\ \frac{1}{\lambda} &= (2)^2 \cdot 1.097 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{\infty} \right) \\ \frac{1}{\lambda} &= 4 \cdot 1.097 \times 10^7 \cdot \frac{1}{4} = 1.097 \times 10^7 \text{ m}^{-1} \\ \lambda &= \frac{1}{1.097 \times 10^7} = 9.116 \times 10^{-8} \text{ m} \\ \lambda &= 91.16 \text{ nm}\end{aligned}$$

Spectral region:

Far Ultraviolet

Verification by energy:

$$E = \frac{1240}{91.16} = 13.6 \text{ eV} \quad (\text{ionization energy from } n=2 \text{ for He}^+)$$

Exercise

Exercise on the Balmer Series: The Balmer series corresponds to all electronic transitions where the electron arrives at the energy level $n_f = 2$. This series produces lines in the visible domain of the electromagnetic spectrum.

a) **Wavelength calculation:**

An excited electron in a hydrogen atom de-excites by going from the $n_i = 3$ level to the $n_f = 2$ level.

- 1) Calculate the wavelength λ (in nm) of the photon emitted during this transition. Use the Rydberg formula:

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

- 2) Is this emitted radiation visible to the naked eye? Justify your answer. (The visible domain extends approximately from 400 nm to 800 nm).

b) **Energy calculation:**

- (1) Calculate the energy (in Joules, then in electronvolts) of the photon emitted during the $n_i = 4 \rightarrow n_f = 2$ transition.
- (2) Compare this energy to that of the $n_i = 3 \rightarrow n_f = 2$ transition. Which is more energetic? Why is this logical?

Solution

a. Transition $n_i = 3 \rightarrow n_f = 2$

a.1 Wavelength calculation The Rydberg formula is written as:

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

Numerical application:

$$\frac{1}{\lambda} = 1.097 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

First, calculate the difference of the inverse squares:

$$\frac{1}{4} - \frac{1}{9} = \frac{9}{36} - \frac{4}{36} = \frac{5}{36} \approx 0.1389$$

Therefore:

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times \frac{5}{36} = 1.097 \times 10^7 \times 0.1389$$

$$\frac{1}{\lambda} = 1.524 \times 10^6 \text{ m}^{-1}$$

To obtain the wavelength:

$$\lambda = \frac{1}{1.524 \times 10^6} = 6.56 \times 10^{-7} \text{ m}$$

Conversion to nanometers ($1 \text{ nm} = 10^{-9} \text{ m}$):

$$\lambda = 6.56 \times 10^{-7} \text{ m} = 6.56 \times 10^{-7} \times 10^9 \text{ nm} = 656 \text{ nm}$$

$$\lambda = 656 \text{ nm}$$

This wavelength corresponds to the H_α line (first Balmer line).

a.2 Visibility to the naked eye The visible domain extends approximately from 400 nm to 800 nm. Our calculated wavelength $\lambda = 656 \text{ nm}$ lies well within this interval:

$$400 \text{ nm} < 656 \text{ nm} < 800 \text{ nm}$$

Yes, this radiation is visible to the naked eye.

Justification: It corresponds to the red color in the visible spectrum (this is the red line of hydrogen, characteristic of nebulae in astrophysics).

b. Transition $n_i = 4 \rightarrow n_f = 2$

b.1 Calculation of the photon energy **Method:** First calculate the wavelength using the Rydberg formula, then the energy with $E = \frac{hc}{\lambda}$.

Wavelength calculation:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = 1.097 \times 10^7 \left(\frac{1}{2^2} - \frac{1}{4^2} \right)$$

$$\frac{1}{4} - \frac{1}{16} = \frac{4}{16} - \frac{1}{16} = \frac{3}{16} = 0.1875$$

$$\frac{1}{\lambda} = 1.097 \times 10^7 \times 0.1875 = 2.057 \times 10^6 \text{ m}^{-1}$$

$$\lambda = \frac{1}{2.057 \times 10^6} = 4.86 \times 10^{-7} \text{ m} = 486 \text{ nm}$$

Energy calculation in Joules:

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}) \times (3.00 \times 10^8)}{4.86 \times 10^{-7}}$$

$$E = \frac{1.988 \times 10^{-25}}{4.86 \times 10^{-7}} = 4.09 \times 10^{-19} \text{ J}$$

Conversion to electronvolts:

$$E = \frac{4.09 \times 10^{-19}}{1.602 \times 10^{-19}} = 2.55 \text{ eV}$$

$$E = 4.09 \times 10^{-19} \text{ J} = 2.55 \text{ eV}$$

This transition corresponds to the H_β line (blue-green line).

b.2 Comparison with the $n_i = 3 \rightarrow n_f = 2$ transition Calculate the energy of the first transition:

$$\lambda_{3 \rightarrow 2} = 656 \text{ nm} = 6.56 \times 10^{-7} \text{ m}$$

$$E_{3 \rightarrow 2} = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3.00 \times 10^8}{6.56 \times 10^{-7}}$$

$$E_{3 \rightarrow 2} = \frac{1.988 \times 10^{-25}}{6.56 \times 10^{-7}} = 3.03 \times 10^{-19} \text{ J}$$

$$E_{3 \rightarrow 2} = \frac{3.03 \times 10^{-19}}{1.602 \times 10^{-19}} = 1.89 \text{ eV}$$

Comparison:

$$E_{4 \rightarrow 2} = 2.55 \text{ eV} > E_{3 \rightarrow 2} = 1.89 \text{ eV}$$

The $4 \rightarrow 2$ transition is more energetic than the $3 \rightarrow 2$ transition

Why is this logical?

According to the hydrogen atom energy diagram:

- The energy of levels is given by $E_n = -\frac{13.6 \text{ eV}}{n^2}$
- The energy of the emitted photon corresponds to the energy difference between levels: $\Delta E = E_{n_f} - E_{n_i} = 13.6 \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$

The larger n_i is, the larger the difference $\left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ becomes (since $\frac{1}{n_i^2}$ decreases), so the emitted energy increases.

Visualization:

- Transition $3 \rightarrow 2$: $\Delta E = 13.6 \left(\frac{1}{4} - \frac{1}{9} \right) = 13.6 \times 0.1389 = 1.89 \text{ eV}$
- Transition $4 \rightarrow 2$: $\Delta E = 13.6 \left(\frac{1}{4} - \frac{1}{16} \right) = 13.6 \times 0.1875 = 2.55 \text{ eV}$

We find exactly our results.

Exercise

Electron Configuration Exercise:

Consider the following elements: ${}^2\text{He}$, ${}^9\text{F}$, ${}^{11}\text{Na}$, ${}^{12}\text{Mg}$, ${}^{17}\text{Cl}$, ${}^{19}\text{K}$, ${}^{24}\text{Cr}$, ${}^{26}\text{Fe}$, ${}^{26}\text{Fe}^{2+}$, ${}^{29}\text{Cu}$, ${}^{22}\text{Ti}$, ${}^{22}\text{Ti}^{2+}$, ${}^{38}\text{Sr}$, ${}^{35}\text{Br}$.

- I. Give the electron configuration of these elements, specifying their period, their group, their atomic number, their name, and their family (column).
- II. Identify the element(s) corresponding to each of the following statements:
 1. Elements whose last electron has quantum numbers $n = 3, l = 1$.
 2. Elements whose last electron has quantum numbers $n = 5, l = 0$.
 3. Elements with 6 valence electrons.
 4. Transition metals.
 5. Halogens.
 6. Noble gases.
 7. Elements belonging to the same period as chromium and the same group as fluorine.
 8. Classify: ${}^4\text{Be}$, ${}^{20}\text{Ca}$, ${}^{22}\text{Ti}$, ${}^{24}\text{Cr}$, ${}^{29}\text{Cu}$, ${}^{38}\text{Sr}$ in increasing order of atomic radius, ionization energy, and electronegativity.

Solution

I. Electron configuration and classification:

Z	Symbol	Electron Configuration	Period	Group (No.)	Family
2	He	$1s^2$	1	VIIIA (18)	Noble Gases
9	F	$[\text{He}] 2s^2 2p^5$	2	VIIA (17)	Halogens
11	Na	$[\text{Ne}] 3s^1$	3	IA (1)	Alkali metals
12	Mg	$[\text{Ne}] 3s^2$	3	IIA (2)	Alkaline earth metals
17	Cl	$[\text{Ne}] 3s^2 3p^5$	3	VIIA (17)	Halogens
19	K	$[\text{Ar}] 4s^1$	4	IA (1)	Alkali metals
22	Ti	$[\text{Ar}] 4s^2 3d^2$	4	IVB (4)	Transition metals
24	Cr	$[\text{Ar}] 4s^1 3d^5$ (Exception)	4	VIB (6)	Transition metals
26	Fe	$[\text{Ar}] 4s^2 3d^6$	4	VIII B (8)	Transition metals
29	Cu	$[\text{Ar}] 4s^1 3d^{10}$ (Exception)	4	IB (11)	Transition metals
35	Br	$[\text{Ar}] 4s^2 3d^{10} 4p^5$	4	VIIA (17)	Halogens
38	Sr	$[\text{Kr}] 5s^2$	5	IIA (2)	Alkaline earth metals

Note on ions: To form a transition metal cation, we remove **first** the electrons from the outermost valence shell (ns before $(n-1)d$).

- Ti^{2+} : Remove the 2 $4s$ electrons. Config: $[\text{Ar}] 3d^2$ (not $[\text{Ar}] 4s^2$).
- Fe^{2+} : Remove the 2 $4s$ electrons. Config: $[\text{Ar}] 3d^6$ (not $[\text{Ar}] 4s^2 3d^4$).

II. Identification of elements:

1. **Last electron** ($n = 3, l = 1$): This is a $3p$ subshell.
 - Cl ($\dots 3p^5$): The last electron is indeed in $3p$.
 - **Answer: Cl (Chlorine).**
2. **Last electron** ($n = 5, l = 0$): This is a $5s$ subshell.
 - Sr ($\dots 5s^2$) corresponds.
 - **Answer: Sr (Strontium).**
3. **6 valence electrons:**
 - Normally, this corresponds to column **VIA** ($ns^2 np^4$). No element in the list is in this case.
 - However, for transition metals, we count the $ns + (n-1)d$ electrons.
 - **Chromium (Cr)** has configuration $4s^1 3d^5$, i.e., $1 + 5 = 6$ valence electrons.
 - **Answer: Cr (Chromium).**
4. **Transition metals:** These are the d -block elements.
 - **Answer: Ti, Cr, Fe, Cu.**
5. **Halogens:** Group **VIIA** (column 17), configuration $ns^2 np^5$.
 - **Answer: F, Cl, Br.**

6. **Noble gases:** Group **VIIIA** (column 18), saturated shell.
 • **Answer: He.**
7. **Same period as Chromium and same group as Fluorine:**
 • Period of Chromium = 4.
 • Group of Fluorine = Halogen (17).
 • The sought element is the halogen of the 4th period.
 • **Answer: Br (Bromine).**
8. **Periodic classification:** Elements to classify: Be (P2), Ca, Ti, Cr, Cu (P4), Sr (P5).
 • **Atomic Radius (R):**
 – In a column, R increases with n ($\text{Be} < \text{Ca} < \text{Sr}$).
 – In a period, R decreases as Z increases ($\text{Ca} > \text{Ti} > \text{Cr} > \text{Cu}$).
 – **Increasing order:** $\text{Be} < \text{Cu} < \text{Cr} < \text{Ti} < \text{Ca} < \text{Sr}$
- **Ionization Energy (EI) and Electronegativity (χ):** They vary generally in the opposite direction to atomic radius (the smaller the atom, the more it retains its electrons).
 – **Increasing order:** $\text{Sr} < \text{Ca} < \text{Ti} < \text{Cr} < \text{Cu} < \text{Be}$
- Note: Beryllium (Period 2) is significantly more electronegative and harder to ionize than the transition metals of Period 4.

Exercise

Exercise on Nuclei and Ions Composition:

- a) For each atom or ion below, calculate:
- The number of protons
 - The number of neutrons
 - The number of electrons
- ${}^{55}_{25}\text{Mn}$, ${}^{40}_{18}\text{Ar}$, ${}^{96}_{42}\text{Mo}$, ${}^{48}_{22}\text{Ti}$, ${}^{207}_{82}\text{Pb}^{+2}$, ${}^{80}_{35}\text{Br}^{-}$, ${}^{122}_{51}\text{Sb}^{+3}$, ${}^{31}_{15}\text{P}^{3-}$.
- b) Give the complete electron configuration of each corresponding neutral atom.
- c) Which of these ions are isoelectronic with a noble gas? Specify the noble gas.
- d) Classify the neutral atoms in increasing order of:
- Atomic radius
 - Ionization energy
 - Electronegativity
- e) Calculate the approximate atomic mass of the element bromine, knowing that there are two stable isotopes: ${}^{79}\text{Br}$ (50.69% abundance) and ${}^{81}\text{Br}$ (49.31% abundance).
- f) Is the ${}^{122}_{51}\text{Sb}^{+3}$ ion stable? Justify in terms of neutron/proton ratio.

Solution

- a) **Composition of nuclei and ions:** Reminder:
- Protons = Z (lower index)
 - Neutrons = $A - Z$ (upper index - lower index)
 - Electrons = $Z - \text{charge}$

Species	Protons (Z)	Neutrons ($A - Z$)	Charge	Electrons
${}^{55}_{25}\text{Mn}$	25	$55 - 25 = \mathbf{30}$	0	25
${}^{40}_{18}\text{Ar}$	18	$40 - 18 = \mathbf{22}$	0	18
${}^{96}_{42}\text{Mo}$	42	$96 - 42 = \mathbf{54}$	0	42
${}^{48}_{22}\text{Ti}$	22	$48 - 22 = \mathbf{26}$	0	22
${}^{207}_{82}\text{Pb}^{+2}$	82	$207 - 82 = \mathbf{125}$	+2	$82 - 2 = \mathbf{80}$
${}^{80}_{35}\text{Br}^{-}$	35	$80 - 35 = \mathbf{45}$	-1	$35 - (-1) = \mathbf{36}$
${}^{122}_{51}\text{Sb}^{+3}$	51	$122 - 51 = \mathbf{71}$	+3	$51 - 3 = \mathbf{48}$
${}^{31}_{15}\text{P}^{3-}$	15	$31 - 15 = \mathbf{16}$	-3	$15 - (-3) = \mathbf{18}$

- b) **Electron configuration of neutral atoms:**
- Mn** ($Z = 25$) : $[\text{Ar}] 4s^2 3d^5$
 - Ar** ($Z = 18$) : $1s^2 2s^2 2p^6 3s^2 3p^6$ (Noble gas)

- **Mo** ($Z = 42$) : $[Kr] 5s^1 4d^5$ (Exception to Klechkowski's rule, like Chromium)
 - **Ti** ($Z = 22$) : $[Ar] 4s^2 3d^2$
 - **Pb** ($Z = 82$) : $[Xe] 6s^2 4f^{14} 5d^{10} 6p^2$
 - **Br** ($Z = 35$) : $[Ar] 4s^2 3d^{10} 4p^5$
 - **Sb** ($Z = 51$) : $[Kr] 5s^2 4d^{10} 5p^3$
 - **P** ($Z = 15$) : $[Ne] 3s^2 3p^3$
- c) **Ions isoelectronic with a noble gas:** A species is isoelectronic with a noble gas if it has a saturated shell configuration ($ns^2 np^6$).
- **Br⁻** (36 e^-): Isoelectronic with **Krypton (Kr)**.
 - **P³⁻** (18 e^-): Isoelectronic with **Argon (Ar)**.
 - **Pb²⁺** (80 e^-): No (pseudo-noble gas configuration s^2 , stable ion but not noble gas configuration).
 - **Sb³⁺** (48 e^-): No (pseudo-noble gas configuration $d^{10} s^2$).
- d) **Periodic classification of neutral atoms:** Elements: P (**P3**), Ar (**P3**), Ti (**P4**), Mn (**P4**), Br (**P4**), Mo (**P5**), Sb (**P5**), Pb (**P6**).
- **Atomic radius:** Increases downwards and leftwards.
 $\text{Ar} < \text{P} < \text{Br} < \text{Mn} < \text{Ti} < \text{Sb} < \text{Mo} < \text{Pb}$
 (Note: Argon is very small because it is an isolated atom without a standard covalent bond like the others, but we follow the general Z_{eff} trend).
 - **Ionization energy and Electronegativity:** Increase upwards and rightwards.
 $\text{Pb} < \text{Mo} < \text{Ti} < \text{Sb} < \text{Mn} < \text{P} < \text{Br} < \text{Ar}$
- e) **Average atomic mass of Bromine:** The average mass is the weighted average of isotopic masses. Here, we approximate the isotopic mass by the mass number A .

$$M_{\text{avg}} = \frac{\sum(x_i M_i)}{100}$$

$$M_{\text{avg}} = \frac{(50.69 \times 79) + (49.31 \times 81)}{100}$$

$$M_{\text{avg}} = \frac{4004.51 + 3994.11}{100} = \frac{7998.62}{100} \approx \mathbf{79.99 \text{ amu}}$$

We indeed find the periodic table value: 79.9

- f) **Stability of the $^{122}_{51}\text{Sb}^{3+}$ ion:** Nuclear stability depends on the nucleus, not the electrons. We look at the N/Z ratio.

$$N = 71, \quad Z = 51 \quad \Rightarrow \quad \frac{N}{Z} = \frac{71}{51} \approx 1.39$$

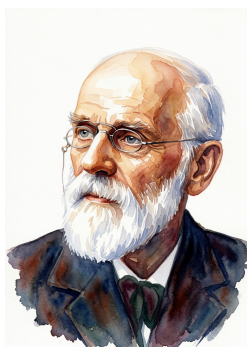
Justification: For light nuclei ($Z < 20$), stability is achieved for $N/Z \approx 1$. For heavy nuclei ($Z > 20$), more neutrons are needed to compensate for proton repulsion; the stability ratio gradually increases up to 1.5 (for Lead). With $Z = 51$, a ratio of **1.39** is quite consistent with the "band of stability". Isotopes 121 and 123 are stable; 122 is actually unstable (radioactive β^+ or β^-), but for a first-year exercise without a Segré chart, the theoretical argument expected is: "The ratio is greater than 1, which is necessary for a heavy nucleus to dilute the Coulomb repulsion of protons".

Transition

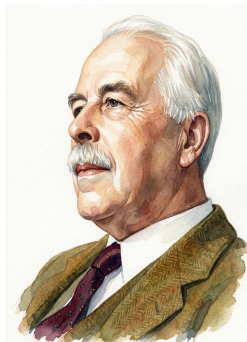
After having explored in detail the **structure of the atom** — consisting of a central nucleus (protons + neutrons) surrounded by electrons distributed in successive electron shells according to increasing energy, and organized in the periodic table which reveals reactivity trends — we now move on to the study of the **molecule**, the chemical entity resulting from the stable association of several atoms.

It is precisely the electron configuration of the **outer shells** (or valence electrons) of these atoms that determines their ability to associate: elements tend to achieve a **stable octet configuration** (like noble gases) by modifying their electron distribution. Depending on the nature of the elements involved and their **relative electronegativity**, the valence electrons will then be either **completely transferred** (ionic bond forming ions), or **equally shared** (nonpolar covalent bond, like H_2), or **polarized shared** (polar covalent bond, like HCl). Thus, the molecule emerges as the direct product of these electronic interactions initiated at the atomic level, laying the foundations for all of compound chemistry.

The Beginning of Structural Chemistry



Johannes Diderik van der Waals (1837-1923): Dutch physicist. He studied the liquid and gaseous states, which led him to discover short-range cohesion forces, named van der Waals forces. Nobel Prize winner in Physics in 1910.



Gilbert Newton Lewis (1875-1946): American chemist and physicist. In 1904, he proposed the octet rule, which describes the tendency of atoms to surround themselves with eight (8) valence electrons. In 1916, he introduced his theory of electron sharing in chemical bonds, identifying the covalent bond as a sharing of electrons between two atoms.



Robert Sanderson Mulliken (1896-1986): American physicist and chemist. Known for his work with **Hund** on molecular orbitals, in which electrons occupy quantum states that extend throughout the molecule. This theory is also called the "**Hund-Mulliken** theory." It explains the structure of molecules.



Linus Carl Pauling (1901-1994): American chemist and physicist. He was one of the first chemists to receive the Nobel Prize in Chemistry in 1954 for his work describing the nature of the chemical bond. In 1939, he published a book on *The Nature of the Chemical Bond*, in which he developed the concept of hybridization of atomic orbitals.



Ronald James Gillespie (1924): London-born chemist, specialist in molecular geometry, professor of chemistry at McMaster University in Canada. He developed the VSEPR (Valence Shell Electron Pair Repulsion) model of molecular geometry with Professor Ronald Nyholm. He wrote several books on VSEPR theory.

Chapter 2.

Chemical Bonding

Proteins, carbohydrates, and other important biomolecules are aggregates of atoms held together by attractive forces called chemical bonds.

Several types of chemical bonds exist, dictated primarily by the electronegativity difference $\Delta\chi$ between the two atoms that form the bond.

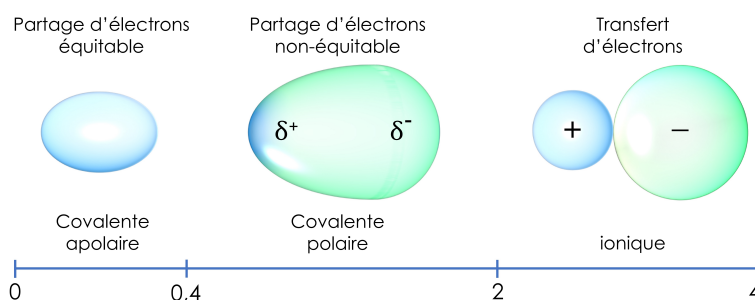


Figure 2.1 Chemical bond as a function of electronegativity difference $\Delta\chi$.

2.1. Lewis Representation of a Chemical Bond

Chemical bonds form between atoms when they seek to share their valence electrons in order to obtain a completely filled peripheral electron shell (octet rule for most atoms, duet rule for hydrogen).

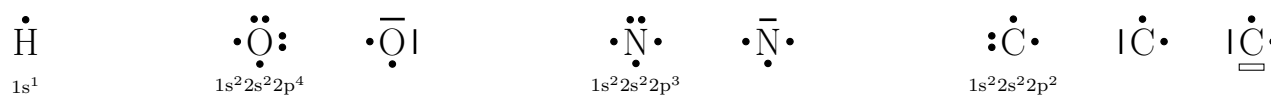
A shell saturated with electrons confers great stability to the whole. When two atoms approach each other, the electrons in their valence shells rearrange to reduce their potential energy. This energy reaches a minimum when the two atoms are separated by a precise distance. This distance, measured from one atomic nucleus to the other, is called the **bond length**. The corresponding energy drop is the **bond energy**.

To facilitate understanding of chemical bonds, several approaches exist. Initially, we use the Lewis representation. This was developed by **Gilbert Newton Lewis**, American physicist and chemist, in 1916.⁽²⁶⁾

In the Lewis representation, each atom is denoted by its atomic symbol. This representation only considers valence electrons (outer shell):

- Electrons are represented by dots arranged around the symbol.
- An electron pair can be represented by two dots or by a line.
- The bond between two atoms is represented by a line connecting their symbols.

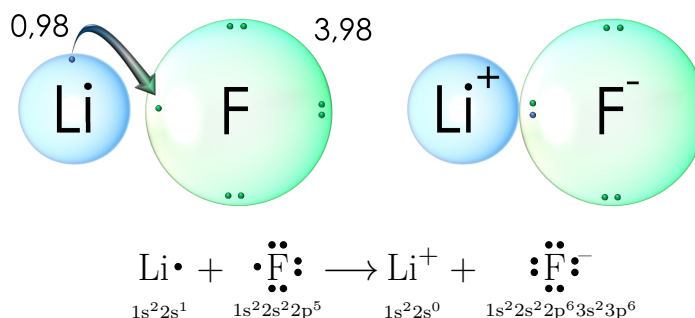
Here are some examples:



In the case of oxygen, we have two unpaired electrons and two paired electron pairs (lone pairs or non-bonding pairs). These can also be represented by lines (non-bonding pairs).

Sometimes, empty quantum boxes are represented in the Lewis representation. For example, in the case of carbon, its electron configuration shows two unpaired electrons in the **p** subshell and one empty box. This is also represented by an empty box in the Lewis representation.

Ionic bond: results from electrostatic attraction between ions of opposite signs (cation and anion); there is a transfer of electrons (caused by an electronegativity difference greater than 2). A bond that generally forms between metallic atoms (electron donors), families **IA**, **IIA**, and **IIIA**, and non-metallic atoms (electron acceptors) from families **VIA** and **VIIA**.



In a molecule like H_2 (Figure 2.2), since the two atoms are identical, they have the same electronegativity and the electron pair that constitutes the covalent bond will be shared equally between the two atoms. The bond thus formed is called a nonpolar covalent bond (or pure covalent bond), because the electron pair is evenly distributed between the two atoms.

On the other hand, in a molecule like HF (Figure 2.3), where there is a large electronegativity difference (ΔEN) between the two atoms, the electron pair will not be distributed equitably between the two nuclei as in H_2 . Indeed, since **F** is much more electronegative than **H**, it will attract the electrons more strongly, thus deforming the electron cloud of the formed bond. Since the electron density will be greater around fluorine, the molecule will have a positive part and a negative part. It is important to realize that the **H** and **F** atoms do not carry real charges, but partial charges, denoted δ^+ and δ^- . The molecule therefore has a dipole, i.e., two poles and a polar covalent bond in which the pair is shared unequally between the two atoms.

When the electronegativity difference is large, the bond is so polar and the partial charges are so large that they approach the charge of an electron (as if the electron were completely transferred); in this case, the bond is ionic.

Atoms of two elements with very different electronegativities therefore tend to form ionic bonds with each other (like those of **NaCl** and **CaO**), because the atom with lower electronegativity donates one or more electrons to the other atom. Such a bond generally involves a metal atom (except when the cation is a polyatomic cation like NH_4^+) and a non-metal atom. On the other hand, atoms whose electronegativities are slightly different tend to form polar covalent bonds with each other, because the deformation of the electron cloud is usually smaller.

Most covalent bonds involve non-metal atoms. Atoms of the same element, or atoms of different elements with the same electronegativity, can unite through a pure (or nonpolar) covalent bond. These trends and characteristics are consistent with the definitions of ionization energy and electron affinity seen earlier.

There is no real boundary between a polar covalent bond and an ionic bond. Only experimental measurements, such as the electrical conductivity of molten solids, allow us to determine whether a substance consists of one type of bond rather than another. However, here are some rules to distinguish the two types of bonds:

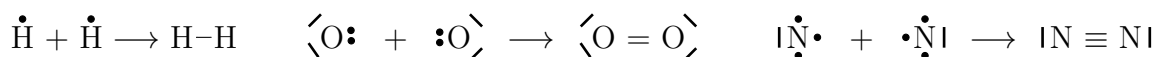
- If the electronegativity difference (ΔEN) is less than 0.5, the bond is nonpolar covalent.
- If the electronegativity difference is between 0.5 and 1.6, the bond is polar covalent.
- If the electronegativity difference is greater than 2.0, the bond is ionic.
- When the electronegativity difference is between 1.7 and 2.0 and a metal participates in the bond, the bond is ionic. If the bond involves non-metals, it is polar covalent.

Sometimes, chemists use the percentage of ionic character to describe the nature of a bond. A pure ionic bond would have an ionic character value of 100% (no known bond has this value), while a purely covalent bond (as in the case of H_2) has an ionic character value of 0%. As Figure 2.1 demonstrates, the pure (nonpolar) covalent bond and the ionic bond are extremes; between them lies the polar covalent bond.

In the case of simple chemical species, it is easy, using the charge carried by each atom, to calculate the percentage of ionic character. For example, if the **HCl** molecule were an ionic compound, the electron would be transferred from hydrogen to chlorine to form **H** and **Cl** ions. With an extra electron, the charge carried by the chlorine atom would correspond to the charge of the electron, i.e., $-1.6 \times 10^{-19} \text{C}$. The hydrogen atom would carry the same charge, with opposite sign, i.e., $+1.6 \times 10^{-19} \text{C}$. However, experiment shows that the charge carried by the chlorine atom in the **HCl** molecule is rather $-2.7 \times 10^{-20} \text{C}$, which represents 17% of the charge of an electron. This means that the chemical species **HCl** is only slightly ionic; that is why this molecule is considered covalent.

$$\text{Percentage of ionic character} = \frac{|\delta|}{e^-} \times 100\%$$

Nonpolar covalent bond: the association between two atoms with a very small or zero electronegativity difference (two identical atoms). The electron sharing will be equitable, and the electrons will orbit around the atoms (the two forming the bond) on a trajectory called a molecular orbital.



Polar covalent bond: Unlike the nonpolar covalent bond, in this case there is a moderate electronegativity difference in the range of 0.4 to 2. Consequently, the electron cloud is denser on the side of the more electronegative atom.

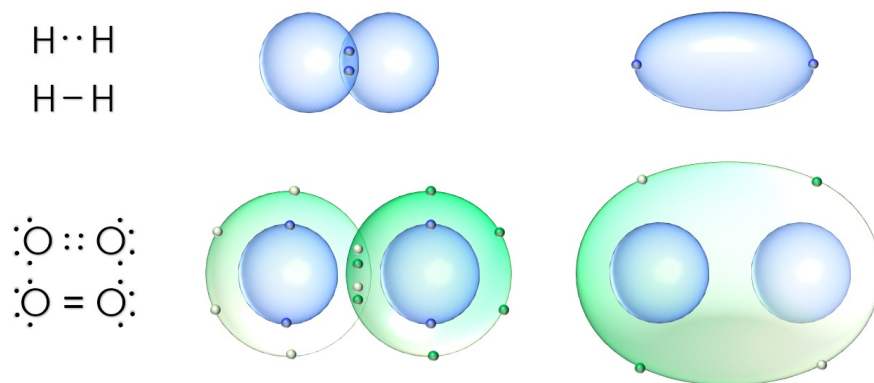


Figure 2.2 Illustration of a nonpolar covalent bond (H_2 and O_2)

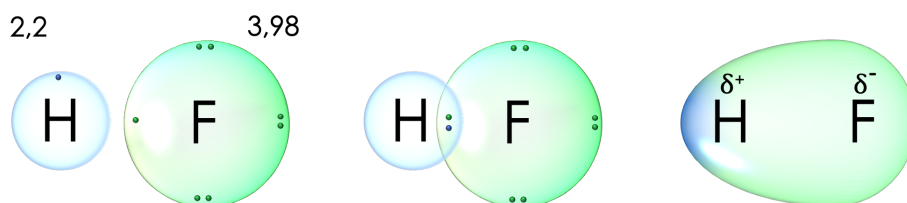
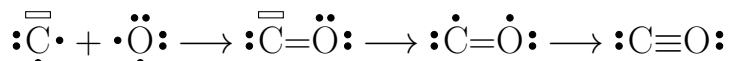


Figure 2.3 Illustration of a polar covalent bond (HF)

Polar coordinate (dative) covalent bond: This type of covalent bond is between two atoms where the two shared electrons in the bond come from the same atom.



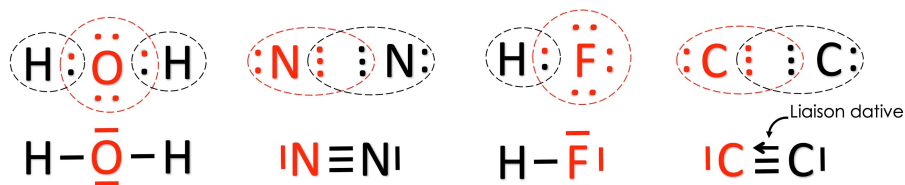
In the carbon monoxide example, both atoms participate with two electrons to form a double bond, but this form shows some instability. Oxygen will participate with the two electrons from its lone pair to create a new bond (i.e., oxygen will give carbon an electron that will occupy the empty box), an action favored by the presence of an empty box in carbon. Thus, the two shared electrons in the bond come from oxygen and form a coordinate bond.

2.1.1. The Duet and Octet Rules:

For a molecule, stability corresponds to the lowest possible energy state. During bond formation, atoms tend to adopt a lower energy electronic configuration, often close to that of the nearest noble gas in the periodic table. Within the Lewis model framework, this tendency is summarized by the duet rule and the octet rule.

Duet rule: Atoms whose first K shell is the valence shell (notably **H** and **He**) are stable when this shell contains **2 electrons** ($1s^2$ configuration). This is the case for helium, and for Li^+ and Be^{2+} ions, which achieve this configuration by losing electrons.

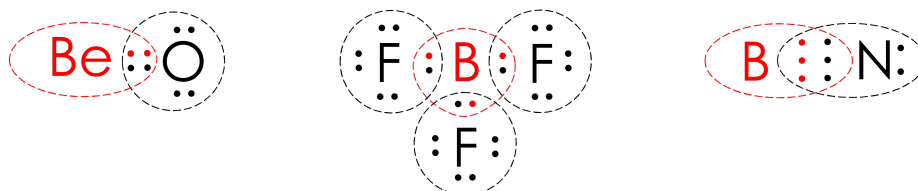
Octet rule: Many non-metal atoms, particularly those in the second period (**C**, **N**, **O**, **F**), tend to achieve a stable configuration with **eight electrons** in their valence shell. This configuration is achieved by sharing electrons (covalent bonds) or by gaining/losing electrons (ion formation).



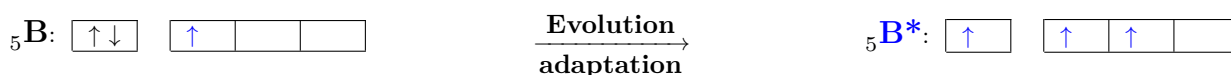
Important limits and exceptions:

- Duet and first shell:** The duet rule applies only to atoms whose valence shell is the first shell (K). This shell can only accommodate **2 electrons** at most, so it concerns mainly **hydrogen** (H) and **helium** (He).
- Hypovalent compounds:** Some light elements, particularly **beryllium** (Be) and **boron** (B), form so-called **hypovalent** compounds. The central atom has fewer than eight electrons in its valence shell, as in BeH_2 , BH_3 , or BF_3 .

- **Noble gases:** They naturally have a saturated valence electron configuration (ns^2np^6) with **8 electrons**, which explains their great stability and low chemical reactivity.
- **Octet expansion and hypervalency:** From the **third period** onward, elements such as **P, S, Cl, Br, I**, and even some noble gases like **xenon** (Xenon forms stable compounds where its octet is expanded, illustrating the flexibility of rules beyond the second period), can accommodate **more than eight electrons** in their valence shell. These compounds, called **hypervalent** (e.g., PCl_5 , SF_6 , XeF_4), show that the octet rule is a trend and not an absolute law.

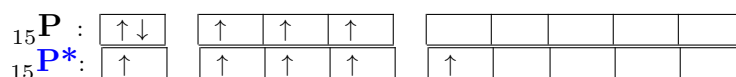


In the case of BF_3 , Boron as the central atom, in its ground state, has three valence electrons: one unpaired in the p subshell and two in the s ($\text{B}: 1s^2 2s^2 2p^1$). To form bonds with the three ligands such as Fluorine, it must go to an excited state ($\text{B}^*: 1s^2 2s^1 2p^2$) in order to have three unpaired electrons. The electron from the s subshell will move to the p subshell alone in an atomic orbital (its new quantum box). The following figure illustrates this explanation.

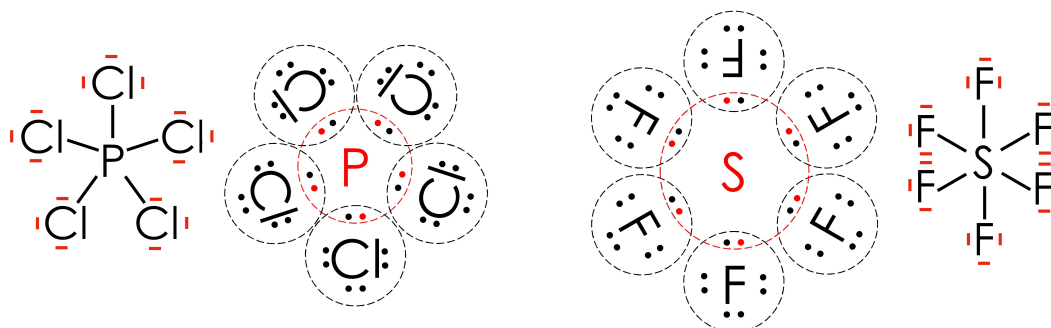


Concerning atoms in the third row, the octet rule is generally invalidated because hybridization with d orbitals allows increasing the capacity of the valence shell, or extending the valence; this is called hypervalency.

In the case of PCl_5 , phosphorus as the central atom ($\text{P}: 1s^2 2s^2 2p^6 3s^2 3p^3$) has three valence electrons. To form bonds with the five chlorine ligands, it must evolve ($\text{P}^*: 1s^2 2s^2 2p^6 3s^1 3p^3 3d^1$). These five electrons will form bonds with chlorine electrons (to form five bonding pairs), meaning ten electrons, and we call this hypervalency (more than eight).



In SF_6 we find the same thing, hypervalency with twelve electrons around the central atom (Sulfur $\text{S}: 1s^2 2s^2 2p^6 3s^2 3p^4$) which excites to accommodate six ligands ($\text{S}^*: 1s^2 2s^2 2p^6 3s^1 3p^3 3d^2$).



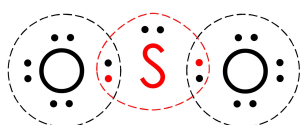
2.1.2. How to Draw a Lewis Formula for a Molecule:

To handle more complex cases, several methods exist. We will take the simplest one to successfully draw this formula:

- 1. Electron configuration and valence:** Count the total number of valence electrons (add 1 e⁻ per negative charge, subtract 1 e⁻ per positive charge).
- 2. Identify the central atom:** The central atom **A** is generally the least electronegative; the ligands **X** are more numerous and more electronegative: $\chi_{(A)} < \chi_{(X)}$ (χ : electronegativity). H is never central.
- 3. Lewis skeleton: single bonds:** Connect atoms with single bonds (each bond = 2 e⁻).
- 4. Distribution of pairs and compliance with octet/duet:** Redistribute electrons respecting the octet and duet rules if possible (except exceptions: B, Al may be deficient).
 - Start with bonding pairs between atoms.
 - For non-bonding pairs, start with ligands then the central atom if any remain.
 - (**Note:** several models are possible—resonance/isomers depending on context).
- 5. Check: formal charges (and chemical consistency):** Calculate the formal charge of each atom = valence electrons – non-bonding electrons – $\frac{1}{2}$ bonding electrons).

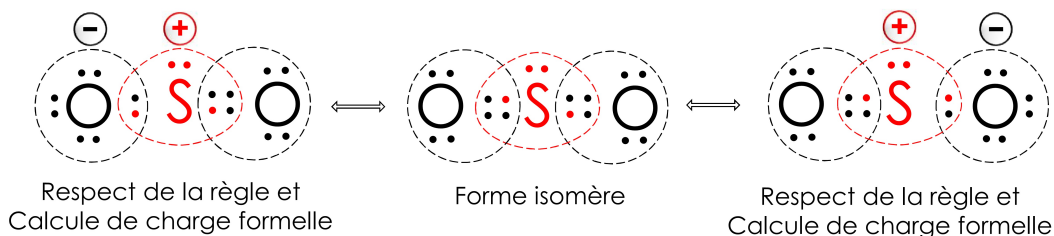
We will take examples to illustrate these steps well.

For sulfur dioxide **SO₂**, we have a total of 18 valence electrons, six for each atom ($6 \times 3 = 18$). The second step is the redistribution of electrons. Since we have two ligands, we will eliminate 4 electrons (two for each pair), leaving 14. Now each ligand takes 6 (to have 8 electrons around each ligand). At this stage, 2 remain and will be for the central atom. We will translate these steps in the following figure.



Redistribution des électrons

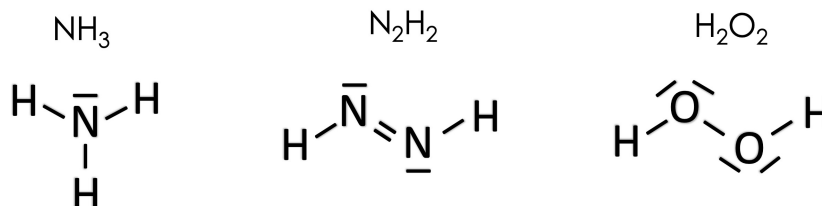
atom	valence electrons	non-bonding electrons	number of bonds	formal charge
S	6	2	3	+1
O	6	6	1	-1
O	6	4	2	0

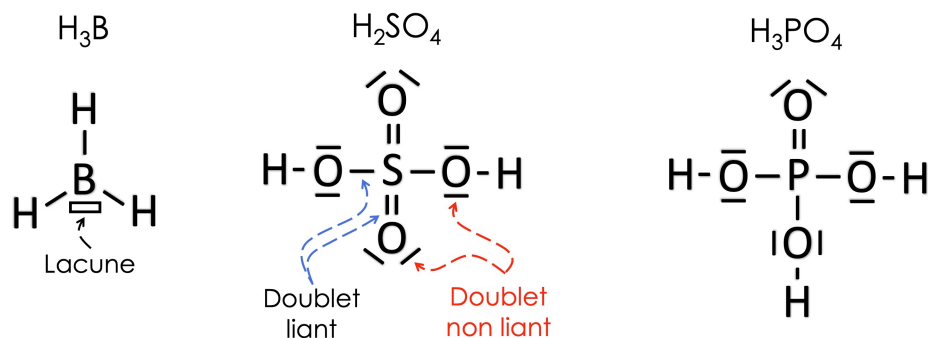


Formal charge calculation of the isomeric form:

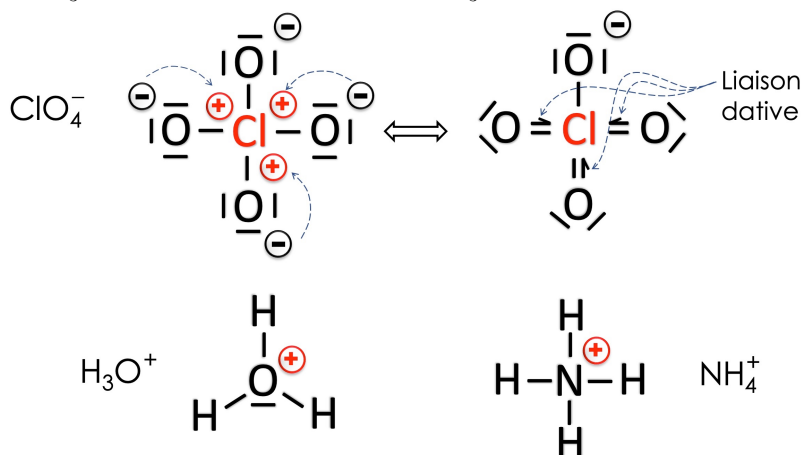
atom	valence electrons	non-bonding electrons	number of bonds	formal charge
S	6	2	4	0
O	6	4	2	0
O	6	4	2	0

Here are some examples of Lewis models for neutral or ionic molecules.





The borane example (BH_3) illustrates **electron deficiency**. The central atom B ($1s^2 2s^2 2p^1$) adopts an sp^2 **hybridization** ($\text{B}^*: 1s^2 2s^1 2p^2$), generating **three unpaired electrons** for the three B–H bonds (see [Page 63](#)). This hybridization leaves an **empty p_z orbital** (vacancy), which must be represented in the Lewis structure, as with AlCl_3 . This deficiency gives BH_3 its **Lewis acid** character, like AlCl_3 .



atom	valence electrons	non-bonding electrons	number of bonds	formal charge
Cl	7	0	4	+3
O	6	6	1	-1

atom	valence electrons	non-bonding electrons	number of bonds	formal charge
Cl	7	0	7	0
O	6	6	1	-1
O	6	4	2	0

In the case of ions, such as ClO_4^- , it is very important to calculate the formal charge (for isomeric forms) to find the location of the latter and consequently conclude whether there is a dative bond or not. In this example, we find three (three positive charges mean an electron deficiency, and the existence of three negative charges forming three coordination bonds, as mentioned in the example). Sometimes we do not find any, as visible in the last two examples of the Hydroxonium ion H_3O^+ and ammonium NH_4^+ .

Exercise

1. Draw the Lewis structures of the following compounds: HNO_2 , ammonium ion (NH_4^+), phosphate ion (PO_4^{3-}), ozone (O_3), sulfite ion (SO_3^{2-}), H_2CO , AlCl_3 , H_2SO_4 , IF_4^- .
2. Based on the electronic structure of the phosphorus atom, explain the formation of PCl_3 and PCl_5 molecules.
3. Both chlorides PCl_3 and PCl_5 exist. Explain why only the compound NCl_3 is known while NCl_5 does not exist.
4. Halogen atoms (group 17) all have 7 valence electrons. However, a notable difference is observed in their ability to form hypervalent compounds with fluorine: iodine heptafluoride (IF_7) is stable and well known, whereas bromine heptafluoride (BrF_7) has never been synthesized.

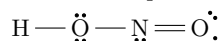
Explain this difference based on the atomic properties of Bromine and Iodine.

Solution

1. Draw the Lewis structures

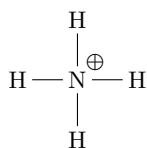
1) HNO_2 (nitrous acid)

- Valence electrons: $1(\text{H}) + 5(\text{N}) + 2 \times 6(\text{O}) = 18$.
- Most stable skeleton: $\text{H}-\text{O}-\text{N}-\text{O}$ (H bonded to O).
- After saturating the O atoms, the octet of N imposes a multiple bond:



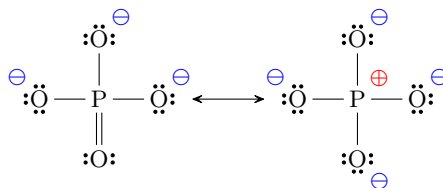
2) Ammonium ion NH_4^+

- Valence electrons: $5 + 4 \times 1 - 1 = 8$.
- Lewis: 4 single N-H bonds, no lone pairs on N, formal charge +1 on N.

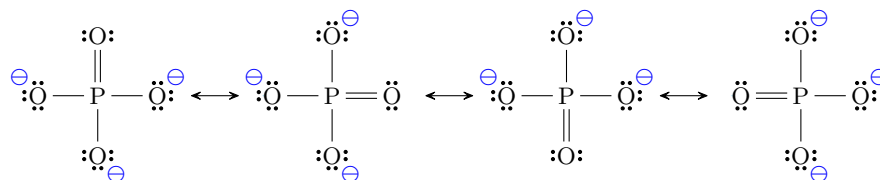


3) Phosphate ion PO_4^{3-}

- Available valence electrons: $5 + 4 \times 6 + 3 = 32$.
- One possible representation with four single P-O bonds leads to a large separation of formal charges: P^+ and four oxygens O^- .
- A more common representation, which reduces charge separation, consists of one $\text{P}=\text{O}$ bond and three $\text{P}-\text{O}^-$ bonds.

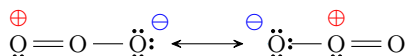


- The resonance hybrid reflects delocalization of the negative charge $\ominus$ over the four oxygens, making the P-O bonds overall equivalent.



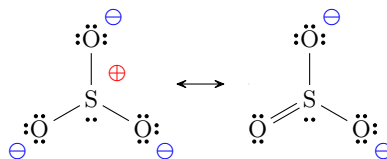
4) Ozone O_3

- Valence electrons: $3 \times 6 = 18$.
- The two main resonance structures are:

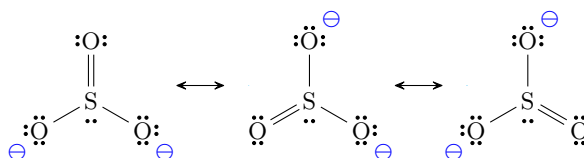


5) Sulfite ion SO_3^{2-}

- Valence electrons: $6 + 3 \times 6 + 2 = 26$.
- After 3 S-O bonds and completion of octets of O, one pair remains on S.
- The first formal charge calculation reveals that sulfur has a positive charge or oxygen a negative charge.

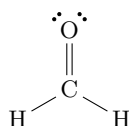


- To reduce formal charges, we classically write: 1 $\text{S}=\text{O}$ bond, 2 $\text{S}-\text{O}^-$ bonds, with 3 resonance forms.



7) **Formaldehyde H_2CO**

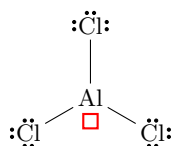
- Valence electrons: $2 \times 1 + 4 + 6 = 12$.
- The central atom is Carbon (least electronegative atom besides H).
- With 2 single C–H bonds and 1 single C–O bond, carbon lacks 2 electrons for its octet.
- To complete Carbon's octet without creating formal charges, we form a double bond C=O.



- Formal charges: $\text{CF}(\text{C}) = 4 - (0 + 4) = 0$; $\text{CF}(\text{O}) = 6 - (4 + 2) = 0$.
- Conclusion: This unique structure is very stable because it respects the octet rule for C and O, and all formal charges are zero. There are no significant resonance forms (no delocalization).

8) **Aluminum chloride AlCl_3**

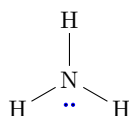
- Valence electrons: $3 + 3 \times 7 = 24$.
- The central atom Al forms 3 single bonds with Cl atoms.
- Each Cl completes its octet with 3 lone pairs.
- **Conclusion:** Al is surrounded by only 6 electrons (incomplete octet). This molecule is electron-deficient.



- Formal charges: $\text{CF}(\text{Al}) = 3 - 0 - 3 = 0$; $\text{CF}(\text{Cl}) = 7 - 6 - 1 = 0$.
- **Major consequence:** Because of this electron vacancy (empty box) (in red), AlCl_3 eagerly seeks an electron pair to complete its octet.
- It is therefore a powerful **Lewis acid**.

9) **Ammonia NH_3**

- Valence electrons: $5 + 3 = 8$.
- The central atom N forms 3 single bonds with Hydrogen atoms.
- Remaining: $8 - (3 \times 2) = 2$ electrons, i.e., **1 lone pair** on nitrogen.
- Nitrogen respects the octet rule (6 bonding electrons + 2 from lone pair = 8).

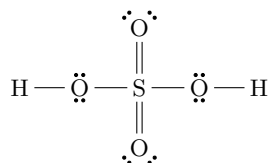


- Formal charges: $\text{CF}(\text{N}) = 5 - 2 - 3 = 0$; $\text{CF}(\text{H}) = 1 - 0 - 1 = 0$.
- **Major consequence:** The presence of this available lone pair (in blue) makes NH_3 a **Lewis base** (electron pair donor).

10) **Sulfuric acid H_2SO_4**

- Valence electrons: $2 \times 1 + 6 + 4 \times 6 = 32$.
- The 2 Hydrogens are bonded to Oxygens (acid -OH function).
- If we strictly respect the octet for Sulfur (4 single bonds), we obtain Sulfur charged +2 and two Oxygens charged -1.

- To minimize these charges, we form two double bonds S=O (hypervalency of sulfur, 12 electrons).

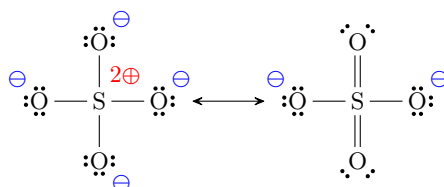


- Formal charges: $\text{CF}(\text{S}) = 6 - (0 + 6) = 0$; all Oxygens are neutral.
- The hypervalent structure is energetically favored because it eliminates excessive charge separation.

To better understand the structure of sulfuric acid, we must go through:

11) **Sulfate ion SO_4^{2-}**

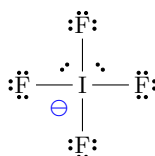
- Valence electrons: $6 + 4 \times 6 + 2$ (negative charges) = 32.
- Strict Octet Approach:** 4 single dative bonds. Sulfur is +2, the four Oxygens are -1. Huge charge separation.
- Extended Octet Approach** (Hypervalency): We form 2 double bonds to cancel the charge on Sulfur.
- There are 6 possibilities to place these 2 double bonds over the 4 positions (equivalent by resonance).



- Formal charges: $\text{CF}(\text{S}) = 0$. The two singly bonded Oxygens each carry a -1 charge.
- This structure with 12 valence electrons around Sulfur is the most energetically stable.

12) **Tetrafluoroiodate ion IF_4^-**

- Valence electrons: $7 + 4 \times 7 + 1$ (negative charge) = 36.
- The central atom I forms 4 single bonds with F atoms.
- Remaining: $36 - (4 \times 8 \text{ for F}) = 4$ electrons, i.e., **2 lone pairs** on Iodine.
- Iodine is surrounded by 4 bonds + 2 lone pairs = 6 electron pairs (Hypervalency, 12 electrons).



- Formal charges: $\text{CF}(\text{I}) = 7 - (4 + 4) = -1$. The negative charge is carried by the central atom.

2. **Formation of PCl_3 and PCl_5 (based on the electronic structure of P)**

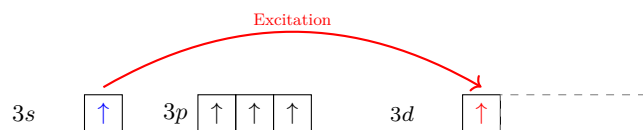
To understand the difference, we need to examine the quantum boxes (orbitals) of the valence shell of Phosphorus.

A. Ground state: Formation of PCl_3 Electronic structure of Phosphorus ($Z=15$): $[\text{Ne}] 3s^2 3p^3$.



- Phosphorus has **3 unpaired electrons** in its $3p$ orbitals.
- It can therefore form **3 simple covalent bonds** with 3 Chlorine atoms.
- $\Rightarrow$ Formation of **PCl_3** (The P atom respects the octet rule).

B. Excited state: Formation of PCl_5 Phosphorus belongs to the **3rd period**. It has empty **3d orbitals** that are energetically accessible. We can promote an electron from the 3s shell to the 3d shell (hypervalency phenomenon).



- Phosphorus now has **5 unpaired electrons** ($1s + 3p + 1d$).
 - It can form **5 covalent bonds**.
 - $\Rightarrow$ Formation of PCl_5 (Expansion of the valence shell).
3. **Why NCl_5 does not exist (but NCl_3 exists)**
- This is a fundamental limit related to the atom's period:
- Nitrogen (N)** ($Z=7$) belongs to the **2nd period**. Its valence shell is $n = 2$ ($2s$ and $2p$ orbitals).
 - Impossibility:** There are no "2d" orbitals. Nitrogen cannot promote electrons to increase its valence beyond 4.
 - It is stuck with the strict octet rule: it can form 3 bonds (NCl_3) thanks to its 3 unpaired p electrons, but can never accommodate 10 electrons to form NCl_5 .

Atom	Period	Valence Orbitals	Possible molecules
Nitrogen (N)	2	$2s, 2p$ (No 2d)	NCl_3 only
Phosphorus (P)	3	$3s, 3p, 3d$	PCl_3 and PCl_5

4. **Why IF_7 exists while BrF_7 does not exist?**

Although Iodine (I) and Bromine (Br) share the same valence configuration (ns^2np^5) and access to d orbitals (theoretical hypervalency possible), chemical reality is dictated by geometry.

- a) **The determining factor: Radius and Atomic surface area** The fundamental difference is the size of the central atom:
- Iodine** ($n = 5$) has a large atomic radius ($r \approx 133$ pm). This large size offers a sufficient **spherical surface area** to accommodate 7 Fluorine atoms around the nucleus without mutual steric hindrance.
 - Bromine** ($n = 4$) is significantly smaller ($r \approx 114$ pm). Its available surface area is too limited to accommodate 7 ligands. The Fluorine atoms would be forced too close to each other, creating insurmountable steric repulsions that destabilize the molecule.
- b) **Secondary factor: Electronegativity** Forming XF_7 forces the central atom to reach the extreme oxidation state +7. Iodine, being less electronegative than Bromine, better supports this massive loss of electron density to the Fluorine atoms.

2.1.3. Limits and Insufficiencies of the Lewis Model:

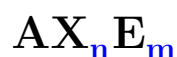
The **Lewis** model satisfactorily interprets the fundamental mechanisms of bond formation and breaking. However, it does not provide information on the geometric orientation of bonds, nor does it explain the magnetic properties of molecules or molecular ions.

2.2. Geometry of Covalent Structures: Gillespie's Model (VSEPR)

In 1940, at Oxford University (UK), researchers **Nevil Sidgwick** and **Herbert Powell**⁽²⁷⁾ proposed a correlation between molecular geometry and the number of valence electrons. This idea was taken up by **Ronald Gillespie** and **Ronald Sydney Nyholm** in 1957⁽²⁸⁾ at University College London to propose a more detailed theory. One of them, **Gillespie**, later moved to Canada (McMaster University, Ontario) and continued to develop this theory.

This method, called **VSEPR** (abbreviation for *Valence Shell Electron Pair Repulsion*), is considered an extension of **Gilbert Newton Lewis's** ideas (1916) on chemical bonds. It allows predicting the geometry of structures (molecular or ionic). It is a method that studies the repulsion forces created by electron pairs in the valence shell of the central atom, and consequently determines the angle between two bonds (between two ligands and the central atom).

To do this, it is very important to write the molecule in the following general form:



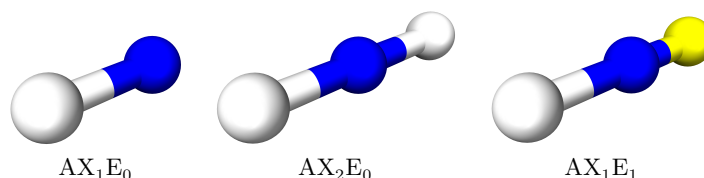
- **A**: Central atom.
- **X**: Atom bonded to the central atom or ligand (white sphere).

- **n**: Number of ligands.
- **E**: Lone pair of the central atom (yellow sphere).
- **m**: Number of lone pairs of the central atom.

Gillespie established several models classified according to the sum **n+m** called the steric number or coordination number; this function gives us the nature of the structure (the framework).

2.2.1. Diagonal Geometry ($n+m = 1$ or 2):

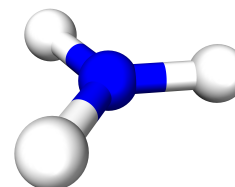
In this case, we have a linear system. There are three possibilities: AX_1E_0 , AX_2E_0 (or AX_2), and AX_1E_1 (AXE). The framework can only be linear, and consequently the angle between the two bonds ($\hat{XAX}$) will take the value 180° . This is illustrated in these three respective examples: LiH , $BeCl_2$, and CN^- .



2.2.2. Trigonal Geometry ($n+m = 3$):

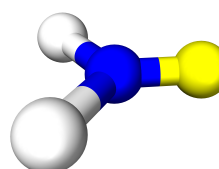
In this case, we have a coplanar system (the three motifs lie in the same plane). There are two possibilities.

AX_3E_0 has a geometry with three identical vertices, so the same repulsion force is exerted on all sides. Consequently, the angle between two bonds is constant, equal to 120° ($360^\circ/3 = 120^\circ$? Because 360° is the angle of a plane, and 3 as three identical ligands). The geometric shape of this model is called triangular planar (example: BF_3).

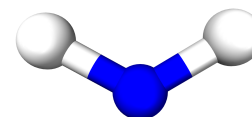


AX_3E_0

AX_2E_1 also has a three-vertex geometry, except that only two are similar; the third is occupied by a lone pair. This lone pair occupies more space than a bonding pair, and consequently there is a small contraction or compression in the angle between the two ligands and the central atom ($\hat{XAX}$ less than 120°). The geometric shape of this model is called bent or V-shaped, as in the example of ozone O_3 or sulfur dioxide SO_2 .

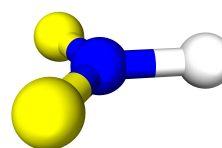


AX_2E_1

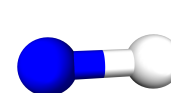


Bent Shape

The last possibility with trigonal base geometry ($m+n=3$) is AX_1E_2 . Here again, we have two similar vertices, but they are lone pairs, and the last is occupied by a bonding pair. The repulsion forces will impose a very stable linear structure, so the angle between the central atom and the single ligand is 180° , as in the case of O_2 .



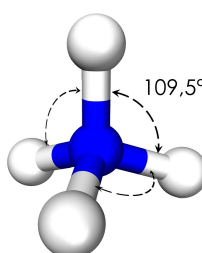
AX_1E_2



Linear Shape

2.2.3. Tetrahedral Geometry ($n+m = 4$):

"tetra" means four and "hedron" is from ancient Greek, synonym for Face of a geometric solid. So a tetrahedron is a geometric shape with four identical faces (identical vertices, identical repulsion force, and identical bond angle = $109.47^\circ = 109^\circ 28'$), also known as a regular tetrahedron.



AX_4E_0

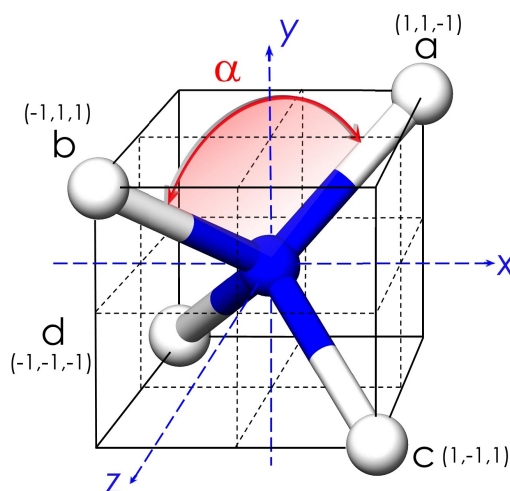


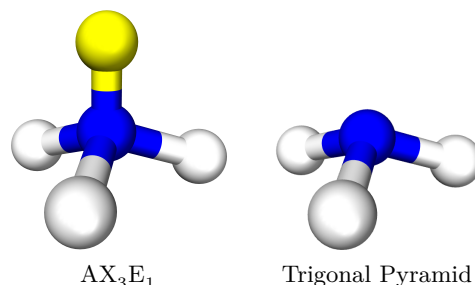
Figure 2.4 Regular tetrahedral geometry: bond angle sp^3 with $\alpha=109.5^\circ$

Where does the value 109.5° come from? A brief geometry reminder is necessary to find this value. We need to know that the shape of a regular tetrahedron can be illustrated in a perfect cube (a geometric shape with identical faces, angles, and edges, and the angle $\mathbf{X}\hat{\mathbf{A}}\mathbf{X}$ denoted α), the angle we seek is the one between the central atom and the two vertices that form a diagonal of one of the faces. The most suitable equation to find our unknown is:

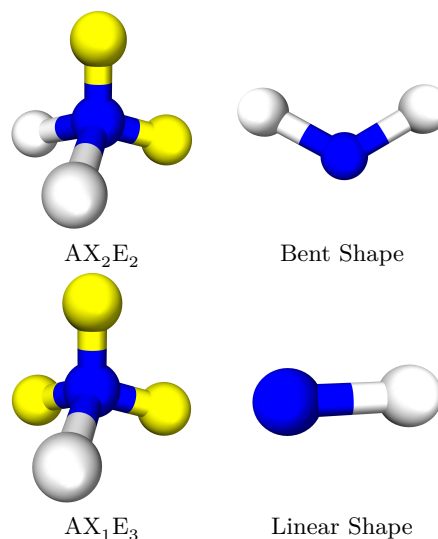
$$a \cdot b = \|a\| \cdot \|b\| \cos \alpha \Rightarrow \cos \alpha = \frac{a \cdot b}{\|a\| \cdot \|b\|} = \frac{\begin{pmatrix} 1 \\ 1 \\ -1 \end{pmatrix} \cdot \begin{pmatrix} -1 \\ 1 \\ 1 \end{pmatrix}}{\sqrt{1^2 + 1^2 + (-1)^2} \cdot \sqrt{(-1)^2 + 1^2 + 1^2}}$$

$$\cos \alpha = \frac{1 \cdot (-1) + 1 \cdot (1) + (-1) \cdot (1)}{\sqrt{3} \cdot \sqrt{3}} = \frac{-1}{3} \Rightarrow \alpha = \cos^{-1} \left(\frac{-1}{3} \right) = 109.5^\circ$$

Formula $\mathbf{AX}_4\mathbf{E}_0$ appears in a regular tetrahedron. But if we substitute one bonding pair with a lone pair (so $\mathbf{AX}_4\mathbf{E}_0$ becomes $\mathbf{AX}_3\mathbf{E}_1$), there will be an increase in repulsion forces, hence a deformation and a change in the $\mathbf{X}\hat{\mathbf{A}}\mathbf{X}$ angle value (109.5° becomes 107.4°) due to electron pair repulsion. Because of this, the regular tetrahedron transforms into a trigonal pyramid (ammonia NH_3 exhibits this configuration).

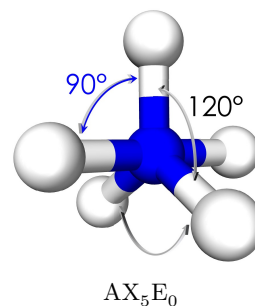


For $m+n=4$, the base geometric shape is tetrahedral, but the presence of a lone pair causes deformation and a change in the $\mathbf{X}\hat{\mathbf{A}}\mathbf{X}$ angle value. The more lone pairs present, the greater the deformation. We will see this in the two following examples: $\mathbf{AX}_2\mathbf{E}_2$ and $\mathbf{AX}_1\mathbf{E}_3$. The common point is the base shape, but the difference will be in the final shape (without considering the lone pairs). Among the molecules with this configuration, H_2O (bent) and HCl (linear).

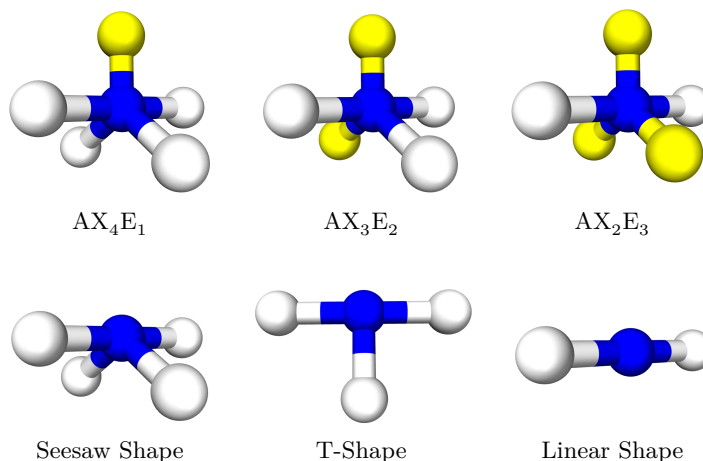


2.2.4. Trigonal Bipyramidal Geometry ($n+m = 5$):

As its name indicates, we have a trigonal pyramid structure attached to another identical one (face to face). It can also be found under another name such as triangular diamond. It is a structure where the central atom is bonded to five identical ligands located at each vertex; it is an AX_5E_0 (case of: PCl_5). This is one of the rare cases where bond angles are not identical, which is simply explained by the fact that there is no geometric arrangement that can result in five equal angles in space.

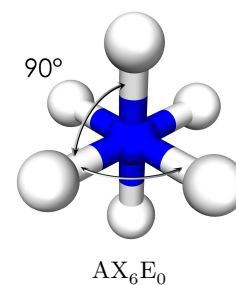


For a steric number of five, we have several possibilities. To see them, it suffices to substitute a bonding pair with a lone pair, and each case has its own structure. Formula AX_4E_1 (for example: SF_4) shows a deformation on all angles; some have shrunk and others expanded, giving a shape called seesaw. Formula AX_3E_2 (for example: ClF_3 or BrF_3) with two lone pairs, and formula AX_2E_3 (for example: KrF_2 or XeF_2) with three lone pairs. The deformation in the framework is significant, giving respectively a "T-shaped" and a linear shape.



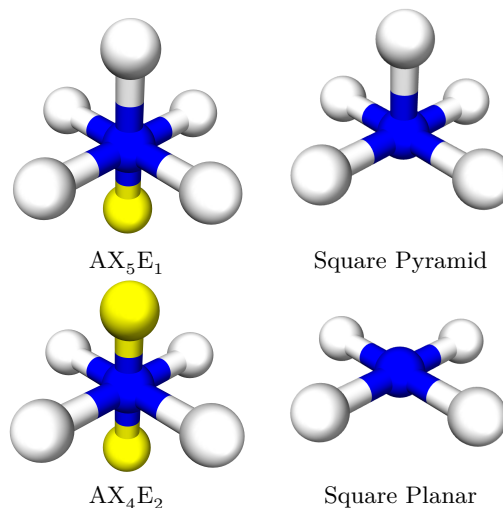
2.2.5. Octahedral Geometry ($n+m = 6$):

An octahedron is a geometric shape with eight faces (square bipyramid), hence the prefix octa (eight). This is the case where we have six pairs surrounding the central atom. In the absence of a lone pair (AX_6) like SF_6 , the geometry is that of a perfect octahedron, and the angle between two bonds is the same = 90° .



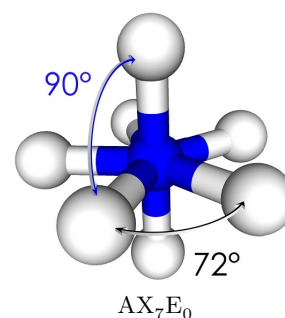
Square Pyramid: When the central atom has one lone pair (AX_5E_1) like Bromine in BrF_5 , it occupies one of the six equivalent directions of the octahedron. This is the case of a square pyramid geometry. With an angle of 84.9° between the square base and the apex of the pyramid (vertical axis), while the angle remains 90° at the base (the square).

Square Planar: In this case, the molecule has two lone pairs (AX_4E_2) for example: XeF_4 , which will be placed on the same axis, resulting in cancellation of repulsion forces, and the angle value remains constant (90°) at the base (square plane).

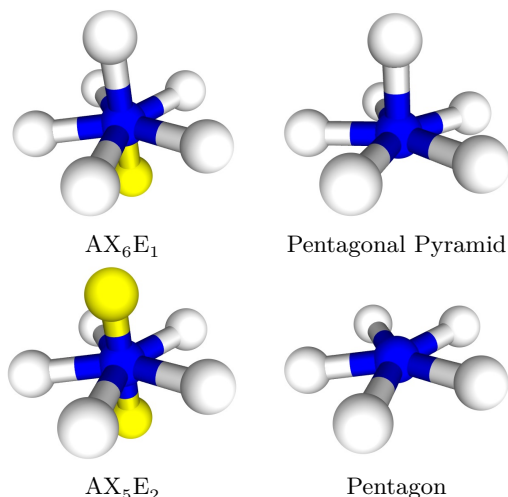


2.2.6. Pentagonal Bipyramidal Geometry ($n+m=7$):

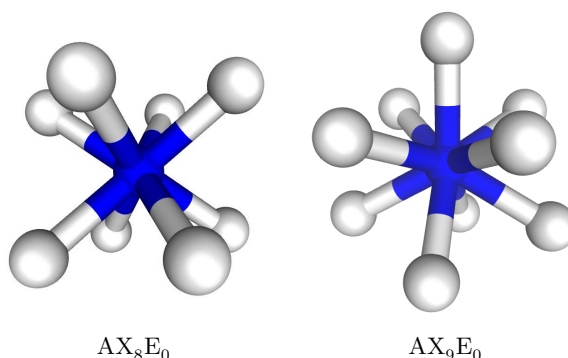
The name of this geometry well summarizes the configuration of the seven vertices present. A pentagonal base ("pent" means five and "gone" means angle) – to determine the $\mathbf{XAX}$ value, simply divide the total angle of a plane by five ($360^\circ/5 = 72^\circ$). As in the previous geometric shape, the two remaining ligands are located facing the pentagonal plane, forming a right angle of 90° (this is the case of $\mathbf{IF}_7$).



In this case, there are only two possibilities. The first case, $\mathbf{AX}_6\mathbf{E}_1$ (such as $\mathbf{XeOF}_5$), we have a single contraction of the 90° angle caused by the presence of the lone pair. The second case, $\mathbf{AX}_5\mathbf{E}_2$, we have only one angle located in the pentagonal base (for example: $\mathbf{XeF}_5^-$).



Other Geometric Shapes: There are several geometric shapes that change according to their steric number or the presence of lone pairs. For steric numbers 8 and 9, we have respectively square antiprism and tricapped trigonal prism shapes.



2.2.7. Limits and Insufficiencies of the Gillespie Model:

Even though this method allows satisfactory prediction of molecular geometry, it is more difficult to apply and insufficient for more complex molecules. However, there are more advanced models that can overcome these limitations, such as Molecular Orbital (**MO**) theory.

Molecules, with their atoms, electrons, and nucleons, are not fixed structures in time and space. Their relative positions vary with time and environment. Consequently, this model has been eclipsed by quantum mechanics and computational chemistry.

2.3. Linear Combination of Atomic Orbitals (LCAO):

This method consists of combining or superimposing atomic orbitals (**AO**) (those of atoms participating in chemical bonds) to obtain (by calculation) molecular orbitals (**MO**).

Unlike in an atom, the electron cloud in a molecule is modified; it depends on the atoms forming the bond. Calculations in this model allow approaching the new wave function (**MO** wave function) based on that of each element taken individually (**AO** wave function).

This method is particularly used to describe diatomic molecules. It allows explaining why some molecules exist and others do not, the relative strength of chemical bonds, as well as the origin of certain physical properties such as dipole moment and diamagnetism or paramagnetism of molecules.

2.3.1. Linear Combination:

The notion of linear combination refers to two sets: Vectorial and Scalar of mathematical objects, namely a set of vectors from a vector space on one hand, and numbers or scalars from a numerical space such as the set of real numbers on the other hand.

We then define an external operation such that any element can be expressed as a sum of products of a scalar and a vector. The number of terms in this product depends on the dimension of the chosen vector space. If the vector space is two-dimensional, then each linear combination will have two terms; if the vector space is three-dimensional, then each linear combination will have three terms, and so on.

Taking an example: If variables x and y belong to a set of real numbers, and a and b are integers, then the expression representing the real number z in the form of a linear combination of the integers a and b .

$$z = ax + by$$

2.3.2. Atomic and Molecular Orbitals:

Electrons are described by atomic orbitals in the case of isolated atoms, and molecular orbitals in the case of molecules (sets of atoms). The wave function of **AOs** is the reference to exact solutions obtained with the hydrogen atom, which considerably simplified their determination. This is no longer possible in the case of **MOs**; therefore, other strategies exist, namely **LCAO**, which expresses the combination of **AOs**. The following relation can translate this method.

$$\Psi = \sum c_i \cdot \psi$$

In this sum, a numerical coefficient c_i is the combination coefficient of the atomic orbital ψ in the molecular orbital Ψ .

To determine these coefficients of the **AOs**, we rely on the variation theorem. A choice of **AOs** is important for calculating the coefficients; for example:

- We do not consider the **AOs** of the core.

- We restrict the development to the **AOs** occupied in the ground state of the atom (valence orbitals).

As for isolated atoms, we can write a molecular Schrödinger equation for molecules. Solving this equation will lead to molecular wave functions (or molecular orbitals) whose square represents the probability of electron presence. This solution is rigorously possible only in the simplest case, that of the H^{2+} molecular ion. For more complex molecules, we resort to approximations.

2.3.3. Formation of a Chemical Bond:

2.3.3.1. Mathematical Aspect of a Chemical Bond:

The exact solution of **Schrödinger's** equation is quite complex, but it is possible to use an approximate solution method called linear combination of atomic orbitals. This method consists of considering that the molecular wave function is a Linear Combination of Atomic Orbitals. We will take the example of dihydrogen H_2 , and the atomic orbitals to consider are the two $1s$ of the hydrogen atoms. Let us call these two atoms **A** and **B**, and the functions ψ_A and ψ_B , two well-defined mathematical expressions that express the wave function of each atomic orbital. In the **LCAO** method, we consider that the molecular orbital Ψ_{AB} is a linear combination of these two atomic orbitals ψ_A and ψ_B .

$$\Psi_{AB} = a\psi_A + b\psi_B$$

In reality, only the square of the wave function (which expresses the probability of electron presence in space) has physical meaning.

$$\Psi_{AB}^2 = a^2\psi_A^2 + 2ab\psi_A\psi_B + b^2\psi_B^2$$

This expression contains a term:

- that appears only for atom **A** ($a^2\psi_A^2$) corresponds to the probability of finding the electron very close to nucleus **A**.
- that appears only for atom **B** ($b^2\psi_B^2$) corresponds to the probability of finding the electron very close to nucleus **B**.

- mixed term where both atoms **A** and **B** appear ($2ab \psi_A \psi_B$), which corresponds to the probability of finding the electron neither very close to nucleus **A** nor very close to nucleus **B**, i.e., between the two atoms **A** and **B**, which corresponds to the formation of the chemical bond between these two atoms as in the Lewis model.

For symmetry reasons, atoms **A** and **B** play the same role, so there is no reason for the electron to be closer to **A** than to **B** or vice versa. The probability of finding the electron near **A** is therefore equal to the probability of finding it near **B**, and thus:

$$a^2 \psi_A^2 = b^2 \psi_B^2$$

Moreover, in this case, the orbitals ψ_A and ψ_B are completely identical, and there is no reason to distinguish them. So we have $a^2 = b^2$, i.e., $a = \pm b$. We will therefore have two solutions for Ψ_{AB} :

$$\Psi_{AB} = a\psi_A + a\psi_B = a(\psi_A + \psi_B)$$

$$\Psi_{AB} = a\psi_A - a\psi_B = a(\psi_A - \psi_B)$$

These two expressions will simultaneously be solutions of the Schrödinger equation. Thus, we obtain two molecular orbitals from the two atomic orbitals. These two molecular orbitals are different:

- the function $(\psi_A + \psi_B)$ is called bonding because it corresponds to an increase in the probability of electron presence between atoms **A** and **B**, which corresponds to bond creation.
- conversely, the function $(\psi_A - \psi_B)$ is called antibonding because it corresponds to a decrease in the probability of electron presence between atoms **A** and **B**, which corresponds to bond destruction.

To further simplify understanding of the problem and its solution, we will simplify the model: one electron instead of two, which leads us to $\mathbf{H}_2^+$ instead of $\mathbf{H}_2$.

If the electron is close to the nucleus of atom **A**, it uses the atomic orbital ψ_A , and if it is close to the nucleus of atom **B**, it uses the atomic orbital ψ_B . The molecular wave function Ψ_{AB} is a linear combination of the two atomic wave functions ψ_A and ψ_B . Let us call:

$$\Psi_{AB}^+ = a\psi_A + a\psi_B = a(\psi_A + \psi_B)$$

$$\Psi_{AB}^- = a\psi_A - a\psi_B = a(\psi_A - \psi_B)$$

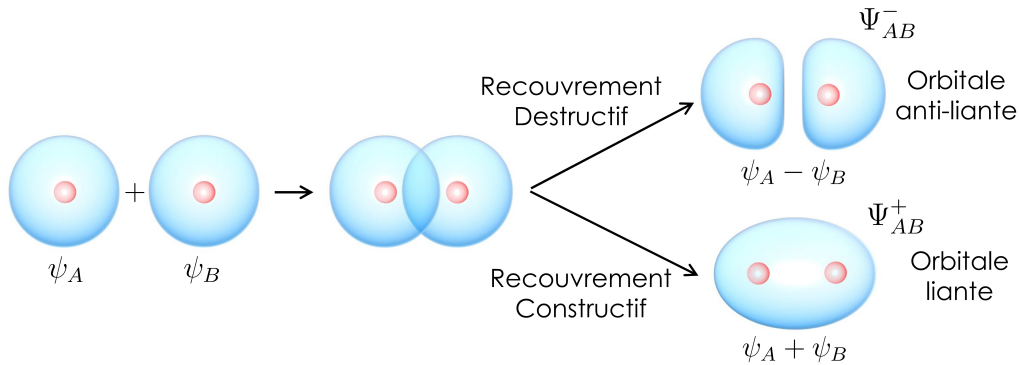


Figure 2.5 Different types of overlap

The wave function of the 1s atomic orbital (of the hydrogen atom, see [Page 29](#)) ($\Psi_{(1,0,0)}$ 1s which corresponds to ψ_A and ψ_B since they are identical) is:

$$\psi_A = \psi_B = \sqrt{\frac{1}{\pi a_0^3}} \cdot e^{-\left(\frac{r}{a_0}\right)}$$

The probability density $|\Psi(r)|^2$ is the notion of finding the particle (in our case the electron) at radius r ($0 \leq r \leq \infty$), and using the probability $P_n(r)$ to find the particle in a volume V around r , we will have this equation (level $n=1$, since it is the 1s):

$$P_1 = |\Psi_{AB}^+|^2 \cdot dV$$

$$\int_V |\Psi_{AB}^+|^2 dV = 1$$

$$\int_V (a^2 \psi_A^2 + 2a^2 \psi_A \psi_B + a^2 \psi_B^2) dV = 1$$

$$a^2 \int_V \psi_A^2 dV + 2a^2 \int_V \psi_A \psi_B dV + a^2 \int_V \psi_B^2 dV = 1$$

Knowing that $\psi_A = \psi_B$ because they are identical s -type atomic orbitals, and these are normalized wave functions, therefore:

$$\int_V \psi_A^2 dV = \int_V \psi_B^2 dV = 1$$

And we are left with only the mixed term that represents the bond between the two hydrogen atoms, so we have an overlap (called S) between the two wave functions:

$$\int_V \psi_A \psi_B dV = S \quad \text{with: } 0 \leq S \leq 1$$

This integral gives a measure of the interpenetration of the two atomic orbitals.

- When the two atoms are very far apart, the two atomic clouds (or atomic orbitals) are sufficiently separated that their overlap can be neglected. The overlap integral is zero $S = 0$.
- When the two atoms approach, the two atomic orbitals take simultaneously non-zero values in the bonding zone around the center of the molecule. In the limit of fusion of the two nuclei, the two orbitals become identical and the overlap integral becomes equal to a normalization integral $S = 1$.

If we symbolically represent the two $1s$ orbitals as spheres, the intersection zone of these geometric shapes then symbolizes the extent of overlap between the atomic orbitals.

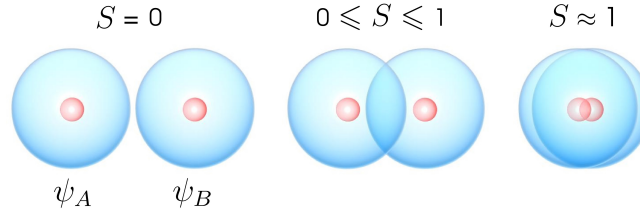


Figure 2.6 Overlap between atomic orbitals

The closer S is to 1 (the larger it is), the stronger the overlap, and the stronger the bond. To find out, we need to calculate the overlap coefficient a .

$$a^2 \int_V \psi_A^2 dV + 2a^2 \int_V \psi_A \psi_B dV + a^2 \int_V \psi_B^2 dV = 1$$

$$a^2(1 + 2S + 1) = 1 \quad \Leftrightarrow \quad a = \sqrt{\frac{1}{2(1 + S)}}$$

Thus, the expression of the wave function of the molecular orbital Ψ_{AB}^+ is:

$$\Psi_{AB}^+ = \sqrt{\frac{1}{2(1 + S)}}(\psi_A + \psi_B)$$

We will do the same for the other molecular orbital:

$$a^2 \int_V \psi_A^2 dV - 2a^2 \int_V \psi_A \psi_B dV + a^2 \int_V \psi_B^2 dV = 1$$

$$a^2(1 - 2S + 1) = 1 \quad \Leftrightarrow \quad a = \sqrt{\frac{1}{2(1 - S)}}$$

$$\Psi_{AB}^- = \sqrt{\frac{1}{2(1 - S)}}(\psi_A - \psi_B)$$

Concerning the energy of the molecular orbital, it is necessary to use the variational method, which is based on the fact that by varying a function to obtain the lowest average energy, we will maximize the rate of the lowest energy eigenvalue present in the linear combination.

$$\langle \Psi_{AB} | H | \Psi_{AB} \rangle = E \langle \Psi_{AB} | \Psi_{AB} \rangle$$

Within the framework of the **LCAO** method, it is written:

$$\langle a\psi_A + b\psi_B | H | a\psi_A + b\psi_B \rangle = E \langle a\psi_A + b\psi_B | a\psi_A + b\psi_B \rangle$$

Taking into account the linearity of the integrals:

$$\begin{aligned} \langle a\psi_A + b\psi_B | H | a\psi_A + b\psi_B \rangle &= \langle a\psi_A | H | a\psi_A \rangle + \langle a\psi_A | H | b\psi_B \rangle \dots \\ &= a^2 \langle \psi_A | H | \psi_A \rangle + ab \langle \psi_A | H | \psi_B \rangle \dots \end{aligned}$$

To simplify the notation, we set:

- $\langle \psi_i | H | \psi_i \rangle = \alpha_i$ Called the Coulomb integral, it approximately represents the energy of an electron occupying the orbital ψ_i in the isolated atom i . α_i is negative and its absolute value should increase with the electronegativity of i .
- $\langle \psi_i | H | \psi_j \rangle = \beta_{ij}$ Called the resonance integral, its absolute value gives a measure of the bond strength between the two atoms. It is an increasing function of the overlap integral S_{ij} .
- $\langle \psi_i | \psi_j \rangle = S_{ij}$ Called the overlap integral.
- $\langle \psi_i | \psi_i \rangle = S_{ii} = 1$, since the **AOs** are normalized.

For this model, the two atoms being identical, we have: $\alpha_1 = \alpha_2$ and $\beta_{12} = \beta_{21}$, which further simplifies our equation:

$$(a^2 + b^2)\alpha + 2ab\beta = E(a^2 + b^2 + 2abS)$$

In this equation, α , β , and S are parameters; a , b and E are unknowns. Now let us choose a and b to minimize E (the minimum is obtained when the partial derivatives of the energy E with respect to the various coefficients are zero).

$$\frac{\partial E}{\partial a} = \frac{\partial E}{\partial b} = 0$$

We obtain the system of secular equations:

$$(\alpha - E)a + (\beta - ES)b = 0$$

$$(\beta - ES)a + (\alpha - E)b = 0$$

These equations are linear and homogeneous in a and b . For a solution to exist, the secular determinant must be zero:

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

We find two possible solutions:

$$E_1 = \frac{\alpha + \beta}{1 + S} \quad \text{and} \quad E_2 = \frac{\alpha - \beta}{1 - S}$$

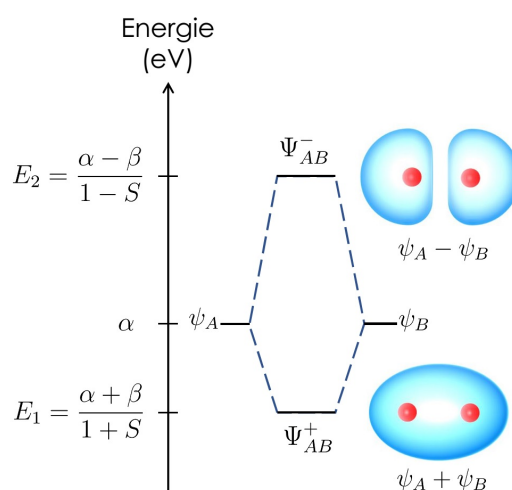


Figure 2.7 Correlation diagram of molecular orbitals

E_1 is the energy of the first molecular orbital (ψ_{AB}^+) and E_2 is the energy of the second (ψ_{AB}^-); these are the only possible energies for an electron belonging to a diatomic like H_2 . It should not be forgotten that α and β have negative

values and S is by nature less than 1 (a value that would correspond to perfect overlap of orbital ψ_B onto orbital ψ_A). Both energies are negative, and E_1 is lower than E_2 . See Figure 2.7.

In this molecular orbital Ψ_{AB}^+ , the electron binds the nuclei (it tends to bring them closer); this orbital is called bonding. Once occupied (by electrons), it decreases the energy of the molecule. However, in the molecular orbital Ψ_{AB}^- , the electron does not bind the nuclei but tends to push them apart; it is antibonding. If it is occupied, it increases the energy of the molecule.

2.3.3.2. Analysis of Molecular Orbitals

The two orbitals ψ_A and ψ_B are identical; therefore, they will be symmetric. Considering the combinations of atomic orbitals in the molecular orbital expressions, it appears that the functions of the two atomic orbitals overlap in the interatomic space. The nature of this overlap will determine the nature of the considered molecular orbital.

- The orbital Ψ_{AB}^+ : in the interatomic space, the functions add. The probability of finding electrons in this region of space also increases. This is a sharing of two electrons in the interatomic space: This is the definition of a bond. Ψ_{AB}^+ is a bonding molecular orbital.
- The orbital Ψ_{AB}^- : in the interatomic space, the functions subtract. So we add a positive function ψ_A to a negative function ($-\psi_B$). The mathematical functions defining ψ_A and ψ_B are the same, so exactly at equal distance from the nuclei of atoms A and B , this sum is zero. This surface associated with a wave function (molecular orbital Ψ_{AB}^-) is called a nodal surface. On this surface, the probability of finding electrons is zero. Ψ_{AB}^- is an antibonding molecular orbital.

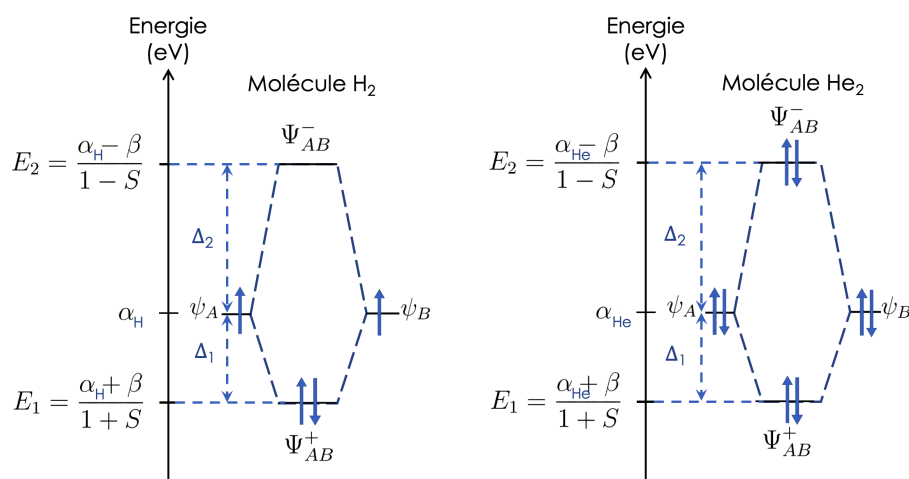


Figure 2.8 Energy diagram of Molecular Orbitals for H₂ (left) and He₂ (right)

2.3.3.3. Energy Analysis

Each atomic orbital ψ_A and ψ_B is associated with an energy level of value α . The energies of the molecular orbitals E_1 and E_2 are distributed on either side of this intermediate value Figure 2.8. The difference between α and E_1 is therefore smaller than that between α and E_2 . This difference accounts for the stability of molecules relative to separated atoms.

2.3.3.4. Physical Aspect of a Chemical Bond

In the Lewis model, bonding resulted from the sharing of an electron pair between two atoms; this simple idea remains broadly valid in the quantum model, where chemical bonding arises from the overlap of two atomic orbitals to produce two molecular orbitals.

There are two types of overlap, leading to two different types of bonds. We will focus only on bonds involving atomic orbitals of type s or p .

Sigma type bonds: Axial overlap leads to σ type bonds. We find this between s type atomic orbitals (Figure 2.9), between p_z orbitals (Figure 2.12), and even between s and p_z (Figure 2.13). It should be noted that by convention, the z axis is the overlap axis (the bond axis); thus, this type of overlap is found mainly on this axis and occurs when the two interacting orbitals point toward each other.

As shown in the derivations, the atomic orbitals ψ_A and ψ_B are completely identical, so we have $a^2 = b^2$, i.e. $a = \pm b$. Two cases therefore arise: an overlap with $+\psi_B$ and another with $-\psi_B$. One should bear in mind that the sign of the

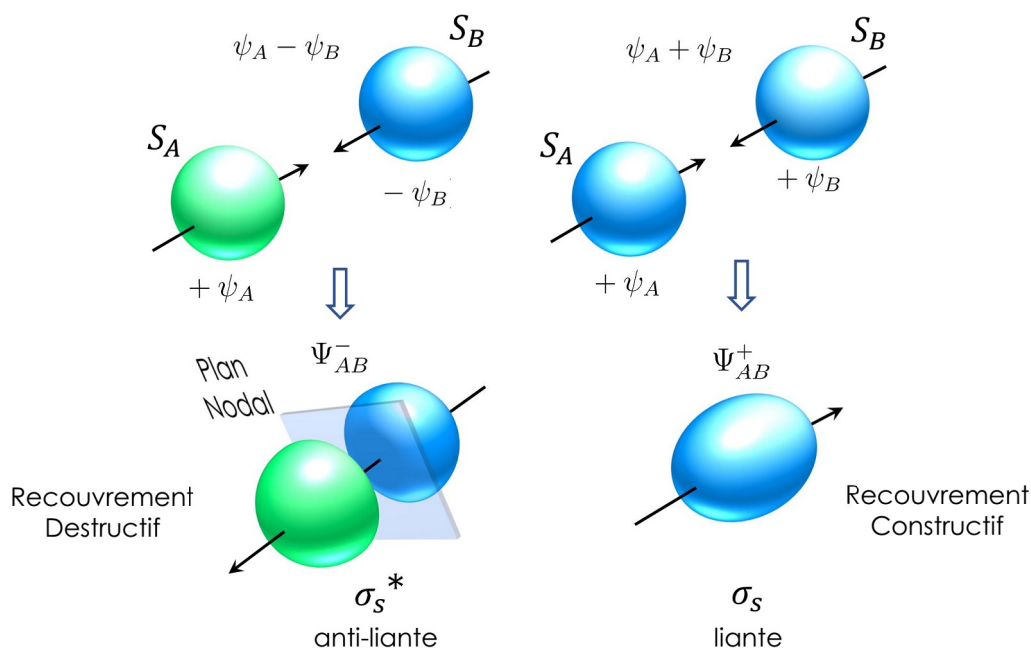


Figure 2.9 Axial overlap between s -type orbitals

wave function carries no physical meaning by itself, except that its modulus reflects the probability of finding electrons in space. It is important to understand that a sign difference for a single electron is irrelevant, but as soon as several electrons occupying several orbitals are considered, they can interfere constructively or destructively in a way that fundamentally depends on these signs. We can therefore say that the electron distribution in molecules can only be determined if the signs of these wave functions are known.

To gain a clearer understanding, we consider the case of H_2 , dihydrogen — the simplest example of a diatomic model. Each H contributes a $1s$ atomic orbital (AO), giving rise to two molecular orbitals (MO) **Figure 2.8**: the bonding σ_s (or Ψ_{AB}^+) and the antibonding σ_s^* (or Ψ_{AB}^-).

In general, from n atomic orbitals, we can construct n molecular orbitals.

Note: For homonuclear diatomic molecules, it is useful to describe a molecular orbital by identifying its symmetry — the behavior of the wave function when inverted through the center of inversion. If we take any point on the bonding σ orbital and project it through the molecular center to an equal distance on the other side, we arrive at an identical value of the wave function (**Figure 2.10**). This pseudo-symmetry, called *gerade* (German for “even”), is denoted by a subscript *g*, as in σ_g . Conversely, the same procedure applied to the antibonding orbital yields the opposite sign of the wave function. This *ungerade* (“odd symmetry”) is denoted by a subscript *u*, as in σ_u . This inversion symmetry classification does not apply to diatomic molecules formed from atoms of two different elements (heteronuclear), since these molecules have no center of inversion.

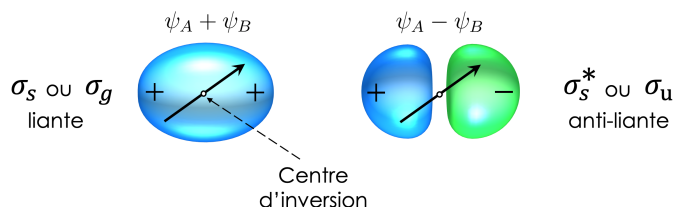


Figure 2.10 Inversion center of the σ -type wave function.

In the dihydrogen molecule, there are two electrons to accommodate; these can enter σ_s with paired spins (as required by the **Pauli** principle). The ground-state configuration is therefore $1(\sigma_s)^2$ or $(\sigma_{1s})^2$, meaning the atoms are linked by a bond consisting of an electron pair in a sigma-type molecular orbital.

At this point, molecular orbital theory defines the bond order — also called the bond index L_n — deduced from the

following equation:

$$L_n = \frac{1}{2} (\text{number of bonding electrons} - \text{number of antibonding electrons})$$

Applying this to dihydrogen gives $L_n = 1$, meaning there is a single bond in H_2 :

$$L_n = \frac{1}{2} (2 - 0) = 1$$

Another case must be highlighted to better understand the two types of overlap. In the case of helium He_2 , the importance of the antibonding orbital becomes evident when considering the hypothetical existence of this molecule. The MO energy diagram of He_2 (Figure 2.8) bears a strong qualitative resemblance to that of H_2 ; a total of four electrons occupy the molecular orbitals. The electronic configuration is $1(\sigma_s)^2 1(\sigma_s^*)^2$, sometimes written as $(\sigma_{1s})^2 (\sigma_{1s}^*)^2$. Applying the bond order equation gives $L_n = 0$, meaning no bond exists between the two helium atoms, and hence He_2 does not exist (it is hypothetical):

$$L_n = \frac{1}{2} (2 - 2) = 0$$

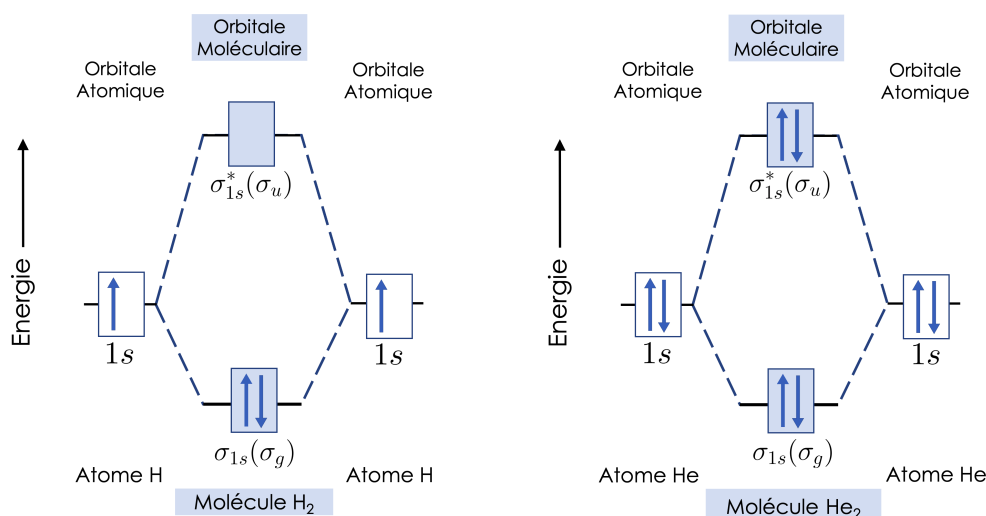


Figure 2.11 Molecular orbital diagram of H_2 (left) and He_2 (right).

The diagrams of the two preceding examples can also be presented in a simpler and more common form (Figure 2.11), with the starting atomic orbitals on the outside as a reference and the molecular orbitals in the center. Recall that the atomic orbitals shown on both sides of the diagram have combined to form the molecular orbitals. They appear on the diagram to show the orbital energies of the isolated atoms relative to those of the molecular orbitals, and to indicate which atomic orbitals form which molecular orbitals.

Using these diagrams, MO theory shows that the two electrons of H_2 reside in the bonding molecular orbital; energetically, these electrons occupy a more stable level than in an isolated atom ($E_{1s} > E_{\sigma_{1s}}$), so hydrogen is more stable when bonded to another atom than in its monoatomic form.

In the case of helium, isolated atoms are slightly more stable than He_2 , so this molecule will not form. We already know that helium atoms are stable and unreactive, and do not combine with one another.

In the case of axial overlap σ_z (or σ_{p_z}) shown in (Figure 2.12), this is generally found in a heteronuclear diatomic molecule (e.g. HF or LiF). The MO diagrams for these molecules are similar (Figure 2.14) to those of homonuclear molecules when the valence orbitals of one atom are sufficiently close in energy to those of the other atom. It is important to know that there are two criteria for combining atomic orbitals (AO):

- **Energy criterion.** AOs of very different energies do not combine. In general, the energies of combined AOs differ by less than 10 eV.
- **Symmetry criterion.** The overlap is zero between AOs of different symmetry types. Their combination leads to no bond regardless of its length.

In heteronuclear models, the energy difference ΔE between the AOs forming the σ_{sp} (or σ_{spz}) MOs must be verified, as shown in (Figure 2.13).

The interaction between overlapping atomic orbitals decreases as the energy difference between them increases. If a large difference exists ($\Delta E > 12$ eV), the molecular orbital is no longer stable relative to an isolated atom. Figure 2.14 presents the MO diagram of HF .

The energy difference between the atomic orbitals in HF is so large that the most stable molecular orbitals are exclusively the fluorine atomic orbitals. However, there is a weak interaction between the $1s$ orbital of hydrogen and the $2p_z$ orbital

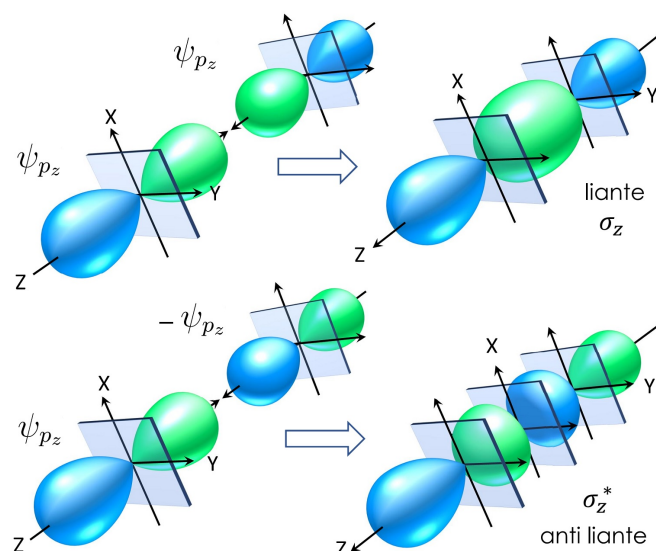


Figure 2.12 Axial overlap between p_z -type orbitals

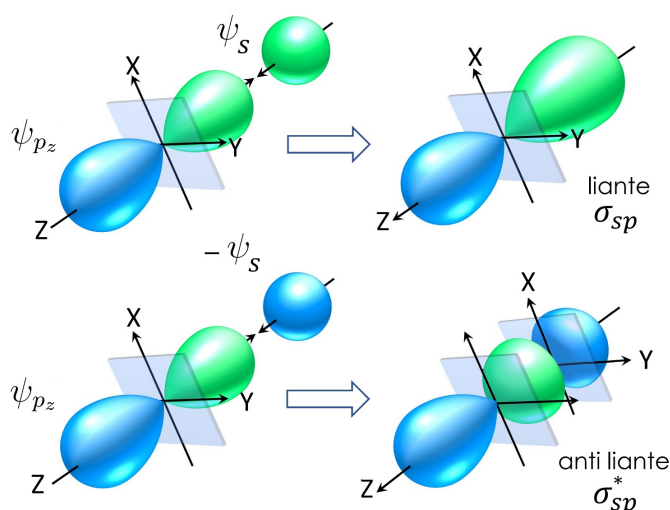


Figure 2.13 Axial overlap between an s -type orbital and a p_z -type orbital

of fluorine directed toward hydrogen (along the overlap axis), since the energy difference is $\Delta E = -13.6 - (-19.9) = 6.3 \text{ eV} < 12 \text{ eV}$.

Two of the eight valence electrons in **HF** occupy this molecular orbital (the covalent bond). The remaining six occupy molecular orbitals that are essentially the remaining $2s$ and $2p$ atomic orbitals of fluorine and do not contribute to bond formation (since they do not participate in the overlap); the electronic configuration is therefore $2s^2 (\sigma_{sp})^2 2(p_x^2 p_y^2)$. The bond order L_n equals 1 since there are only two bonding electrons:

$$L_n = \frac{1}{2}(2 - 0) = 1$$

Pi type bonds: Lateral overlap leads to π -type bonds. This is found between p_x -type atomic orbitals (Figure 2.15), and also between p_y -type orbitals (Figure 2.16).

As a reminder, each type of overlap gives bonding and antibonding possibilities; we just need to specify their energy values.

The $2p_x$ and $2p_y$ orbitals of each atom that constitute the atomic bond are perpendicular to the overlap axis and can overlap laterally. This overlap can be constructive or destructive. The notation π is analogous to “ p ” (the atomic orbital), given the resemblance between them when observing the molecular orbital along the overlap axis.

Overlap along the x and y axes gives degenerate molecular orbitals (they have the same energy). Thus, in homonuclear diatomic molecules (consisting of two atoms of the same element) of the first ten elements, the molecular orbitals derived

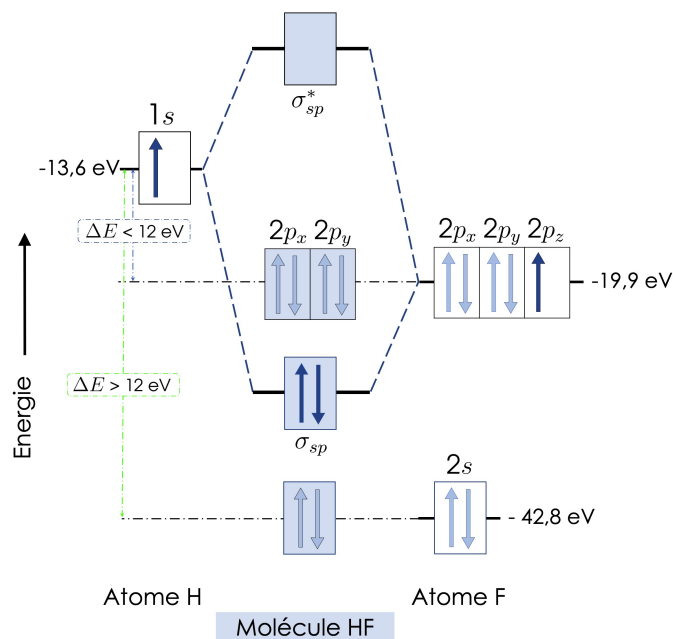


Figure 2.14 Molecular orbital diagram of **HF**

from the p_x and p_y atomic orbitals yield two degenerate bonding orbitals (low energy) and two degenerate antibonding orbitals (high energy).

Several non-metallic elements of the second period exist as homonuclear diatomic molecules: N_2 , O_2 , and F_2 . Molecular orbital theory is useful for describing the bond in these well-known molecules and others less so, such as Li_2 , B_2 , and C_2 . In the second period, the valence shell is formed by $2s$ and $2p$ atomic orbitals. Due to the low energy of the orbitals and inner electrons (core electrons) $1s$, they will not be included in the bonding of second-period element molecules. Each atom has four valence atomic orbitals (s , p_x , p_y , and p_z); there is a total of eight atomic orbitals used to construct the molecular orbital diagram of these diatomic molecules.

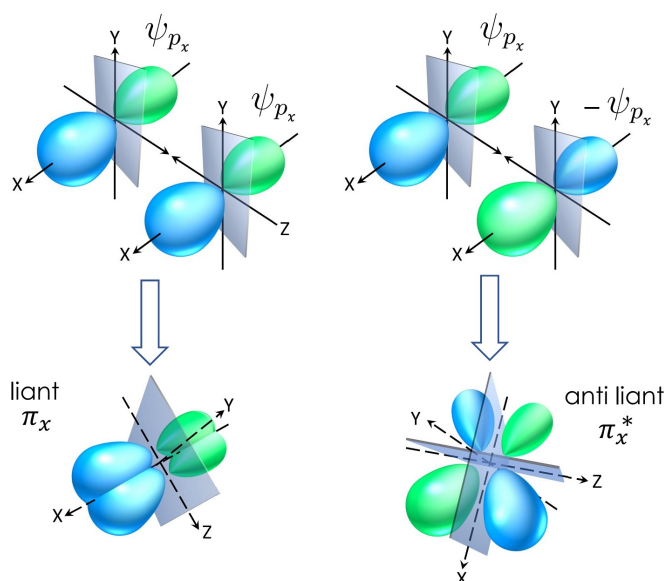


Figure 2.15 Lateral overlap between p_x -type orbitals

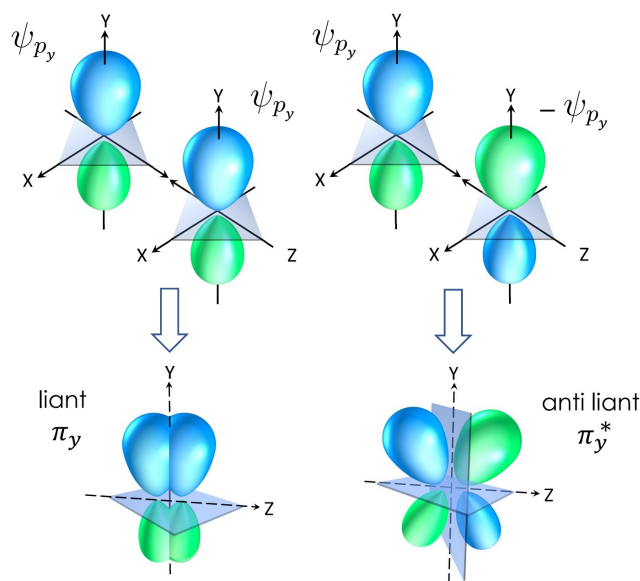


Figure 2.16 Lateral overlap between p_y -type orbitals

Second-period diatomic molecules form σ_s and σ_s^* molecular orbitals from the $2s$ orbitals on both atoms, analogous to those formed from the $1s$ orbitals for H_2 . The $2p$ orbitals combine to give two different types of molecular orbitals. The first set of molecular orbitals comes from the lateral overlap of a p_x or p_y orbital on one atom with a p_x or p_y orbital on the other atom, oriented along the overlap axis.

For these elements, two types of diagrams explain the formation of appropriate chemical bonds: overlap with and without interaction between the s and p_z orbitals, shown respectively in [Figure 2.18](#) and [Figure 2.17](#).

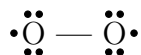
Difluorine molecule: The electronic configuration in F_2 is:

$2(\sigma_s)^2 2(\sigma_s^*)^2 2(\sigma_z)^2 2(\pi_x \pi_y)^4 2(\pi_x^* \pi_y^*)^4$ (see [Figure 2.17](#) on the right). The bond order L_n is equal to 1 (single bond) because there are eight bonding electrons and six in antibonding orbitals.

$$L_n = \frac{1}{2}(8 - 6) = 1$$

The four electrons in the (σ_s) and (σ_s^*) molecular orbitals do not contribute to the bond; the antibonding orbital with its destructive nature prevents bond formation via the bonding orbital (constructive). Consequently, non-bonding pairs find their place on each atom. To summarize the phenomenon: an antibonding pair destroys the bonding pair to give a non-bonding pair. This bond description is consistent with the bond order predicted by the Lewis structure. The lone pairs on nitrogen atoms correspond to electron pairs in the (σ_s) and (σ_s^*) molecular orbitals.

Dioxygen molecule: As indicated previously, valence bond theory predicts that O_2 does not contain unpaired electrons. To show these electrons in this molecule, a structure similar to the following would be needed:

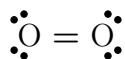


This structure is deficient because it implies the presence of a single covalent bond, whereas experimental measurements show that the molecule contains a double bond, and also because each oxygen atom is surrounded by seven electrons, which violates the octet rule. According to the electronic configuration of oxygen, there are 12 valence electrons total in the O_2 molecule, and according to the molecular orbital diagram, the molecular configuration is as follows:

$2(\sigma_s)^2 2(\sigma_s^*)^2 2(\sigma_z)^2 2(\pi_x \pi_y)^4 2(\pi_x^* \pi_y^*)^2$ (see [Figure 2.17](#) on the left), for a bond order of 2, which is a double bond in this molecule.

$$L_n = \frac{1}{2}(10 - 6) = 2$$

According to **Hund's rule**,⁽²⁹⁾ these electrons are placed in separate orbitals with parallel spins. Molecular orbital theory correctly accounts for experimental observations of a double bond and the presence of two unpaired electrons in O_2 .



Dinitrogen molecule: The electronic configuration in N_2 is $2(\sigma_s)^2 2(\sigma_s^*)^2 2(\sigma_z)^2 2(\pi_x \pi_y)^4$. The bond order L_n is equal to 3 (triple bond) because there are eight bonding electrons and two in antibonding orbitals.

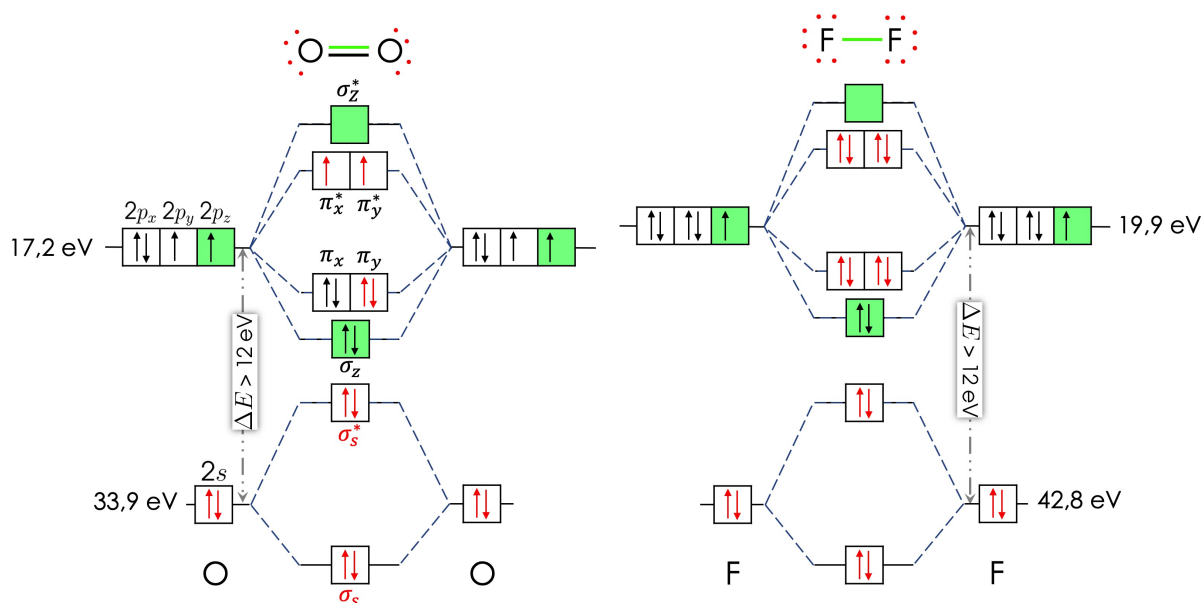


Figure 2.17 Molecular orbital diagram of O_2 (left) and F_2 (right) without interaction between the s and p_z orbitals

$$L_n = \frac{1}{2}(8 - 2) = 3$$

Unlike previous molecules, those that have an energy difference greater than 12 eV between their s and p atomic orbitals, such as nitrogen and boron with respective shifts of 10 and 5 eV, will have an energetic disorder also called sp pollution, manifested by a change in the energetic state of the axial sigma overlap (σ_s and σ_s^*), one gaining stability and the other losing it. The diagram in [Figure 2.18](#) reveals this change and the interaction between s and p .

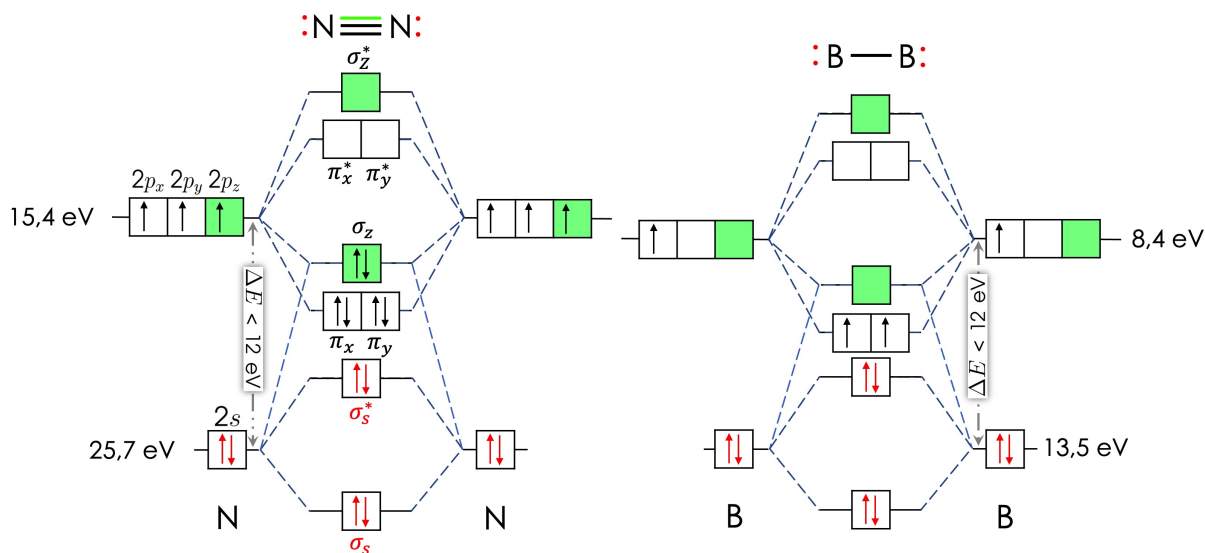


Figure 2.18 Molecular orbital diagram of N_2 (left) and B_2 (right) with interaction between the s and p_z orbitals

2.3.3.5. Magnetic Properties of Molecules

Pauli's principle and **Hund's** rule have been demonstrated through experiments on magnetic properties. Since each electron in an atom induces a magnetic field, the pairing of two electrons of opposite spins in an orbital results in a zero net magnetic field because the magnetic field of one electron cancels that of the other.

A substance is called diamagnetic if all its electrons are paired (electron pairs) and, when subjected to the magnetic field of a magnet, it is repelled out of this field.

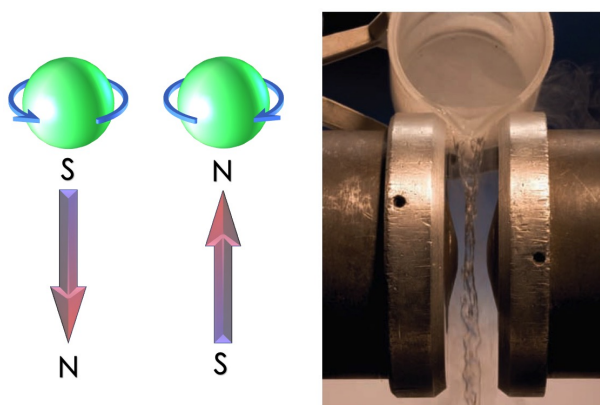


Figure 2.19 Behavior of a liquid diamagnetic substance (**Dia**) in a magnetic field: N_2 (right), corresponding to antiparallel spins (left)

In contrast, a paramagnetic substance (**Para**) is a substance that has one or more unpaired electrons and, when subjected to the magnetic field of a magnet, is attracted into this field.

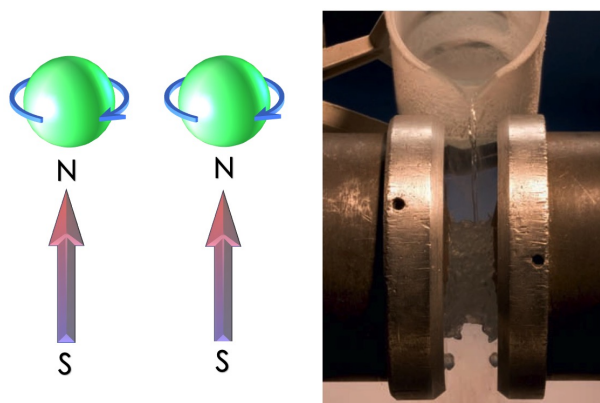


Figure 2.20 Behavior of a liquid paramagnetic substance in a magnetic field: O_2 (right), corresponding to parallel spins (left)

	Li_2	B_2	C_2	N_2	O_2	F_2
σ_z^*	☐	☐	☐	☐	☐	☐
π_x^*, π_y^*	☐	☐	☐	☐	☒ ☒	☒ ☒
σ_z	☐	☐	☐	☒	☒ ☒	☒ ☒
π_x, π_y	☐	☒ ☒	☒ ☒	☒ ☒	☒ ☒	☒ ☒
σ_s^*	☐	☒	☒	☒	☒	☒
σ_s	☒	☒	☒	☒	☒	☒
Bond order	1	1	2	3	2	1
Bond length (pm)	267	159	131	110	121	142
Bond energy (kJ/mol)	104.6	288.7	627.6	941.4	498.7	156.9
Magnetic properties	Dia	Para	Dia	Dia	Para	Dia
With s-p interaction				Without interaction		

Table 2.1 Comparison of bond orders and magnetic properties.

Magnetic property measurements ([Table 2.1](#)) constitute the most obvious proof of specific electronic configurations of elements. Advances in instrumentation over the past 30 years have made it possible to determine the number of

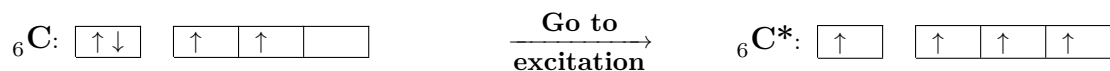
unpaired electrons in certain atoms. Experimentally, we know that the helium atom is diamagnetic (**Dia**) in its ground state, as predicted by the Pauli principle. There is a useful rule to keep in mind: any atom or molecule containing an odd number of electrons is paramagnetic, because for the magnetic effect to cancel, an even number of electrons is required. On the other hand, atoms that contain an even number of electrons can be either diamagnetic or paramagnetic.

2.4. Hybridization of Atomic Orbitals

Hybridization of atomic orbitals is a theoretical model imagined by Linus Pauling (1939) in valence bond theory: the *s*, *p*, *d* orbitals of **the same atom** are "mathematically mixed" to create hybrid orbitals that are all **equivalent in energy and perfectly oriented in space** (sp^3 tetrahedral, sp^2 planar 120° , sp^3d bipyramidal...). VSEPR is an empirical rule that predicts the observable final shape (AX_nE_m) based on electron pair repulsion, while hybridization explains why this shape occurs by showing how the central atom adapts its orbitals. For CH_4 , VSEPR says "tetrahedral" (AX_4), and hybridization shows carbon going from $2s^2 2p^2$ to **4 sp^3 orbitals** at the vertices of a perfect tetrahedron (109.5°). The two models are complementary: VSEPR for quick sketching, hybridization for in-depth understanding.



With the two unpaired electrons located in the $2p$ orbitals (ground state configuration of carbon: $2s^2 2p^2$), valence bond theory naturally predicts the formation of CH_2 (model AX_2E_1 , bond angle 120°), a molecule that would be unstable because the central carbon does not reach the octet rule (only 6 electrons in its valence shell). The simplest stable hydrocarbon is therefore **methane CH_4** , where carbon is surrounded by four equivalent hydrogens. To explain the existence of these four identical **C–H** covalent bonds in length and energy, we must consider an **electronic promotion**: one electron from the $2s$ orbital migrates to an empty $2p$ orbital (absorption of energy), creating a carbon atom in the excited state ($2s^1 2p^3$) with four unpaired electrons perfectly positioned to form the four σ bonds of methane.



The presence of three mutually perpendicular $2p$ orbitals in the excited state electronic configuration might suggest that the molecule has three **C–H** bonds with bond angles of 90° . The fourth **C–H** bond would then come from the overlap of the carbon $2s$ orbital and the $1s$ orbital of a hydrogen atom. This bond would be oriented to minimize interactions with the other three bonds.

However, experimental data show that in CH_4 , the four **C–H** bonds are strictly equivalent: same lengths, same energies, and all **H–C–H** angles are 109.5° , the characteristic angle of tetrahedral geometry.

The **VSEPR** method can certainly predict this tetrahedral geometry (model AX_4 , see [Page 71](#)), and the excited electron configuration does provide four unpaired electrons to form four bonds, but it does not explain either the equivalence of the bonds or the exact value of the observed angles.

The preceding analysis is based on the assumption that the orbitals (*s*, *p*, ...) of atoms involved in a bond are identical to those of isolated atoms. However, this assumption is not verified in many cases, such as methane. To resolve this contradiction, it is necessary to use the concept of **hybridization of atomic orbitals**.

2.4.1. sp^3 Hybridization

In the CH_4 molecule, we find the sp^3 hybrid orbital. It "fuses" the $2s$ orbital and the three $2p$ orbitals to obtain four new orbitals equivalent in energy and shape, and oriented toward the four vertices of a tetrahedron.

The following figure ([Figure 2.21](#)) represents hybridization, which gives a set of four new orbitals called sp^3 hybrid orbitals. The notation of this type of orbital is based on the nature and number of atomic orbitals used to form the hybrids.

In cases where the best description of a molecular structure is obtained by a hybridization model in valence bond theory, it is important to remember the following principles:

- In general, a hybridization model can be used for atoms that participate in covalent bonds, but such a model is most often used only for central atoms.
- The number of hybrid orbitals resulting from a hybridization model is equal to the total number of atomic orbitals combined.
- During covalent bond formation, overlap can occur between hybrid orbitals and pure atomic orbitals or other hybrid orbitals.
- Molecular geometry is determined by the shape and orientation of hybrid orbitals, which differ from the shape and orientation of atomic orbitals.

To illustrate the role of sp^3 hybrid orbitals in bond formation in methane, we represent the hybridization of the central carbon atom using quantum boxes, and orbital overlap in the following figure. sp^3 hybridization should apply not only to AX_4 -type structures (see [Page 71](#), like CH_4 in [Figure 2.22](#) on the right), but also to AX_3E -type structures (like NH_3 in [Figure 2.22](#) in the middle) or AX_2E_2 -type structures (like H_2O in [Figure 2.22](#) on the left).

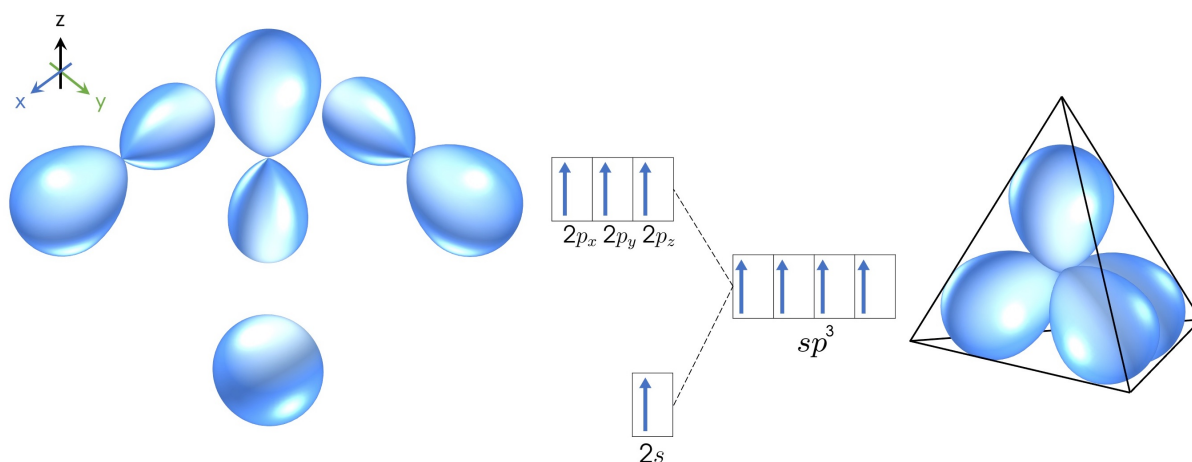


Figure 2.21 sp^3 -type hybridization

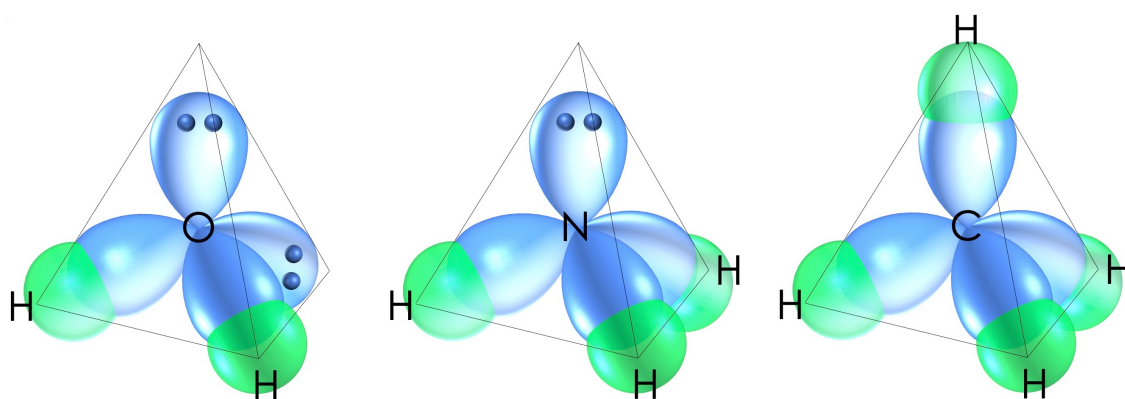
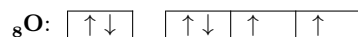


Figure 2.22 sp^3 Hybrid orbitals in different models

In the ammonia molecule NH_3 , sp^3 hybrid orbitals can be formed from the valence shell atomic orbitals of the central nitrogen atom. If we assign the five valence electrons to the four hybrid orbitals, there is one lone pair in one orbital and unpaired electrons in the other three. Overlap between hybrid orbitals containing unpaired electrons and $1s$ orbitals of hydrogen atoms leads to the formation of three N—H bonds. The theoretical value of the H—N—H bond angle, i.e., 109.5° , is close to the observed value, i.e., 107.4° .



A similar hybridization model for H_2O explains the formation of two O—H bonds and the presence of two lone pairs around the oxygen atom. However, the observed value is 104.5° .

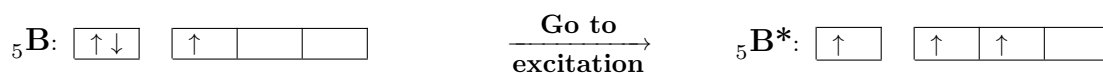


As emphasized in the VSEPR method (Page 71), the fact that bond angles are slightly smaller than those of a tetrahedral structure is explained by the presence of repulsion forces exerted by lone pairs on bonding pairs.

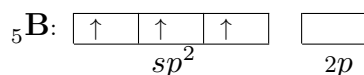
2.4.2. sp^2 Hybridization

The sp^2 hybridization model is particularly useful for describing double covalent bonds, focusing on boron compounds.

The first step of the sp^2 hybridization process involves the promotion of an electron from a $2s$ orbital to an unoccupied $2p$ orbital.



One $2s$ orbital and two $2p$ orbitals occupied by unpaired electrons are transformed into three sp^2 hybrid orbitals, and the remaining $2p$ orbital does not participate in hybridization.



The geometry of the three sp^2 hybrid orbitals is in a plane, with angles of 120° . According to valence bond theory, the BF_3 molecule is triangular planar, and the value of the F—B—F bond angle is 120° (Page 71), exactly the observed value.

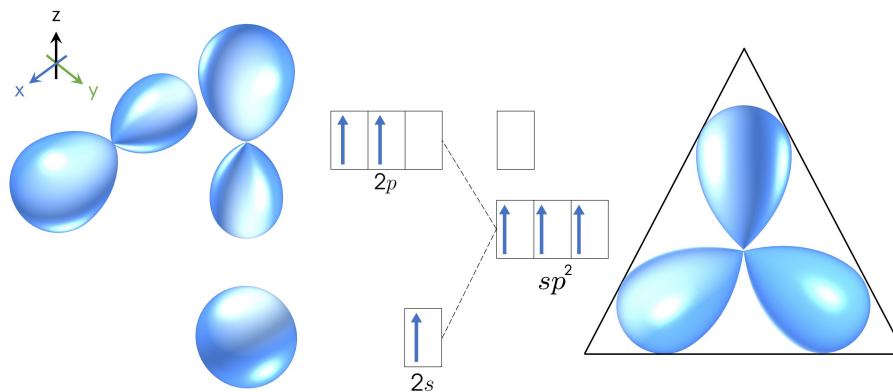


Figure 2.23 sp^2 -type hybridization

2.4.3. Hybrid orbitals sp :

The *sp* hybridization model is particularly useful for describing a triple covalent bond, but let us take a simple example: **BeCl₂**. Beryllium, with its two valence electrons, undergoes excitation — one electron is promoted from the 2s orbital to an initially empty 2p orbital — and these two orbitals then merge (hybridization).

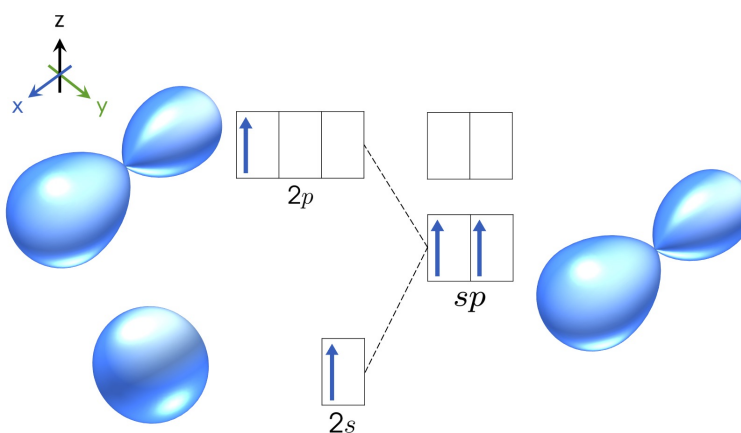


Figure 2.24 *sp*-type hybridization

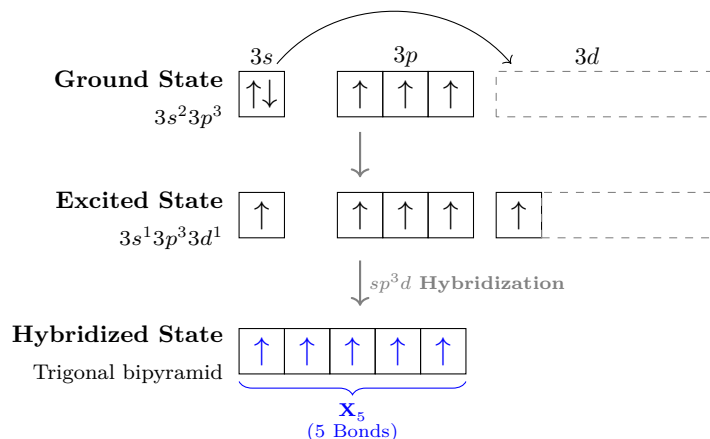
2.4.4. Hybrid orbitals sp^3d :

Any hybridization model involving only s and p orbitals cannot accommodate more than eight valence electrons, i.e. the octet. To apply a hybridization model to structures with an **expanded valence shell**, additional orbitals must be used — specifically orbitals of type d .

For example, **five hybrid orbitals** are required to describe the bonds in PCl_5 , obtained by combining one s orbital, three p orbitals, and one d orbital of the central phosphorus atom.

Atomic phosphorus has the outer configuration $[\text{Ne}] 3s^2 3p^3$, with five valence electrons. To form five σ bonds in PCl_5 , **electronic promotion** occurs: one electron from $3s$ migrates to an empty $3d$ orbital ($3d^0$), giving $3s^1 3p^3 3d^1$.

The five orbitals ($3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{z^2}$) then mix to form **five equivalent sp^3d hybrids**, directed toward the vertices of a **trigonal bipyramid** (VSEPR geometry AX_5).



Five sp^3d hybrid orbitals, each containing one unpaired electron, form five **P–Cl** σ bonds by overlap with the $3p$ orbitals of Cl. This geometry distinguishes two types of bonds:

- **Three equatorial** (120°)
- **Two axial** (90°), due to the slightly higher energy of the hybrids involving d .

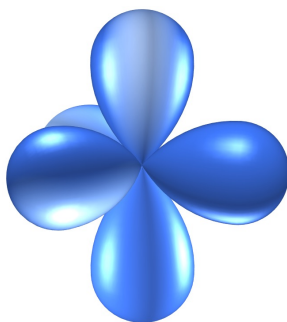
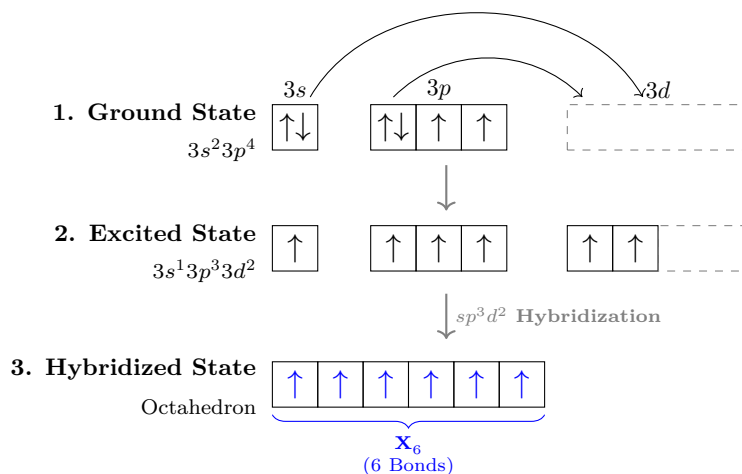


Figure 2.25 sp^3d -type hybridization

2.4.5. Hybrid orbitals sp^3d^2 :

The hybrid orbitals of the central sulfur atom in SF_6 , whose geometry is octahedral, are shown in the following figure. For each bond in SF_6 , the overlap involves one sp^3d^2 hybrid orbital of the sulfur atom and one $2p$ orbital of a fluorine atom.



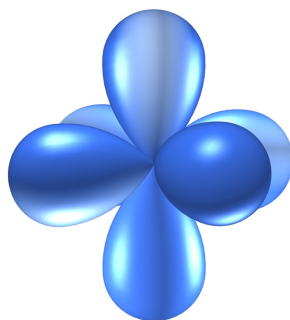


Figure 2.26 sp^3d^2 -type hybridization

The central S atom uses **six sp^3d^2 hybrid orbitals**, each containing one unpaired electron, forming a σ S–F bond by overlap with a $2p$ orbital of fluorine.

This hybridization leads to a **perfect octahedral geometry**:

- Six equivalent bonds directed toward the vertices of a regular octahedron
- Bond angles: 90° (adjacent, 12 pairs) and 180° (opposite, 3 pairs)
- Identical bond length: $d_{\text{S-F}} = 156 \text{ pm}$

All positions are equivalent, unlike PCl_5 (trigonal bipyramidal, sp^3d).

The formation of six equivalent sp^3d^2 hybrid orbitals requires the promotion of one $3s$ electron to a $3d$ orbital, as shown in the energy-level diagram above. This hybridization scheme is characteristic of elements in period 3 and below, which have accessible d orbitals. The resulting octahedral arrangement minimizes electron-pair repulsion according to VSEPR theory, making SF_6 a classic example of hypervalent compounds where the central atom accommodates more than eight valence electrons.

2.4.6. Conclusion:

The two approaches complement each other perfectly:

The VSEPR model and the concept of atomic orbital hybridization are not competing or opposing theories. On the contrary, they represent **two sides of the same coin** in molecular chemistry, each providing a different yet complementary perspective on molecular structure.

- **VSEPR is a purely geometric and empirical model:** It relies solely on the principle of electrostatic repulsion between electron pairs (bonding or non-bonding) around the central atom. Without any reference to atomic orbitals or quantum mechanics, VSEPR classifies molecules according to their AX_nE_m formula and predicts their equilibrium geometry remarkably well. It is a **fast and intuitive prediction tool**, accessible even without advanced knowledge of quantum chemistry.
- **Hybridization is an orbital-based and explanatory model:** Derived from the valence bond theory developed by Pauling, this concept goes to the heart of the atom. It describes how the central atom **mathematically reorganizes its atomic orbitals** (linear combination) to form new hybrid orbitals perfectly oriented in space. Hybridization **justifies a posteriori** why a given geometry is energetically favorable and how bonds can be rigorously equivalent even though the original orbitals (s , p , d) are not.

VSEPR + Hybridization = same geometry, two complementary languages

Why is this the key to success?

Because molecular geometry problems assess **two distinct skills**:

- Your **ability to quickly apply a predictive method** (VSEPR) to determine the shape and polarity.
- Your **ability to justify that shape using an explanatory model** (hybridization) that demonstrates a deep understanding of chemical bonding.

VSEPR = "Draw quickly and correctly"
Hybridization = "Understand and explain"
 The two are inseparable.

In summary, VSEPR provides a rapid and empirical route to predicting molecular shapes, while hybridization offers a rigorous quantum-mechanical justification for those same geometries. Mastering both models equips the chemist with a powerful dual framework: one for efficient prediction, the other for deep conceptual understanding. Together, they form the cornerstone of modern molecular structure analysis, and their complementary use is essential for success in both academic exercises and real-world chemical reasoning.

Table 2.2 VSEPR summary: geometries, angles and hybridizations by AX_nE_m type

n+m	VSEPR	Molecular geometry		Angle	Hybridization	Example
1 & 2	AX_1		Linear	180°	-	LiH
	AX_2				sp	BeCl₂
	AX_1E_1					CN⁻
3	AX_3		Trigonal planar	120°	sp^2	BF₃
	AX_2E_1		Bent	$< 120^\circ$		SO₂
	AX_1E_2		Linear	180°		O₂
4	AX_4		Tetrahedral	109.5°	sp^3	CH₄
	AX_3E_1		Trigonal pyramidal	107.4°		NH₃
	AX_2E_2		Bent	104.5°		H₂O
	AX_1E_3		Linear	180°		HCl
5	AX_5		Trigonal bipyramidal	120° & 90°	sp^3d	PCl₅
	AX_4E_1		Seesaw	180° , 120° & 90°		SF₄
	AX_3E_2		T-shaped	180° & 90°		BrF₃
	AX_2E_3		Linear	180°		XeF₂
6	AX_6		Octahedral	90°	sp^3d^2	SF₆
	AX_5E_1		Square pyramidal			BrF₅
	AX_4E_2		Square planar			XeF₄

Exercise:

1. Give the geometry of the following molecules, specifying the hybridization of the central atom: SiH_4 , CCl_4 , C_2H_2 , BeCl_2 , BF_3 , ClF_3 , XeF_4 and SF_6 .
2. Consider the following organic molecule: $\text{CH}_2=\text{CHCH}_2\text{NH}_2$
 - a) Draw the structural formula of this molecule, specifying the bond angle values.
 - b) Specify the hybridization states of the carbon atoms.
 - c) Identify the atoms that lie in the same plane.

Before you start: Key advice for this exercise

This exercise tests two complementary skills: **VSEPR geometry prediction** and **hybridization assignment**. Here are the essential points to keep in mind before you begin.

1. Count electron domains, not atoms.

- A double or triple bond counts as **one single domain** for VSEPR.
- Lone pairs on the central atom **must be counted** — they occupy space and affect geometry.

2. The hybridization number equals the total number of domains.

Domains = bonds (σ) + lone pairs $\Rightarrow$ hybridization

Domains	Hybridization	Base geometry
2	sp	Linear
3	sp^2	Trigonal planar
4	sp^3	Tetrahedral
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral

3. Distinguish base geometry from molecular geometry.

- **Base geometry**: includes lone pairs (repulsion figure).
- **Molecular geometry**: only the positions of atoms (ignore lone pairs).
- Example: ClF_3 has 5 domains (base = trigonal bipyramidal), but 2 lone pairs occupy equatorial positions $\rightarrow$ molecular shape = **T-shaped**.

4. Watch for exceptions and special cases.

- **Octet rule exceptions**: BeCl_2 (4 e⁻), BF_3 (6 e⁻) — still stable.
- **Hypervalent molecules**: elements from period 3 and beyond (S, Cl, Xe) can use d orbitals $\rightarrow sp^3d$ or sp^3d^2 .
- **Lone pair placement**: for 5 domains, lone pairs go **equatorial** (120°); for 6 domains, they go **opposite** (180°).

5. For organic molecules, analyse each carbon separately.

- **Double bond** = sp^2 (planar, 120°).
- **Triple bond** = sp (linear, 180°).
- **Four single bonds** = sp^3 (tetrahedral, 109.5°).
- **Coplanarity**: all atoms directly attached to an sp^2 carbon lie in the same plane.

6. Final verification checklist.

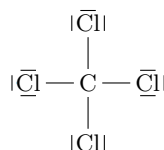
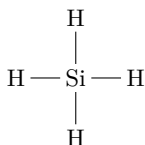
- a) Have I counted **all** electron domains around the central atom?
- b) Does my hybridization match the total number of domains?
- c) Have I correctly placed lone pairs (equatorial for 5, opposite for 6)?
- d) For organic molecules, have I identified the hybridization of **each** carbon?
- e) Are the bond angles consistent with the hybridization I assigned?

Remember: VSEPR gives the *shape*; hybridization gives the *explanation*. The two always agree — if they don't, you have made a mistake somewhere.

Solution

1. Give the geometry of the following molecules, specifying the hybridization of the central atom:

1. **Molecules SiH_4 and CCl_4**

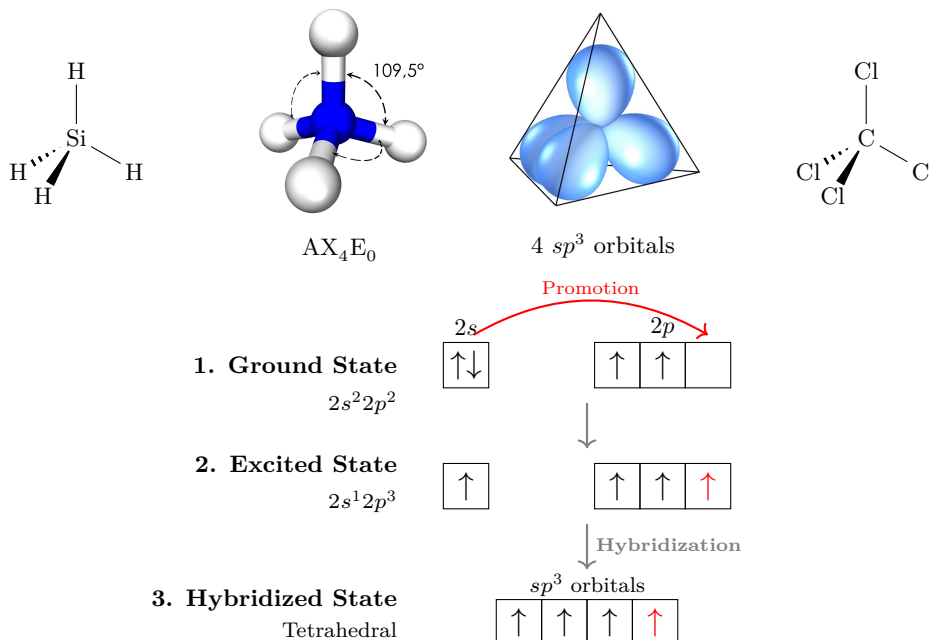


- **Lewis structure:** The central atom (C or Si) belongs to group A4 (column 14) and has 4

valence electrons. It uses all 4 electrons to form 4 single (σ) bonds with the peripheral atoms. No valence electrons remain on the central atom, hence no lone pairs (E_0).

Conclusion: The molecule has 4 equivalent repulsion directions, corresponding to the VSEPR type AX_4 .

- **Geometry:** Tetrahedral (bond angles of 109.5°).
- **Hybridization:** sp^3 (combination of one s orbital and three p orbitals).

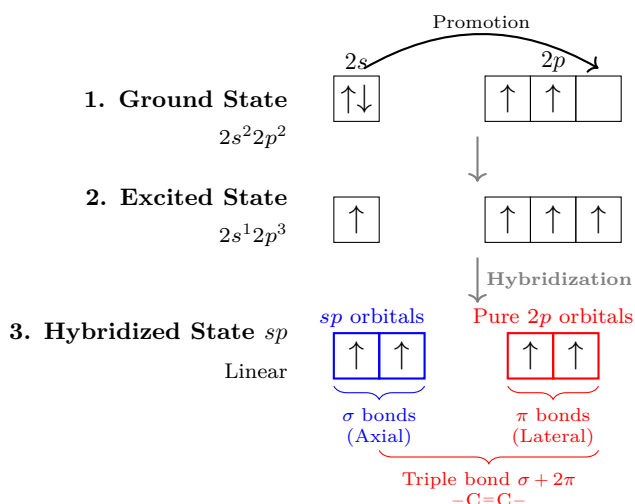


2. Molecule C_2H_2

- **C_2H_2 :** Each carbon is bonded to one H and to the other C via a triple bond. We examine the geometry around one carbon atom.



- In the left-hand structure, each carbon has only 6 valence electrons (2 in the $C-H$ bond, 2 in the single $C-C$ bond, 2 in the lone pair). The octet is incomplete, making this configuration extremely reactive and unstable. By sharing their lone pairs, the two carbons form a triple bond (one σ and two π), allowing each carbon to reach the stable noble-gas configuration (8 valence electrons). The right-hand structure is the only physically correct Lewis representation.



- **Geometric and electronic analysis:**

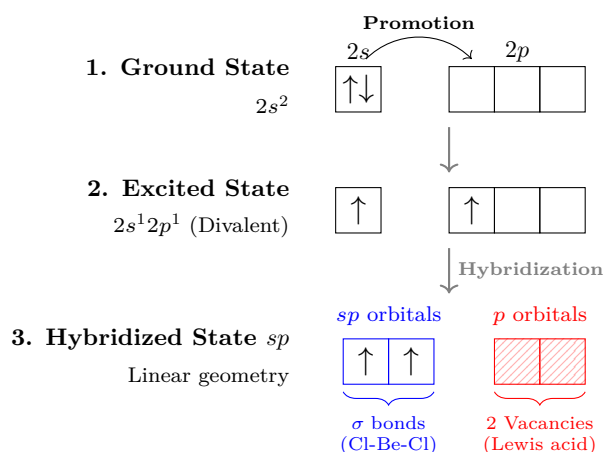
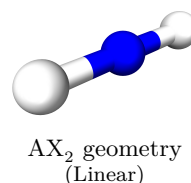
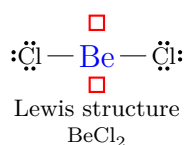
To determine the geometry of acetylene (C_2H_2), each carbon atom must be considered independently as a repulsion center. Although carbon is bonded to the other carbon through an electron-rich triple bond (6 electrons), the VSEPR model treats this electron density as a **single repulsion domain** (a “super-bond”).

Thus, each carbon is surrounded by only two effective bonding directions: one toward hydrogen and one toward the other carbon. To minimize electrostatic repulsions between these two domains, they are forced to point in opposite directions, imposing a 180° angle. This geometric constraint forces carbon to adopt a specific hybridization capable of maintaining this linearity while reserving orbitals for the triple bond.

- **VSEPR type:** AX_2 (2 repulsion domains, no lone pair).
- **Geometry:** **Linear** (bond angle $\widehat{HCC} = 180^\circ$).
- **Hybridization:** sp (combination of one s and one p orbital).
- **Consequence:** The two remaining p orbitals are perpendicular to each other and form the two π bonds.

3. Molecule $BeCl_2$:

- In the linear structure, each chlorine atom donates one electron to form a covalent bond with beryllium. Beryllium, with only 2 valence electrons, forms two single $Be-Cl$ bonds. Although beryllium does not complete the octet (it has only 4 electrons around it), this configuration is stable because beryllium is a classic exception to the octet rule (a 2nd-period element with insufficient valence electrons to reach 8). The linear structure with two single bonds is the only physically correct Lewis configuration for this molecule.



• Geometric and electronic analysis:

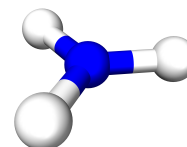
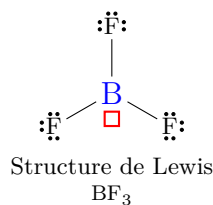
To determine the geometry of beryllium dichloride ($BeCl_2$), we analyze the electronic environment of beryllium, which acts as the unique repulsion center. Beryllium is bonded to two chlorine atoms by two single bonds. According to the VSEPR model, these two bonds constitute two distinct repulsion domains.

To minimize electrostatic repulsions, they are forced to point in opposite directions, imposing an angle of 180° . This geometric constraint forces beryllium to adopt a specific hybridization capable of maintaining perfect linearity, analogous to that observed in acetylene C_2H_2 where each carbon also forms two bonds in a linear geometry.

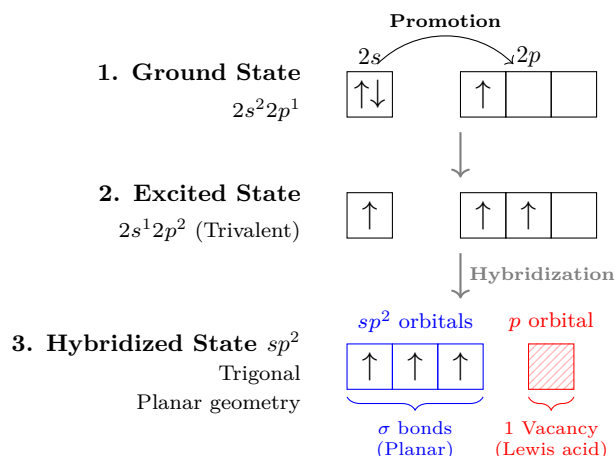
- **VSEPR type:** AX_2 (2 repulsion domains, no lone pair).
- **Geometry:** **Linear** (bond angle $\widehat{ClBeCl} = 180^\circ$).
- **Hybridization:** sp (combination of one s and one p orbital).
- **Note:** Beryllium does not satisfy the octet rule (only 4 valence electrons), but the molecule remains stable due to the linear symmetry and the low electronegativity of beryllium.

4. Molecule BF_3 (Boron trifluoride)

- In the planar structure, each fluorine atom donates one electron to form a covalent bond with boron. Boron, with only 3 valence electrons, forms three single $B-F$ bonds. As with beryllium, boron does not complete the octet (it has only 6 electrons around it), but this configuration is stable because boron is a classic exception to the octet rule (electron deficiency). The planar structure with three single bonds is the physically correct Lewis configuration.



La forme AX₃
(Trigonale plane)



- **Geometric and electronic analysis:**

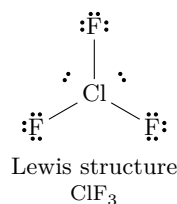
Analysis of the hybridized quantum boxes shows that the 3 sp² orbitals each contain one unpaired electron (blue arrow), ready to form a σ bond with a fluorine atom. No free valence electrons remain on boron: the remaining pure p orbital is completely empty (electron vacancy, hatched red box). With 3 ligands (X₃) and 0 lone pairs (E₀) around the central atom A, we identify a structure of type AX₃.

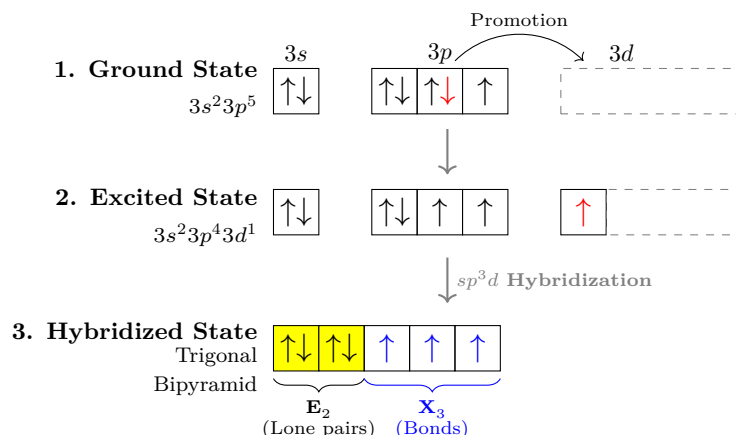
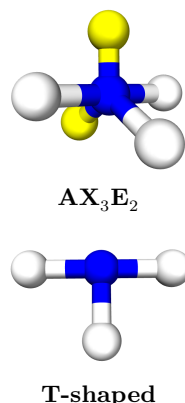
These three equivalent electron domains repel each other and orient toward the vertices of an equilateral triangle, all in the same plane. The bond angles are thus maximized at 120°.

- **Lewis structure:** The central boron (3 valence electrons) forms 3 single bonds and is left with an **electron vacancy** (only 6 electrons around it — an exception to the octet rule).
- **VSEPR type:** AX₃E₀ (3 bonds, 0 lone pairs).
- **Base geometry (repulsion figure):** **Trigonal planar**. The 3 domains occupy the plane with perfect symmetry.
- **Molecular geometry (actual):** **Trigonal planar**. In the absence of lone pairs, the atomic geometry is identical to the repulsion figure. The 3 fluorine atoms form an equilateral triangle around boron.
- **Hybridization:** Sum of domains $n + m = 3 + 0 = 3$. **3 hybrid orbitals** are required. Combination: $1 \times s + 2 \times p = 3$. The hybridization is therefore sp².
- **Bond angles:** The perfect symmetry ensures exact FBF angles of 120°.

5. **Molecule ClF₃ (The classic trap)**

- In this structure, the central chlorine atom forms three single Cl–F bonds and has two lone pairs. This brings the number of valence electrons around chlorine to 10 (3 bonding pairs + 2 lone pairs). Chlorine, a 3rd-period element, undergoes **octet expansion** (hypervalence) by making its empty d orbitals accessible. This is the only configuration that satisfies the total valence electron count ($7 + 3 \times 7 = 28$ electrons, equivalent to 14 pairs, both bonding and non-bonding).





• **Geometric and electronic analysis:**

Analysis of the hybridized quantum boxes directly yields the VSEPR formula: each unpaired electron (single blue arrow) will form a σ bond with a fluorine atom, corresponding to a ligand **X**. Each paired electron set (antiparallel black arrows) represents a lone pair, denoted **E**. With 3 unpaired electrons (X_3) and 2 lone pairs (E_2) around the central atom **A** (chlorine), we immediately identify a structure of type AX_3E_2 .

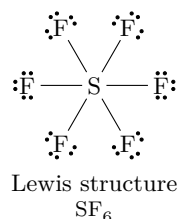
This structure involves 5 total electron domains (3 + 2), imposing a **trigonal bipyramidal** repulsion figure. The critical rule is spatial: lone pairs (**E**), being more voluminous and repulsive than bonds (**X**), preferentially occupy the equatorial positions (120° angles) to minimize electrostatic strain.

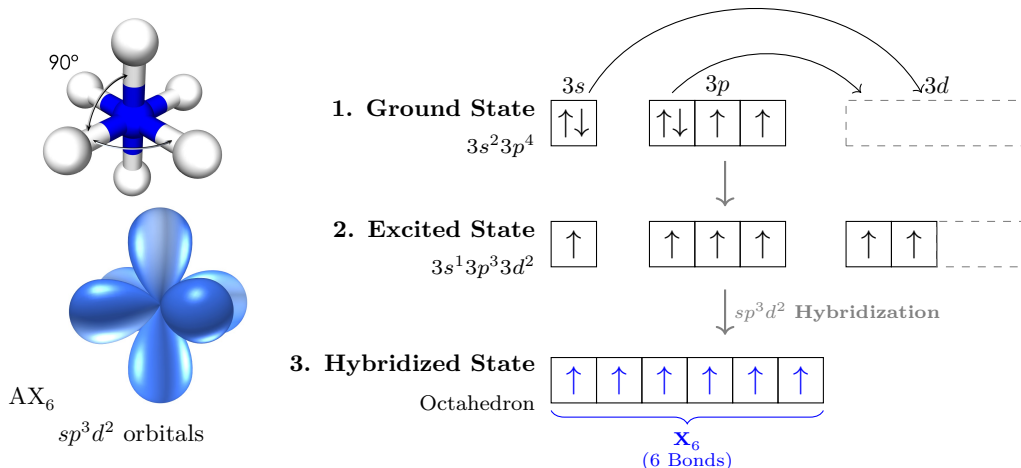
Placing them in axial positions (90° to 3 neighbors) would make the molecule unstable. The fluorine atoms therefore occupy the two remaining axial positions and one equatorial position, giving the molecule its characteristic **T-shape**.

- **Lewis structure:** Central chlorine (7 valence electrons) forms 3 bonds and retains $7 - 3 = 4$ electrons, i.e. **2 lone pairs**.
- **VSEPR type:** AX_3E_2 (3 bonds, 2 lone pairs).
- **Base geometry (repulsion figure): Trigonal bipyramidal.** This shape is imposed by the 5 electron domains ($n + m = 5$): the 3 blue bonds and the 2 yellow lone pairs occupy the vertices of a triangular bipyramid.
- **Molecular geometry (actual): T-shaped.** The two yellow lone pairs, being more voluminous, must occupy the equatorial positions (triangle plane) for more space (120° angles). Mentally “switching off” these two equatorial yellow volumes, only the central atom, the two axial atoms (vertical), and the last equatorial atom remain — forming the letter **T**.
- **Hybridization:** Sum of domains $n + m = 3 + 2 = 5$. **5 hybrid orbitals** are required. Combining in increasing energy order: $1 \times s + 3 \times p + 1 \times d = 5$. The hybridization is therefore sp^3d .
- **Distortion:** The strong repulsion of the two lone pairs compresses the $\widehat{\text{ClF}_{\text{ax}}\text{F}_{\text{eq}}}$ angle to approximately 87.5° (instead of the theoretical 90°).

6. **Molecule SF_6 (Perfect hypervalence)**

- In this emblematic structure, the central sulfur atom forms six identical single **S–F** bonds, with no lone pairs. This brings the number of valence electrons around sulfur to 12 (6 bonding pairs). Sulfur, a 3rd-period element, undergoes **maximum octet expansion** (hypervalence) by hybridizing its orbitals and using its vacant $3d$ orbitals. This stable configuration perfectly satisfies the total valence electron count ($6 + 6 \times 7 = 48$ valence electrons, equivalent to 24 pairs).





• **Geometric and electronic analysis:**

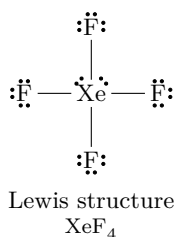
Analysis of the hybridized quantum boxes directly yields the VSEPR formula: each hybrid orbital contains one unpaired electron (blue arrow), ready to form a σ bond with a fluorine atom (ligand **X**). Unlike the previous case, there are no residual lone pairs. With 6 unpaired electrons (X_6) and 0 lone pairs (E_0) around the central atom **A** (sulfur), we identify an ideal structure of type **AX_6** .

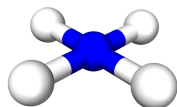
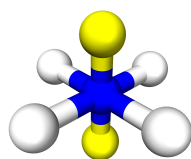
This structure involves 6 equivalent electron domains, imposing a highly symmetric repulsion figure: the **octahedron**. Here, the spatial logic is simplified by the absence of lone pairs. All vertices of the octahedron are geometrically equivalent (90° angles throughout). There is no competition for “more spacious” positions as in the trigonal bipyramid. The 6 fluorine atoms thus occupy the vertices of a regular octahedron around sulfur.

- **Lewis structure:** Central sulfur (6 valence electrons) uses all electrons to form 6 single bonds with fluorine. No free electrons remain ($6 - 6 = 0$).
- **VSEPR type:** **AX_6E_0** (6 bonds, 0 lone pairs).
- **Repulsion figure:** Octahedron (6 equivalent directions).
- **Molecular geometry:** **Regular octahedron**. In the absence of lone pairs, the actual atomic geometry perfectly coincides with the electron repulsion figure.
- **Hybridization:** Sum of domains ($n + m = 6 + 0 = 6$). **6 hybrid orbitals** are required. Combining in increasing energy order: $1 \times s + 3 \times p + 2 \times d = 6$. The hybridization is therefore sp^3d^2 .
- **Bond angles:** The perfect octahedral symmetry ensures exact $\widehat{FSF}$ angles of 90°, with no angular distortion.

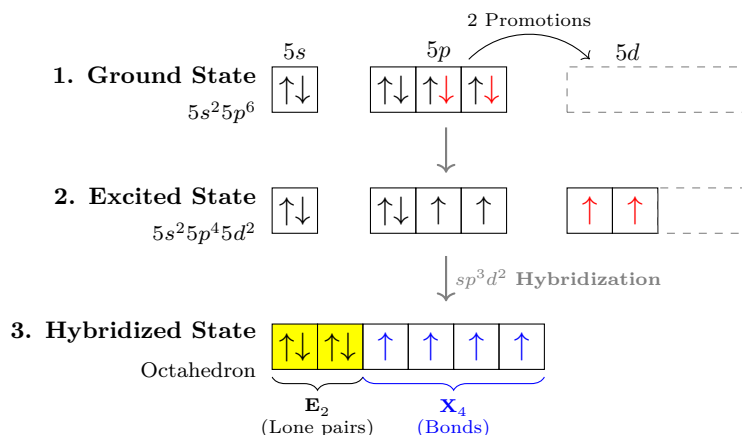
7. **Molecule XeF_4**

- In this particular geometric structure (square planar), the central xenon atom forms four identical single **Xe–F** bonds, but retains **two lone pairs**. This brings the number of valence electrons around xenon to 12 (4 bonding pairs and 2 lone pairs). Xenon, a noble gas from the 5th period, undergoes **octet expansion** (hypervalence) by using its vacant $5d$ orbitals to accommodate the unpaired electrons. This stable configuration perfectly satisfies the total valence electron count ($8 + 4 \times 7 = 36$ valence electrons, equivalent to 18 pairs).





Square planar



• **Geometric and electronic analysis:**

Analysis of the hybridized quantum boxes reveals a key difference from the previous case: we have 6 hybrid orbitals, but not all are occupied by unpaired electrons. We count 4 unpaired electrons (blue arrows) that will form σ bonds with fluorine (X), and 2 already-paired doublets (black arrows) that constitute the lone pairs (E). With 4 ligands and 2 lone pairs around xenon (A), we identify a structure of type AX_4E_2 .

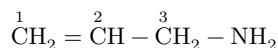
This structure still involves 6 electron domains (4 + 2), imposing the **octahedral** repulsion figure. However, spatial competition is fierce. The two lone pairs (E) are much more voluminous and repulsive than single bonds.

To minimize strain, these two lone pairs must be as far apart as possible. In an octahedron, maximum separation corresponds to 180° . The lone pairs therefore occupy opposite (axial) positions, leaving the equatorial plane to the 4 fluorine atoms.

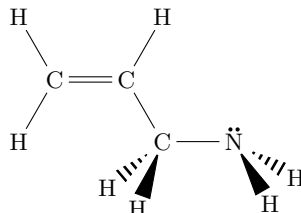
- **Lewis structure:** Central xenon (8 valence electrons) forms 4 single bonds and retains $8 - 4 = 4$ electrons, i.e. **two lone pairs**.
- **VSEPR type:** AX_4E_2 (4 bonds, 2 lone pairs).
- **Base geometry (repulsion figure): Octahedron.** This is the shape obtained when all electron domains are considered without distinction (the 4 blue bonds plus the 2 yellow lone pairs ●).
- **Molecular geometry (actual): Square planar.** To visualize the actual molecule, mentally “switch off” the lone pairs (the yellow zones ●). Removing these two yellow volumes above and below the plane, only the 4 fluorine atoms remain, forming a perfect square around xenon. The molecule is therefore planar.
- **Hybridization:** Sum of domains: $n + m = 4 + 2 = 6$. **6 hybrid orbitals** required. As for SF_6 : $1 \times s + 3 \times p + 2 \times d = 6$. The hybridization is always $sp^3 d^2$.
- **Bond angles:** Although lone pairs are present, their symmetric placement (180° apart) cancels their distortion effects on the equatorial plane. Repulsions perfectly balance, maintaining exact FXeF angles of 90° .

2. **Mixed molecule: Allylamine** $\text{CH}_2=\text{CH}-\text{CH}_2-\text{NH}_2$

For clarity, we number the carbon chain from left to right:



a) **Structural formula and bond angles:**



- **Around C₁ and C₂ (double bond):** Each carbon has 3 repulsion domains (type AX_3). The geometry is **trigonal planar**.

$$\text{Angles } \widehat{\text{HCH}} \text{ and } \widehat{\text{CCC}} \approx 120^\circ$$

- **Around C₃ (single bond):** Carbon bonded to 4 atoms (2H, 1C, 1N). Type **AX₄**. Geometry: **tetrahedral**.

$$\text{Angle } \widehat{\text{HCH}} \approx 109.5^\circ$$

- **Around nitrogen (N):** Nitrogen has 3 bonds and 1 lone pair. Type **AX₃E₁**. Geometry: **trigonal pyramidal**. The lone pair slightly compresses the bond angles.

$$\text{Angle } \widehat{\text{HNH}} \approx 107^\circ$$

b) **Hybridization states of the carbon atoms:**

To determine hybridization, we count the direct neighbors (σ bonds) and lone pairs.

Atom	VSEPR domains	Type	Hybridization
C ₁	3 (2 single + 1 double)	Planar	sp^2
C ₂	3 (2 single + 1 double)	Planar	sp^2
C ₃	4 (4 single bonds)	Tetrahedral	sp^3
N	4 (3 single + lone pair)	Tetrahedral	sp^3

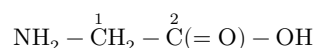
c) **Coplanar atoms:**

The double bond C₁ = C₂ prevents rotation and imposes a rigid planar geometry.

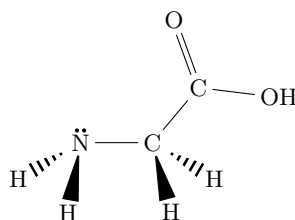
- The **necessarily coplanar** atoms are the two double-bond carbons (C₁, C₂) and the 4 atoms directly bonded to them.
- **List of 6 coplanar atoms:** C₁, C₂, the two H atoms bonded to C₁, the H bonded to C₂, C₃, and nitrogen N.

3. **Mixed molecule: Glycine (2-aminoacetic acid): NH₂–CH₂–COOH**

For clarity, we number the carbon chain from left to right:



a) **Structural formula and bond angles:**



- **Around nitrogen (N):** 3 bonds + 1 lone pair (type **AX₃E**). Geometry: **trigonal pyramidal**.

$$\widehat{\text{HNH}} \approx 107^\circ, \quad \widehat{\text{CNH}} \approx 107\text{--}109^\circ$$

- **Around C₁ (α -carbon):** 4 bonds (type **AX₄**). Geometry: **tetrahedral**.

$$\widehat{\text{HCH}}, \widehat{\text{NCC}} \approx 109.5^\circ$$

- **Around C₂ (carboxyl carbon):** 3 domains (1 double C=O + 2 single). Type **AX₃**. Geometry: **trigonal planar**.

$$\widehat{\text{OCO}} \approx 120^\circ, \quad \widehat{\text{CCO}} \approx 120^\circ$$

- **Around O (hydroxyl, -OH):** 2 bonds + 2 lone pairs (type **AX₂E₂**). Geometry: **bent**.

$$\widehat{\text{COH}} \approx 105\text{--}110^\circ$$

- **Around O (carbonyl, =O):** 1 double bond + 2 lone pairs. Terminal atom — no molecular geometry to describe.

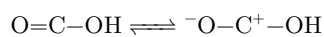
b) **Hybridization states:**

Atom	σ bonds	Lone pairs	VSEPR type	Hybridization
N	3	1	AX ₃ E	sp^3
C ₁	4	0	AX ₄	sp^3
C ₂	3	0	AX ₃	sp^2
O (=O)	1	2	–	sp^2
O (-OH)	2	2	AX ₂ E ₂	sp^3

c) **Coplanar atoms:**

- The carboxyl group $-\text{COOH}$ imposes a rigid plane due to the $\text{C}=\text{O}$ double bond and partial resonance.
- **Necessarily coplanar:** C_2 , $\text{O}(=\text{O})$, $\text{O}(-\text{OH})$, $\text{H}(\text{OH})$, and C_1 (directly bonded).
- **List of 5 coplanar atoms:** C_1 , C_2 , both O atoms, H of OH.
- Nitrogen and its hydrogens are **not** in this plane (free rotation around $\text{C}_1\text{-N}$, and N is sp^3 pyramidal).

d) **Resonance effect of $-\text{COOH}$:** Delocalization imposes coplanarity through resonance:



Angle $\widehat{\text{OCO}} \approx 123^\circ$ (peptide-like rigidity)

- This partial resonance reinforces the **coplanarity** of the $-\text{COOH}$ group.
- The two C-O bonds have intermediate character (bond order ≈ 1.5 in the carboxylate COO^-).
- The angle $\widehat{\text{OCO}}$ remains close to 120° but may vary slightly depending on the degree of delocalization.

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